

DESCRIPTION

TITLE OF INVENTION: PROCESSING AID, MASTER BATCH,
THERMOPLASTIC RESIN COMPOSITION, MOLDED BODY, AND
5 PRODUCTION METHODS THEREFOR

TECHNICAL FIELD

[0001]

The disclosure relates to processing aids,
10 masterbatches, thermoplastic resin compositions, and molded
articles, and production methods thereof.

BACKGROUND ART

[0002]

15 In processing of melt-fabricable thermoplastic
resins, rapid extrusion is required to achieve improved
productivity and low cost. Still, melt-fabricable
thermoplastic resin compositions inevitably have a critical
shear rate and extrusion at a rate higher than this
20 critical shear rate causes a rough surface called melt
fracture, resulting in failure in providing a good molded
article.

[0003]

Techniques for improving the processibility of
25 thermoplastic resins have been proposed. For example,
Patent Literature 1 proposes a technique involving use of
ethylene-vinyl alcohol and Patent Literature 2 proposes a
technique involving use of a surfactant and polyethylene
glycol. However, the effects thereof are insufficient.

30

CITATION LIST

- Patent Literature

[0004]

Patent Literature 1: JP H01-215840 A

35 Patent Literature 2: US 2023/0031000 A1

SUMMARY OF INVENTION

- Technical Problem

[0005]

5 The disclosure aims to provide a processing aid and a masterbatch capable of improving the processibility of thermoplastic resins, a thermoplastic resin composition and a molded article containing these, and production methods thereof.

10

- Solution to Problem

[0006]

 The disclosure (1) relates to a processing aid having a surface free energy of 28.5 mN/m or more, the processing aid being substantially free from fluorine.

15

[0007]

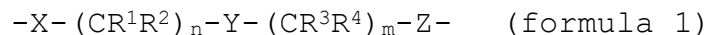
 The disclosure (2) relates to the processing aid according to the disclosure (1), wherein the processing aid has a surface free energy of 29.0 to 55.0 mN/m.

20

[0008]

 The disclosure (3) relates to the processing aid according to the disclosure (1) or (2), wherein the processing aid contains a structural unit represented by the following formula 1:

25



wherein X is a single bond or a divalent group optionally containing a functional group;

 Y and Z are each independently a group constituted by at least one selected from the group consisting of a single bond, -O-, -C(=O)-, -C(=O)O-, -OC(=O)O-, -C(=NR')-, -C(=NR')O-, -OC(=NR')O-, -S-, -S(=O)-, -S(=O)O-, -OS(=O)O-, -S(=O)₂-, -S(=O)₂O-, -OS(=O)₂O-, -P(=O)-, -P(=O)O-, -OP(=O)O-, -P(=O)₂-, -P(=O)₂O-, -OP(=O)₂O-, -NR'-, and -C(OR')R'-, wherein R's at respective occurrences are each

35 independently a hydrogen atom or a C1-C10 hydrocarbon

group;

R^1 , R^2 , R^3 , and R^4 are each independently a hydrogen atom or a C1-C10 hydrocarbon group; and

n and m are each independently an integer of 0 to 10,
 5 with at least one of X, Y, or Z being $-C(=O)-$, $-C(=O)O-$, $-OC(=O)O-$, or $-C(OR')R'-$.

[0009]

The disclosure (4) relates to the processing aid according to the disclosure (3), wherein, in the formula 1,
 10 X is a divalent group constituted by at least one selected from the group consisting of X^1 and X^2 ,

X^1 is a group constituted by at least one selected from the group consisting of $-C(=O)-$, $-C(=NR')-$, $-S(=O)_2-$, $-NR'-$, $-CR'R'-$, and $-C(OR')R'-$, wherein R's at respective
 15 occurrences are each independently a hydrogen atom or a C1-C10 hydrocarbon group; and

X^2 is a C1-C12 aromatic hydrocarbon group optionally containing a substituent.

[0010]

20 The disclosure (5) relates to the processing aid according to the disclosure (4), wherein, in the formula 1, X is a divalent group containing at least one selected from the group consisting of $-C(=O)-$, $-CR'R'-$, and $-C(OR')R'-$, wherein R's at respective occurrences are each
 25 independently a hydrogen atom or a C1-C10 hydrocarbon group.

[0011]

The disclosure (6) relates to the processing aid according to any one of the disclosures (3) to (5),
 30 wherein, in the formula 1, Y and Z are each independently a group constituted by at least one selected from the group consisting of a single bond, $-O-$, $-C(=O)-$, $-C(=O)O-$, $-C(=NR')-$, $-C(=NR')O-$, $-S-$, $-S(=O)_2-$, $-S(=O)_2O-$, $-NR'-$, and $-C(OR')R'-$, wherein R's at respective occurrences are each
 35 independently a hydrogen atom or a C1-C10 hydrocarbon

group.

[0012]

The disclosure (7) relates to the processing aid according to the disclosure (6), wherein, in the formula 1,
5 Y and Z are each independently a group constituted by at least one selected from the group consisting of a single bond, -O-, -C(=O)-, and -C(=O)O-.

[0013]

The disclosure (8) relates to the processing aid
10 according to any one of the disclosures (1) to (7), wherein the processing aid has a melt flow rate of 0.001 to 100 g/10 min at 190°C and a 2.16 kgf load.

[0014]

The disclosure (9) relates to the processing aid
15 according to any one of the disclosures (1) to (8), wherein the processing aid includes at least one selected from the group consisting of polybutylene adipate terephthalate, polybutylene succinate, polylactic acid, and an ethylene-vinyl alcohol copolymer.

20 [0015]

The disclosure (10) relates to a masterbatch containing: the processing aid according to any one of the disclosures (1) to (9); and a thermoplastic resin (A).

[0016]

25 The disclosure (11) relates to the masterbatch according to the disclosure (10), wherein the thermoplastic resin (A) includes a polyolefin resin.

[0017]

The disclosure (12) relates to the masterbatch
30 according to the disclosure (10) or (11), wherein the thermoplastic resin (A) includes metallocene-catalyzed linear low-density polyethylene.

[0018]

The disclosure (13) relates to the masterbatch
35 according to any one of the disclosures (10) to (12),

wherein a difference in surface free energy between the processing aid and the thermoplastic resin (A) is 1.5 mN/m or more.

[0019]

5 The disclosure (14) relates to the masterbatch according to any one of the disclosures (10) to (13), wherein a difference in surface free energy between the processing aid and the thermoplastic resin (A) is 4.0 to 45 mN/m.

10 [0020]

 The disclosure (15) relates to the masterbatch according to any one of the disclosures (10) to (14), wherein a mass ratio of the thermoplastic resin (A) to the processing aid (thermoplastic resin (A):processing aid) is

15 92:8 to 70:30.

[0021]

 The disclosure (16) relates to a thermoplastic resin composition containing: at least one of the processing aid according to any one of the disclosures (1) to (9) or the

20 masterbatch according to any one of the disclosures (10) to (15); and a thermoplastic resin (B).

[0022]

 The disclosure (17) relates to the thermoplastic resin composition according to the disclosure (16), wherein

25 the thermoplastic resin (B) includes a polyolefin resin.

[0023]

 The disclosure (18) relates to the thermoplastic resin composition according to the disclosure (16) or (17), wherein the thermoplastic resin (B) includes metallocene-

30 catalyzed linear low-density polyethylene.

[0024]

 The disclosure (19) relates to the thermoplastic resin composition according to any one of the disclosures (16) to (18), wherein a difference in surface free energy

35 between the processing aid and the thermoplastic resin (B)

is 1.5 mN/m or more.

[0025]

The disclosure (20) relates to the thermoplastic resin composition according to any one of the disclosures
5 (16) to (19), wherein a difference in surface free energy between the processing aid and the thermoplastic resin (B) is 4.0 to 45 mN/m.

[0026]

The disclosure (21) relates to the thermoplastic
10 resin composition according to any one of the disclosures (16) to (20), wherein the processing aid is contained in an amount of 0.1 to 1.0% by mass.

[0027]

The disclosure (22) relates to a molded article
15 containing the thermoplastic resin composition according to any one of the disclosures (16) to (21).

[0028]

The disclosure (23) relates to the molded article according to the disclosure (22), wherein the molded
20 article is in a form of a tube, a film, or a sheet.

[0029]

The disclosure (24) relates to a method for producing the processing aid according to any one of the disclosures
(1) to (9), including a mixing step and an ejecting step.

25 [0030]

The disclosure (25) relates to a method for producing the masterbatch according to any one of the disclosures
(10) to (15), including a mixing step and an ejecting step.

[0031]

30 The disclosure (26) relates to a method for producing the thermoplastic resin composition according to any one of the disclosures (16) to (21), including a mixing step and an ejecting step.

[0032]

35 The disclosure (27) relates to a method for producing

the molded article according to the disclosure (22) or (23), including a molding step.

- Advantageous Effects of Invention

5 [0033]

The disclosure can provide a processing aid and a masterbatch capable of improving the processibility of thermoplastic resins, a thermoplastic resin composition and a molded article containing these, and production methods
10 thereof.

DESCRIPTION OF EMBODIMENTS

[0034]

The disclosure is described in detail below.

15 [0035]

<Processing aid>

The processing aid of the disclosure has a surface free energy of 28.5 mN/m or more and is substantially free from fluorine.

20 [0036]

The processing aid of the disclosure can provide good processibility (in particular, good extrusion processibility). The development of the processing aid of the disclosure is based on the finding that surface free
25 energy strongly correlates with processibility and that maintaining the surface free energy within a specific range leads to particularly good processibility.

[0037]

The processing aid of the disclosure preferably has a
30 surface free energy of 28.6 mN/m or more, more preferably 29.0 mN/m or more, while preferably 55.0 mN/m or less, more preferably 50.0 mN/m or less, still more preferably 45.0 mN/m or less, further preferably 40.0 mN/m or less, even more preferably 35.0 mN/m or less.

35 The surface free energy can be calculated by the

methods in EXAMPLES.

[0038]

The processing aid of the disclosure is substantially free from fluorine. The phrase "substantially free from
5 fluorine" means that the processing aid has a fluorine content of 10 ppm or less (preferably 1 ppm or less, more preferably 0.1 ppm or less). The processing aid of the disclosure is particularly preferably free from fluorine (has a fluorine content of 0% by mass).

10 [0039]

The processing aid of the disclosure preferably contains a structural unit represented by the following formula 1, and is more preferably a polymer containing a structural unit represented by the following formula 1:

15 $-X-(CR^1R^2)_n-Y-(CR^3R^4)_m-Z-$ (formula 1)

wherein X is a single bond or a divalent group optionally containing a functional group;

Y and Z are each independently a group constituted by at least one selected from the group consisting of a single
20 bond, $-O-$, $-C(=O)-$, $-C(=O)O-$, $-OC(=O)O-$, $-C(=NR')-$, $-C(=NR')O-$, $-OC(=NR')O-$, $-S-$, $-S(=O)-$, $-S(=O)O-$, $-OS(=O)O-$, $-S(=O)_2-$, $-S(=O)_2O-$, $-OS(=O)_2O-$, $-P(=O)-$, $-P(=O)O-$, $-OP(=O)O-$, $-P(=O)_2-$, $-P(=O)_2O-$, $-OP(=O)_2O-$, $-NR'-$, and $-C(OR')R'-$, wherein R's at respective occurrences are each
25 independently a hydrogen atom or a C1-C10 hydrocarbon group;

R^1 , R^2 , R^3 , and R^4 are each independently a hydrogen atom or a C1-C10 hydrocarbon group; and

n and m are each independently an integer of 0 to 10,
30 with at least one of X, Y, or Z being $-C(=O)-$, $-C(=O)O-$, $-OC(=O)O-$, or $-C(OR')R'-$.

[0040]

When the processing aid of the disclosure is the polymer, its surface free energy varies depending on the
35 mole fraction of chain ends in the processing aid, which is

calculated using the following calculation method. A higher chain end content leads to a higher surface free energy, whereas a lower chain end content leads to a lower surface free energy. The mole fraction of chain ends of the processing aid of the disclosure is preferably 0.00001 to 0.00450 mol%.

Calculation method:

When the polymer amount (g) is set to 1 g:

Monomer amount (mol) = 1 g/Monomer molecular weight (g/mol)

10 Number of monomers (units) = Monomer amount (mol) $\times$ 6.02×10^{23}

Here, assuming the number average molecular weight of the polymer is M_n :

15 Number of polymer chains (chains) = Number of monomers (units)/ M_n

Number of polymer chain ends (units) = Number of polymer chains (chains) $\times$ 2

Number of moles of chain ends (mol) = Number of polymer chain ends (units)/ 6.02×10^{23}

20 Mole fraction of chain ends (mol%) = Number of moles of chain ends (mol)/Monomer amount (mol)
[0041]

The mole fraction of chain ends varies depending on the oligomer (a component with a molecular weight of 5000 g/mol or less) content in the processing aid. A higher oligomer content leads to a higher mole fraction of chain ends, whereas a lower oligomer content leads to a lower mole fraction of chain ends. The oligomer content can be reduced by purification. The purification is performed by a method including dropping the polymer dissolved in a good solvent into a poor solvent and collecting the resulting precipitate, for example.

[0042]

35 In the formula 1, preferably, X is a divalent group constituted by at least one selected from the group

consisting of X^1 and X^2 ,

wherein X^1 is a group constituted by at least one selected from the group consisting of $-C(=O)-$, $-C(=NR')-$, $-S(=O)_2-$, $-NR'-$, $-CR'R'-$, and $-C(OR')R'-$, wherein R' 's at respective
 5 occurrences are each independently a hydrogen atom or a C1-C10 hydrocarbon group; and

X^2 is a C1-C12 aromatic hydrocarbon group optionally containing a substituent.

[0043]

10 In the formula 1, X is more preferably a divalent group containing at least one selected from the group consisting of $-C(=O)-$, $-CR'R'-$, and $-C(OR')R'-$, wherein R' 's at respective occurrences are each independently a hydrogen atom or a C1-C10 hydrocarbon group.

15 [0044]

In the formula 1, R' 's at respective occurrences are preferably each independently a hydrogen atom or a C1-C7 hydrocarbon group, more preferably a hydrogen atom or a C1-C4 hydrocarbon group, still more preferably a hydrogen atom
 20 or a C1 hydrocarbon group.

[0045]

In the formula 1, Y and Z are preferably each independently a group constituted by at least one selected from the group consisting of a single bond, $-O-$, $-C(=O)-$, $-C(=O)O-$, $-C(=NR')-$, $-C(=NR')O-$, $-S-$, $-S(=O)_2-$, $-S(=O)_2O-$, $-NR'-$, and $-C(OR')R'-$, wherein R' 's at respective occurrences
 25 are each independently a hydrogen atom or a C1-C10 hydrocarbon group.

[0046]

30 In the formula 1, Y and Z are preferably each independently a group constituted by at least one selected from the group consisting of a single bond, $-O-$, $-C(=O)-$, and $-C(=O)O-$.

[0047]

35 In the formula 1, R^1 , R^2 , R^3 , and R^4 are preferably

each independently a hydrogen atom or a C1-C7 hydrocarbon group, more preferably a hydrogen atom or a C1-C4 hydrocarbon group, still more preferably a hydrogen atom or a C1 hydrocarbon group.

5 [0048]

In the formula 1, n and m are preferably each independently an integer of 0 to 8, more preferably an integer of 0 to 6, still more preferably an integer of 0 to 4, particularly preferably an integer of 0 to 2.

10 [0049]

The polymer may contain a structural unit other than the structural unit represented by the formula 1. Examples of the structural unit other than the structural unit represented by the formula 1 include structural units
15 derived from: glycol compounds such as ethylene glycol, propylene glycol, butanediol, heptanediol, hexanediol, octanediol, nonanediol, decanediol, 1,4-cyclohexanedimethanol, neopentyl glycol, glycerol, pentaerythritol, bisphenol A, polyethylene glycol, polypropylene glycol, and polytetramethylene glycol;
20 dicarboxylic acids such as oxalic acid, adipic acid, sebacic acid, azelaic acid, dodecanedioic acid, malonic acid, glutaric acid, cyclohexanedicarboxylic acid, terephthalic acid, isophthalic acid, phthalic acid, naphthalenedicarboxylic acid, bis(p-carboxyphenyl)methane, anthracenedicarboxylic acid, 4,4'-diphenyl ether
25 dicarboxylic acid, sodium 5-sulfoisophthalate, and tetrabutylphosphonium 5-isophthalate; hydroxycarboxylic acids such as glycolic acid, hydroxypropionic acid, hydroxybutyric acid, hydroxyvaleric acid, hydroxycaproic
30 acid, and hydroxybenzoic acid; and lactones such as caprolactone, valerolactone, propiolactone, undecalactone, and 1,5-oxepan-2-one.

[0050]

35 The amount of the structural unit represented by the

formula 1 in the processing aid of the disclosure is preferably 0.1% by mass or more, more preferably 1% by mass or more, still more preferably 10% by mass or more, particularly preferably 20% by mass or more, while
5 preferably 99.9% by mass or less, more preferably 99% by mass or less, still more preferably 95% by mass or less.
[0051]

Examples of the processing aid include polybutylene adipate terephthalate (PBAT), polylactic acid (PLA),
10 polybutylene succinate (PBS), polybutylene succinate adipate (PBSA), and an ethylene-vinyl alcohol copolymer (EVOH). The processing aid preferably includes at least one selected from the group consisting of PBAT, PLA, PBS, and EVOH, more preferably at least one selected from the
15 group consisting of PBAT, PLA, PBS, and EVOH, still more preferably at least one selected from the group consisting of PLA and EVOH.

The processing aid preferably does not include polyethylene glycol (PEG).
20 [0052]

The ethylene-vinyl alcohol copolymer has an ethylene content of preferably 10 mol% or more, more preferably 20 mol% or more, still more preferably 30 mol% or more, while preferably 60 mol% or less, more preferably 50 mol% or
25 less, still more preferably 40 mol% or less. The ethylene-vinyl alcohol copolymer having an ethylene content within this range can lead to a better effect of improving the processibility.

The ethylene content herein is determined by nuclear
30 magnetic resonance (NMR) analysis.
[0053]

The ethylene-vinyl alcohol copolymer is preferably one obtained by saponifying an ethylene-vinyl ester copolymer, and is particularly preferably one obtained by
35 saponifying an ethylene-vinyl acetate copolymer.

[0054]

The ethylene-vinyl alcohol copolymer has a degree of saponification of preferably 80 to 100 mol%.

[0055]

5 Copolymerization of ethylene and vinyl acetate may involve use of a different fatty acid vinyl ester (e.g., vinyl propionate or vinyl pivalate). The ethylene-vinyl alcohol copolymer may contain 0.0002 to 0.2 mol% of a vinylsilane compound as a copolymerized component.

10 Examples of the vinylsilane compound include vinyltrimethoxysilane, vinyltriethoxysilane, vinyltri(β -methoxy-ethoxy)silane, and γ -methacryloxypropylmethoxysilane. Preferably used among these are vinyltrimethoxysilane and vinyltriethoxysilane.

15 [0056]

Copolymerization of ethylene and vinyl acetate may involve the presence of a small amount of a monomer different from the aforementioned fatty acid vinyl ester or vinylsilane compound, such as any of α -olefins such as
20 propylene, isobutylene, α -octene, and α -dodecene; unsaturated acids such as acrylic acid, methacrylic acid, crotonic acid, maleic acid, and itaconic acid, and anhydrides, salts, and mono- or dialkyl esters thereof; nitriles such as acrylonitrile and methacrylonitrile;
25 amides such as acrylamide and methacrylamide; olefin sulfonic acids such as ethylene sulfonic acid, allyl sulfonic acid, and methallyl sulfonic acid and salts thereof; alkyl vinyl ethers, vinyl ketones, N-vinylpyrrolidone, vinyl chloride, and vinylidene chloride.

30 [0057]

The melting point of the processing aid is preferably 65°C or higher, more preferably 70°C or higher, still more preferably 75°C or higher, further preferably 80°C or higher, while preferably 190°C or lower, more preferably
35 185°C or lower, still more preferably 180°C or lower. The

processing aid having a melting point within this range can lead to a better effect of improving the processibility.

The melting point herein is the temperature corresponding to the maximum value on a heat-of-fusion curve at a temperature-increasing rate of 10°C/min using a differential scanning calorimeter (DSC).

[0058]

The processing aid has a melt flow rate (MFR) of preferably 0.001 g/10 min or higher, more preferably 0.01 g/10 min or higher, still more preferably 0.05 g/10 min or higher, further preferably 0.1 g/10 min or higher, particularly preferably 0.5 g/10 min or higher, while preferably 500 g/10 min or lower, more preferably 300 g/10 min or lower, still more preferably 150 g/10 min or lower, further preferably 100 g/10 min or lower, further preferably 40 g/10 min or lower, even more preferably 20 g/10 min or lower, particularly preferably 10 g/10 min or lower. The processing aid having a MFR within this range can lead to a better effect of improving the processibility.

The MFR herein is determined under conditions of 190°C and a 2.16 kgf load in conformity with ASTM D1238.

[0059]

The processing aid of the disclosure may be a mixture of the aforementioned component (component A) and a different component (component B). Examples of the different component include a synergist including at least one selected from the group consisting of a polyol having a melting point of 80°C or lower, polycaprolactone, silicone, and a polyamide-polyether block copolymer.

[0060]

The melting point of the polyol is at least 80°C or lower, preferably 75°C or lower, more preferably 70°C or lower, still more preferably 68°C or lower, while preferably 10°C or higher, more preferably 20°C or higher,

still more preferably 25°C or higher. The polyol having a melting point within this range can lead to a better effect of improving the processibility.

[0061]

5 The polyol can be represented by $A[(OR^{11})_{x2}OR^{12}]_{y2}$, wherein A is commonly alkylene having one or more ether bonds; $y2$ is 2 or 3, $(OR^{11})_{x2}$ is a poly(oxyalkylene) chain having multiple ($x2$) oxyalkylene groups OR^{11} ; R^{11} s are each independently C2-C5 alkylene or, in some embodiments, C2-C3
10 alkylene; R^{12} is hydrogen, alkyl, aryl, arylalkenyl, alkylarylenyl, -C(O)-alkyl, -C(O)-aryl, -C(O)-arylalkenyl, or -C(O)-alkylarylenyl, where -C(O)- bonds to O of OR^{12} ; and $x2$ is 10 to 230000.

[0062]

15 The polyol may be, for example, a homopolymer such as poly(oxypropylene) in which R^{11} is -CH₂CH₂- or poly(oxyethylene) in which R^{11} is -C₃H₆-.

[0063]

20 The polyol may be a chain of randomly distributed oxyalkylene groups (e.g., -OC₂H₄- and -OC₃H₆- units which are copolymers) or a chain including alternating blocks of repeated oxyalkylene groups (e.g., a polymer including a (-OC₂H₄-)_{a1} block and a (-OC₃H₆-)_{b1} block, where $a1 + b1$ is 10 to 230000).

25 [0064]

 In some embodiments, A in the polyol is ethylene, -CH₂-CH(-)-CH₂- (derived from glycerol), CH₃CH₂C(CH₂-)₃ (derived from 1,1,1-trimethylolpropane), poly(oxypropylene), -CH₂CH₂-O-CH₂CH₂-, or -CH₂CH₂-O-CH₂CH₂-O-CH₂CH₂-; and R^{12} is hydrogen, methyl, butyl, phenyl, benzyl, acetyl, benzoyl, or stearyl.

[0065]

35 The polyol may be polyester prepared from a dicarboxylic acid and a poly(oxyalkylene) polymer represented by $A[(OR^{11})_{x2}OR^{12}]_{y2}$, wherein A, R^{11} , and $x2$ are

as defined above; R^{12} is hydrogen; and y_2 is 2.

[0066]

One of the polyols may be used alone or two or more thereof may be used in combination. To achieve an excellent effect of improving the processibility, polyethylene glycol or polyethylene oxide is preferred, and polyethylene glycol is particularly preferred.

[0067]

The polyethylene glycol has a number average molecular weight (M_n) of preferably 1000 or higher, more preferably 3000 or higher, still more preferably 5000 or higher, while preferably 50000 or lower, more preferably 45000 or lower, still more preferably 40000 or lower. The polyethylene glycol having a number average molecular weight within this range can lead to a better effect of improving the processibility.

The number average molecular weight herein is determined by calculation from the hydroxyl value determined in conformity with JIS K0070.

[0068]

The polyethylene oxide has a viscosity average molecular weight (M_v) of preferably 100000 or higher, more preferably 120000 or higher, still more preferably 140000 or higher, while preferably 10000000 or lower, more preferably 1600000 or lower, still more preferably 500000 or lower. The polyethylene oxide having a viscosity average molecular weight within this range can lead to a better effect of improving the processibility.

The viscosity average molecular weight herein is calculated as follows.

An Ostwald viscometer is used to determine at 35°C the specific viscosities η_{sp} of aqueous solutions containing a polymer at various concentrations c (g/dl) in pure water; each specific viscosity is divided by the corresponding polymer concentration to provide the reduced

viscosity; based on the relationship between the resulting reduced viscosity (η_{sp}/c) and the polymer concentration c , with the polymer concentration c being extrapolated to 0, the $[\eta]$ value is calculated. The $[\eta]$ value is substituted
5 into the following formula, whereby the viscosity average molecular weight M is calculated.

$$\text{Formula: } [\eta] = 6.4 \times 10^{-5} M^{0.82}$$

[0069]

The polycaprolactone may be a homopolymer of ϵ -
10 caprolactone or may be a modified polycaprolactone. Examples of the modified polycaprolactone include those modified with, for example, 1,4-butanediol combined during ring-opening polymerization of ϵ -caprolactone and those modified with, for example, an ether or ester group at an
15 end of a polymer.

[0070]

The polycaprolactone has a weight average molecular weight (M_w) of preferably 2000 or higher, more preferably 10000 or higher, still more preferably 25000 or higher,
20 while preferably 100000 or lower, more preferably 95000 or lower, still more preferably 90000 or lower. The polycaprolactone having a weight average molecular weight within this range can lead to a better effect of improving the processibility.

25 The weight average molecular weight herein is determined in polystyrene equivalent by gel permeation chromatography (GPC).

[0071]

The polycaprolactone has a melting point of
30 preferably 80°C or lower, more preferably 75°C or lower, still more preferably 70°C or lower, further preferably 68°C or lower, while preferably 10°C or higher, more preferably 20°C or higher, still more preferably 45°C or higher. The polycaprolactone having a melting point within
35 this range can lead to a better effect of improving the

processibility.

[0072]

The silicone may be basically any organic silicon compound known to those skilled in the art with the term
 5 silicone polymer. An appropriate definition of the silicone is found in Winnacker/Kuchler: "Chemische Technik" [Chemical Technology], R. Dittmeyer, W. Keim, G. Kreysa, A. Oberholz (editor), Vol. 5: "Organische Zwischenverbindungen, Polymere" [Organic Intermediates,
 10 Polymers], Chapter: "Silicones", Wiley-VCH, Weinheim, 2005.
 [0073]

The silicone may be a substituted or unsubstituted linear oligo- or polydiorganosiloxane, a branched silicone polymer, silicone resin, or a crosslinked silicone polymer.
 15 A mixture of various silicone polymers may also be used, of course. As described above, a silicone-containing copolymer may be used, such as a polyether functional silicone, a silicone containing a urea or urethane unit, or a silicone block copolymer with an organic polymer. To
 20 achieve better additivity, particularly preferred is to use a high molecular weight polydiorganosiloxane that can contain a non-silicone component, such as filler, e.g., fine silicic acid particulate, chalk, talc, or a sheet-shaped silicic acid salt.

25 [0074]

Preferably, the silicone polymer corresponds to the formula A $[R^{13}_3SiO_{1/2}]_{a2}[SiR^{13}_2O_{2/2}]_{b2}[R^{13}SiO_{3/2}]_{c2}[SiO_{4/2}]_{d2}$, wherein R^{13} is hydrogen, -OH, or a C1-C18 substituted or unsubstituted hydrocarbon residue; and $a2$, $b2$, $c2$, and $d2$
 30 each mean 0 or an integer, with $a2 + b2 + c2 + d2$ being an integer of 5 to 15000.

[0075]

Examples of the C1-C18 hydrocarbon residue R^{13} include alkyl residues, such as methyl, ethyl, n-propyl,
 35 isopropyl, n-butyl, 2-butyl, isobutyl, tert-butyl, n-

pentyl, isopentyl, neopentyl, a tert-pentyl residue, hexyl residues, e.g., a n-hexyl residue, heptyl residues, e.g., a n-heptyl residue, octyl residues, e.g., a n-octyl residue and an isooctyl residue, a 2,2,4-trimethylpentyl residue, 5 nonyl residues, e.g., a n-nonyl residue, decyl residues, e.g., a n-decyl residue, cycloalkyl residues, e.g., a cyclopentyl residue, a cyclohexyl residue, a 4-ethylcyclohexyl residue, and a cycloheptyl residue, a norbornyl residue, and a methylcyclohexyl residue.

10 Preferred among the alkyl residues are C1-C6 residues, such as methyl and ethyl residues, particularly a methyl residue.

[0076]

Examples of R^{13} also include C1-C18 unsaturated 15 hydrocarbon residues such as alkenyl residues, e.g., a vinyl residue, a 2-propen-2-yl residue, an allyl residue, a 3-buten-1-yl residue, a 5-hexen-1-yl residue, and a 10-undecen-1-yl residue, as well as cycloalkenyl residues (a 2-cyclohexenyl residue, a 3-cyclohexenyl residue, a 20 cyclopentadienyl residue, and a 2-(cyclohex-3-en-1-yl)ethyl residue); aryl residues, e.g., a phenyl residue, a biphenyl residue, and a naphthyl residue; alkaryl residues, e.g., o-, m-, or p-tolyl residue and phenethyl residues (a 2-phenylethyl residue and a 1-phenylethyl 25 residue); as well as aralkyl residues, e.g., a benzyl residue. Preferred C1-C18 unsaturated hydrocarbon residues R^{13} are a vinyl residue and a phenyl residue.

[0077]

Examples of a substituted hydrocarbon residue as the 30 residue R^{13} include halogenated hydrocarbons such as a chloromethyl residue, a 3-chloropropyl residue, a 3-bromopropyl residue, a 3,3,3-trifluoropropyl residue, and a 5,5,5,4,4,3,3-heptafluoropentyl residue, as well as a chlorophenyl residue, a dichlorophenyl residue, and a 35 trifluorotolyl residue.

[0078]

The residue R^{13} is preferably coupled with a silicone polymer represented by the formula A via a Si-C bond, and may be coupled with the silicone polymer via an oxygen atom -O-.

[0079]

R^{13} preferably contains 1 to 6 carbon atoms. Particularly preferred are an ethyl residue, a phenyl residue, a vinyl residue, and a methyl residue.

10 [0080]

Preferably, the number represented by $a^2 + b^2 + c^2 + d^2$ means at least 10, more preferably at least 100, particularly preferably at least 1000 and at most 15000, more preferably at most 10000, particularly preferably at most 7000.

[0081]

Preferably, the number represented by $c^2 + d^2$ means $< 0.1 \times (a^2 + b^2 + c^2 + d^2)$, particularly $c^2 + d^2 < 0.05 \times (a^2 + b^2 + c^2 + d^2)$.

20 [0082]

Preferably at least 50%, more preferably at least 70%, particularly preferably at least 80% of all residues R^{13} mean a methyl residue.

[0083]

25 In principle, every silicone polymer corresponding to the formula A may be used. Still, preferred is a silicone polymer having a dynamic viscosity of higher than 1000 mPa·s, which is measured using a plate-cone system (cone CP50-2) having an opening angle of 2° and a diameter of 50 mm with a rheometer "MCR 302" available from Anton Paar at a measurement temperature of $25.00^\circ\text{C} \pm 0.05^\circ\text{C}$ and a shear rate of 1 sec⁻¹, preferably in conformity with DIN EN ISO3219:1994 and DIN 53019.

[0084]

35 Among these silicones, a silicone polymer having a

very high molecular weight may be used, such as UHMW polysiloxane (ultra-high molecular weight; described in K. J. Ryan, et al., Journal of Vinyl & Additive Technology, March 2000, Vol. 6, No. 1, pp. 7-19).

5 [0085]

UHMW polysiloxane has a degree of polymerization within a range from > 1000 to about 14000, which corresponds to a number average molecular weight from 74 kg/mol to 1000 kg/mol.

10 [0086]

Typical UHMW polysiloxane has a dynamic viscosity from 10 kPa·s to 50 kPa·s, preferably from 15 kPa·s to 30 kPa·s, which is determined using an airborne rotational rheometer preferably in conformity with DIN EN ISO3219:1994 and DIN 53019, where a plate-plate system (diameter 25 mm) having a measurement gap of 0.5 mm is used. The measurement temperature is 25.00°C +/- 0.1°C. The shear rate gradient is 0.1 sec⁻¹. The viscosity described refers to an arithmetic mean of three distinct, independently measured values.

20

[0087]

Owing to its inexpensiveness and effectiveness, particularly preferred among the UHMW polysiloxanes is a high molecular weight polydimethylsiloxane having a dynamic viscosity from 1 kPa·s to 50 kPa·s, preferably from 10 to 40 kPa·s, particularly preferably from 15 to 30 kPa·s (preferably determined by the aforementioned method).

25

[0088]

Examples of the UHMW polysiloxane include commercially available UHMW polysiloxanes such as MULTIBASE® MB50-001 and MULTIBASE® MB50-002 available from Dupont, GENIOPLAST® PELLET S, GENIOPLAST® PELLET P PLUS, GENIOPLAST® PE50S08, and GENIOPLAST® PP50S12 available from Wacker Asahikasei Silicone Co., Ltd., and mixtures of any of these, with MB50-002 and GENIOPLAST® PELLET S being

35

preferred.

[0089]

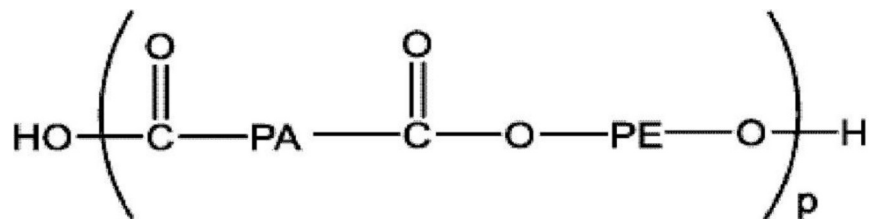
The silicone polymer can be commercially available in the form of pellets or granules or masterbatch for ready-to-use, which may be mixed with thermoplastic granules before additional processing.

[0090]

The polyamide-polyether block copolymer is a copolymer including a polyamide block and a polyether block in the polymer backbone. In the disclosure, such a block copolymer including a polyamide block and a polyether block can also be referred to as a "polyamide/polyether block copolymer". This may also be abbreviated to "PEBA copolymer" or "PEBA".

In some embodiments of the disclosure, the PEBA copolymer can be represented by the following formula:

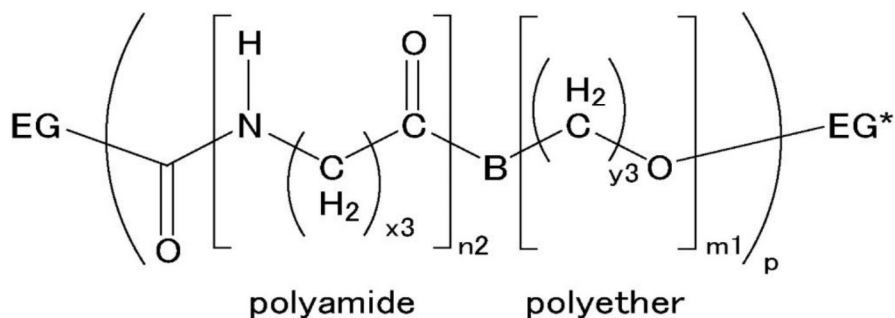
[Chem. 1]



[0091]

wherein PA represents a polyamide block, PE represents a polyether block, and p represents the length of the PEBA copolymer, which represents the total number of the polyamide and polyether blocks. In some embodiments of the disclosure, the PEBA copolymer can be represented by the following formula:

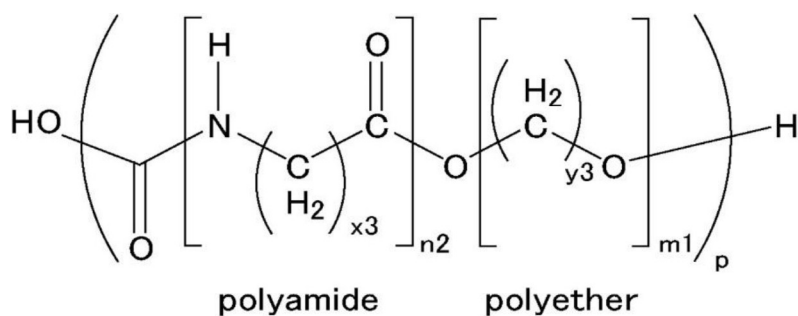
[Chem. 2]



[0092]

wherein EG represents a first unspecified end group; B represents an unspecified crosslinking group; and EG* represents a second unspecified end group, where EG, B, and EG* are determined by a synthesis method used for producing a PEBA copolymer, wherein n2 represents the length of the polyamide block; x3 represents the length of an amide component in the polyamide block; m1 represents the length of the poly(ether) block; y3 represents the length of an ether component in the poly(ether) block; and p represents the length of the PEBA copolymer, which represents the total number of the polyamide and polyether blocks.

In some embodiments of the disclosure, the PEBA copolymer can be represented by the following formula:
[Chem. 3]



[0093]

wherein n2 represents the length of the polyamide block; x3 represents the length of an amide component in the polyamide block; m1 represents the length of the poly(ether) block; y3 represents the length of an ether component in the poly(ether) block; and p represents the

length of the PEBA copolymer, which represents the total number of the polyamide and polyether blocks.

[0094]

The polyamide block in the PEBA copolymer is derived
5 from polyamide-12 (PA-12), polyamide-11 (PA-11), polyamide-6 (PA-6), or polyamide-66 (PA-66).

[0095]

The weight average molecular weight (e.g., Mw and Mn)
of the PEBA copolymer can be determined, for example, by
10 gel permeation chromatography using a narrow molecular weight polymer standard based on a known technique in the technical field (i.e., by size-exclusion chromatography).

[0096]

In an embodiment, the number average molecular weight
15 Mn of the polyamide block in the PEBA copolymer is about 100 to about 15000 g/mol, or about 300 to about 15000 g/mol, or about 600 to about 10000 g/mol, or about 600 to about 5000 g/mol.

The number average molecular weight Mn of the
20 polyether block in the PEBA copolymer is about 100 to about 15000 g/mol, about 100 to about 10000 g/mol, about 100 to about 6000 g/mol, about 100 to about 3000 g/mol, about 200 to about 6000 g/mol, about 200 to about 3000 g/mol, about 250 to about 2000 g/mol, about 750 to about 3500 g/mol, or
25 about 1000 to about 3000 g/mol.

[0097]

The PEBA copolymer has a number average molecular weight Mn of 10000 to 500000 g/mol, including any subrange within these ranges and any number within these ranges. In
30 an embodiment of the disclosure, for example, the number average molecular weight Mn of the PEBA copolymer is 10000 to 400000 g/mol, or 10000 to 300000 g/mol, 10000 to 250000 g/mol, or 15000 to 300000 g/mol, or 20000 to 300000 g/mol, or 15000 to 200000 g/mol, or 20000 to 200000 g/mol, or
35 30000 to 250000 g/mol, or about 25000 to about 75000 g/mol,

or about 50000 to about 75000 g/mol, or about 100000 to about 150000 g/mol.

The number average molecular weight M_n of the PEBA copolymer is at least 10000 g/mol, at least 20000 g/mol, at least 25000 g/mol, exceeding 25000 g/mol, at least 30000 g/mol, exceeding 30000 g/mol, at least 35000 g/mol, exceeding 35000 g/mol, at least 50000 g/mol, or exceeding 50000 g/mol.

[0098]

10 In an embodiment, the PEBA copolymer has a weight average molecular weight M_w of 25000 to 500000 g/mol, including any subrange within these ranges and any number within these ranges. In an embodiment of the disclosure, for example, the weight average molecular weight M_w of the
15 PEBA copolymer is about 100000 to about 250000 g/mol, or about 100000 to about 150000 g/mol, or about 125000 to about 150000 g/mol.

The polyamide and polyether blocks in the PEBA copolymer may be randomly distributed.

20 [0099]

The PEBA copolymer contains a polyamide block and a polyether block and the polyamide block may occupy at least 50% by mass of the copolymer. The PEBA copolymer contains a polyamide block and a polyether block and the polyether
25 block may occupy at least 50% by mass of the copolymer. The PEBA copolymer contains a polyamide block and a polyether block and the ratio by mole of the polyamide block to the polyether block may fall within a range of 1:3 to 3:1, or 1:2 to 2:1, or 3:2 to 1:3, or 2:3 to 3:1, or
30 about 1:1.

[0100]

The PEBA copolymer containing a polyamide block and a polyether block can be prepared by reacting precursors of the polyamide and polyether blocks. For example, a lactam,
35 a polyether diol, and a chain-limiting dioic acid may be

reacted together in the presence of a small amount of water, thereby producing a length-variable PEBA copolymer containing a polyamide block and a polyether block statistically randomly distributed in the block copolymer chain.

5 The polyether block may be derived from poly(oxyethylene), poly(oxypropylene), or poly(tetramethylene ether)glycol, each of which in the natural state may be co-condensed with a polyamide block having a carboxylic acid chain end. A chain-limiting agent may be present during the polycondensation reaction to provide a PEBA copolymer containing a polyamide block and a polyether block randomly distributed in the block copolymer.

15 The polyether block is derived from poly(oxyethylene), poly(oxypropylene), or poly(tetramethylene ether)glycol, each of which are first aminated into polyether diamine and then co-condensed with a polyamide block having a carboxylic acid chain end. A chain-limiting agent may be present during the polycondensation reaction to provide a PEBA copolymer containing a polyamide block and a polyether block randomly distributed in the block copolymer.

The polyether block can be derived from poly(oxyethylene), which is also known as polyethylene glycol (PEG).

The polyether block can be derived from poly(oxypropylene), which is also known as polypropylene glycol (PPG).

30 The polyether block can be derived from poly(tetramethylene ether)glycol (PTMG), which is also known as polytetramethylene oxide (PTMEO) or polytetrahydrofuran (PTHF).
[0101]

35 The PEBA copolymer contains i) a polyamide block

selected from polyamide-12 (PA-12), polyamide-11 (PA-11), polyamide-6 (PA-6), or a mixture of any of these and ii) a polyether block selected from polyethylene glycol (PEG), polypropylene glycol (PPG), polytetrahydrofuran (PTHF), or
5 a mixture of any of these.

[0102]

The PEBA copolymer contains i) a polyamide block selected from polyamide-12 (PA-12), polyamide-11 (PA-11), polyamide-6 (PA-6), or a mixture of any of these and ii) a
10 polyether block which is polyethylene glycol (PEG). In an embodiment of the disclosure, the PEBA copolymer contains i) a polyamide block which is polyamide-12 (PA-12) and ii) a polyether block which is polyethylene glycol (PEG).

[0103]

15 The PEBA copolymer contains 10 to 20 polyamide blocks and 10 to 20 polyether blocks.

[0104]

The PEBA copolymer contains a single species of the polyamide block and a single species of the polyether
20 block.

[0105]

The PEBA copolymer contains i) a polyamide block which is polyamide-12 (PA-12) and ii) a polyether block which is polyethylene glycol (PEG), wherein the polyamide-
25 12 block occupies about 30% by mass to 70% by mass of the copolymer and the polyethylene glycol block occupies about 70% by mass to 30% by mass of the copolymer.

[0106]

The PEBA copolymer contains i) a polyamide block
30 which is polyamide-12 (PA-12) and ii) a polyether block which is polyethylene glycol (PEG), wherein the polyamide-12 block occupies about 40% by mass to 60% by mass of the copolymer and the polyethylene glycol block occupies about 60% by mass to 40% by mass of the copolymer.

35 [0107]

The PEBA copolymer contains i) a polyamide block which is polyamide-12 (PA-12) and ii) a polyether block which is polyethylene glycol (PEG), wherein the polyamide-12 block represents about 45% by mass of the copolymer and the polyethylene glycol block represents about 55% by mass of the copolymer.

[0108]

The PEBA copolymer contains i) 10 to 20 polyamide blocks each of which is polyamide-12 (PA-12) and ii) 10 to 20 polyether blocks each of which is polyethylene glycol (PEG).

[0109]

The PEBA copolymer contains i) a polyamide block which is polyamide-12 (PA-12) and ii) a polyether block which is polyethylene glycol (PEG), and has a number average molecular weight M_n of about 25000 to about 75000 g/mol.

[0110]

The PEBA copolymer contains i) a polyamide block which is polyamide-12 (PA-12) and ii) a polyether block which is polyethylene glycol (PEG), and has a number average molecular weight M_n of about 50000 to about 75000 g/mol. The PEBA copolymer contains i) a polyamide block which is polyamide-12 (PA-12) and ii) a polyether block which is polyethylene glycol (PEG), and has a number average molecular weight M_n of about 66100 g/mol.

[0111]

The PEBA copolymer contains i) a polyamide block which is polyamide-12 (PA-12) and ii) a polyether block which is polyethylene glycol (PEG), and has a weight average molecular weight M_w of about 100000 to about 150000 g/mol.

[0112]

The PEBA copolymer contains i) a polyamide block which is polyamide-12 (PA-12) and ii) a polyether block

which is polyethylene glycol (PEG), and has a weight average molecular weight Mw of about 125000 to about 150000 g/mol.

[0113]

5 The PEBA copolymer contains i) a polyamide block which is polyamide-12 (PA-12) and ii) a polyether block which is polyethylene glycol (PEG), and has a weight average molecular weight Mw of about 134000 g/mol.

[0114]

10 In an embodiment of the disclosure, the PEBA copolymer contains i) a polyamide block which is polyamide-6 (PA-6) and ii) a polyether block which is polyethylene glycol (PEG).

 The PEBA copolymer contains i) a polyamide block
15 which is polyamide-6 (PA-6) and ii) a polyether block which is polyethylene glycol (PEG), wherein the polyamide-6 block represents about 30% by mass to 60% by mass of the copolymer and the polyethylene glycol block represents about 70% by mass to 40% by mass of the copolymer.

20 [0115]

 The PEBA copolymer contains i) a polyamide block which is polyamide-6 (PA-6) and ii) a polyether block which is polyethylene glycol (PEG), wherein the polyamide-6 block represents about 50% by mass to 35% by mass of the
25 copolymer and the polyethylene glycol block represents about 50% by mass to 65% by mass of the copolymer.

[0116]

 The PEBA copolymer contains i) 10 to 20 polyamide blocks each of which is polyamide-6 (PA-6) and ii) 10 to 20
30 polyether blocks each of which is polyethylene glycol (PEG).

[0117]

 The PEBA copolymer contains i) a polyamide block which is polyamide-11 (PA-11) and ii) a polyether block
35 which is polyethylene glycol (PEG). In an embodiment of

the disclosure, the PEBA copolymer contains i) a polyamide block which is polyamide-12 (PA-12) and ii) a polyether block which is polytetrahydrofuran (PTHF).

[0118]

5 The PEBA copolymer contains i) a polyamide block which is polyamide-12 (PA-12) and ii) a polyether block which is polytetrahydrofuran (PTHF), wherein the polyamide-12 block represents about 75% by mass to 10% by mass of the copolymer and the polytetrahydrofuran block represents
10 about 25% by mass to 90% by mass of the copolymer.

[0119]

 The PEBA copolymer contains i) a polyamide block which is polyamide-12 (PA-12) and ii) a polyether block which is polytetrahydrofuran (PTHF), wherein the polyamide-
15 12 block represents about 80% by mass to 60% by mass of the copolymer and the polytetrahydrofuran block represents about 20% by mass to 40% by weight of the copolymer.

[0120]

 The PEBA copolymer contains i) a polyamide block
20 which is polyamide-12 (PA-12) and ii) a polyether block which is polytetrahydrofuran (PTHF), wherein the polyamide-12 block represents about 40% by mass to 60% by mass of the copolymer and the polytetrahydrofuran block represents about 60% by mass to 40% by mass of the copolymer.

25 [0121]

 The PEBA copolymer contains i) a polyamide block which is polyamide-12 (PA-12) and ii) a polyether block which is polytetrahydrofuran (PTHF), wherein the polyamide-
12 block represents about 30% by mass to 10% by mass of the
30 copolymer and the polytetrahydrofuran block represents about 70% by mass to 90% by mass of the copolymer.

 The PEBA copolymer contains i) 10 to 20 polyamide blocks each of which is polyamide-12 (PA-12) and ii) 10 to 20 polyether blocks each of which is polytetrahydrofuran
35 (PTHF).

[0122]

The PEBA copolymer contains i) a polyamide block which is polyamide-12 (PA-12) and ii) a polyether block which is polytetrahydrofuran (PTHF), and has a number
 5 average molecular weight Mn of about 25000 to about 75000 g/mol.

The PEBA copolymer contains i) a polyamide block which is polyamide-12 (PA-12) and ii) a polyether block which is polytetrahydrofuran (PTHF), and has a number
 10 average molecular weight Mn of about 40000 to about 60000 g/mol. In an embodiment of the disclosure, the PEBA copolymer contains i) a polyamide block which is polyamide-12 (PA-12) and ii) a polyether block which is
 15 polytetrahydrofuran (PTHF), and has a number average molecular weight Mn of about 50000 g/mol.

[0123]

The PEBA copolymer contains i) a polyamide block which is polyamide-6 (PA-6) and ii) a polyether block which is polytetrahydrofuran (PTHF).

20 The PEBA copolymer contains i) a polyamide block which is polyamide-11 (PA-11) and ii) a polyether block which is polytetrahydrofuran (PTHF).

The PEBA copolymer is a commercially available elastomer and is marketed under the trade name of PEBAX®.

25 [0124]

The PEBA copolymer is a commercially available elastomer selected from the group consisting of: PEBAX 2533 SA 01, PEBAX 2533 SA 01 MED, PEBAX 2533 SD 02, PEBAX 3533 SA 01, PEBAX 3533 SA 01 MED, PEBAX 3533 SP01, PEBAX 4011,
 30 PEBAX 4033 SA 01, PEBAX 4033 SA 01 MED, PEBAX 4033 SP01, PEBAX 4533 SA 01, PEBAX 4533 SA 01 MED, PEBAX 4533 SP01, PEBAX 5513 SA 01, PEBAX 5513 SP01, PEBAX 5533 SA 01, PEBAX 5533 SA 01 MED, PEBAX 5533 SN 70 BLACK, PEBAX 5533 SP01, PEBAX SA 01, PEBAX 6333 SA 01 MED, PEBAX SP01, PEBAX 6333
 35 SP01, PEBAX 6333 SA 01, PEBAX, PEBAX 3533 SA 01, PEBAX 3533

SA 01 MED, PEBAX 3533 SP01, PEBAX 4011 SA 01, PEBAX 4033 SA 01 MED, PEBAX 4033 SP01, PEBAX 4033 SA 01 MED, PEBAX Clear 2533, PEBAX ES 2533 UV, PEBAX MH 2533, PEBAX MH2030, PEBAX MV 5513 SA 01, PEBAX MV 5513 SA 01 MED, PEBAX MV 5533 SP01, PEBAX MV 5533, PEBAX MV 5533 SP01, PEBAX RNEW® 30R51 SA 01, PEBAX RNEW 35R53 SP01, PEBAX RNEW 70R53 SP01, PEBAX RNEW 55R53 SP01, PEBAX RNEW 63R53 SP01, PEBAX RNEW 70R53 SP01, PEBAX RNEW 70R53 SP01, PEBAX, PEBAX RNEW 72R53 SP01, PEBAX RNEW 80R53 SP 02, and a mixture of any of these.

10 The PEBA copolymer is a commercially available elastomer and is marketed under the trade name of VESTAMID® or VESTAMID E.

[0125]

15 The PEBA copolymer is a commercially available elastomer selected from the group consisting of VESTAMID D, VESTAMID DX, VESTAMID E, VESTAMID EX, VESTAMID Care, VESTAMID Care ML, VESTAMID Care ME, VESTAMID Care ME-B, VESTAMID L, VESTAMID LX, VESTAMID NRG, VESTAMID Terra, VESTAMID X, and a mixture of any of these. Preferred among
20 these is Pebax MV 1072.

[0126]

 The PEBA copolymer may be used in the form of semisolid or viscous liquid, or in the form of powder, pellets, or granules.

25 [0127]

 The total amount of the component A and the synergist in the processing aid of the disclosure is preferably 80% by mass or more, more preferably 90% by mass or more, still more preferably 95% by mass or more, particularly
30 preferably 100% by mass.

[0128]

 Examples of the different component include an anti-agglomerating agent; an ultraviolet absorber; a flame retarder; a reinforcing material such as glass fiber or
35 glass powder; a stabilizer such as mineral or flaky

material; a lubricant such as silicone oil or molybdenum disulfide; a pigment such as titanium dioxide or red iron oxide; a conductive agent such as carbon black; an impact resistance improver such as rubber; an antioxidant such as
5 a hindered phenol- or phosphorus-based antioxidant; a nucleating agent such as metal salt or acetal of sorbitol; and an antiblocking agent.

[0129]

10 The water content of the processing aid of the disclosure is preferably 1.0% by mass or less, more preferably 0.5% by mass or less, still more preferably 0.2% by mass or less, most preferably 0.1% by mass or less. The lower limit may be, but is not limited to, 0% by mass.

[0130]

15 The water content herein is determined by the following method.

The mass of the processing aid of the disclosure is weighed before and after heating at 130°C for 24 hours, and the water content is calculated by the following equation.
20 Three samples are taken, and this calculation is performed for each sample and the values are averaged.

Water content (% by mass) = [(Mass (g) of processing aid before heating) - (Mass (g) of processing aid after heating)] / (Mass (g) of processing aid before heating) × 100
25 [0131]

The processing aid having a water content within the above range can be obtained by any method. For example, a processing aid may be produced using materials with low water content under dry conditions, or a processing aid may
30 be produced using normal materials under normal conditions and water may be removed therefrom by, for example, heat treatment.

[0132]

35 The processing aid of the disclosure may be obtained by a mixing step of mixing the materials of the processing

aid fed to a mixer or the like and an ejecting step of
ejecting the mixture from the mixer, for example. The
disclosure also relates to a method for producing the
aforementioned processing aid including a mixing step and
5 an ejecting step.

[0133]

The process in the mixing step may be, but is not
limited to, mixing (kneading) with a shear force or mixing
without a shear force. To effectively achieve the molding
10 processibility, kneading is preferred, and melt-kneading is
more preferred.

In the case of melt-kneading, the components may be
melted in the mixing step or may be melted before the
mixing step.

15 [0134]

In the production method, the ejecting step may be
followed by a molding step of molding the ejected matter
using a molding machine, for example.

Examples of the process in the molding step include,
20 but are not limited to, extrusion molding, injection
molding, and blow molding. To effectively achieve the
molding processibility, extrusion molding is preferred
among these.

[0135]

25 The extrusion molding is performed using an extruder.
Examples of the extruder include a single-screw extruder, a
twin-screw extruder, and a tandem extruder. The extruder
commonly includes a cylinder, a screw housed in the
cylinder, a die attached to the tip of the cylinder, and a
30 hopper for feeding pellets to the cylinder.

[0136]

The conditions relating to the molding are not
limited and may be set as appropriate in accordance with,
for example, the compositional ratio and amount of the
35 composition as well as the shape and size of a desired

molded article.

[0137]

The processing aid of the disclosure is particularly useful as a processing aid for thermoplastic resin (particularly, polyolefin resin).

[0138]

<Masterbatch>

The masterbatch of the disclosure contains the processing aid of the disclosure and a thermoplastic resin (A).

The processing aid of the disclosure as it is may be added to a target such as a thermoplastic resin; still, adding the processing aid in the form of masterbatch can lead to weighing stability and good dispersibility, i.e., a better effect of improving the processibility.

[0139]

Examples of the thermoplastic resin (A) include a polyolefin polymer (e.g., polyethylene (PE), polypropylene (PP), and an ethylene-propylene copolymer), polystyrene (PS), acrylonitrile styrene (AS) resin (AS), acrylonitrile butadiene styrene (ABS) resin (ABS), methacrylic resin (PMMA), polymethyl pentene (PMP), polybutadiene resin (BDR), polybutene-1 (PB-1), polyvinyl alcohol (PVA), polyacrylonitrile (PAN), polystyrene methacrylate (MS), an ethylene-vinyl acetate copolymer (EVA), an ethylene-vinyl alcohol copolymer, and polyvinyl chloride (PVC). Each of these may be used alone or two or more of these may be used in combination. To achieve a better effect of improving the processibility, a polyolefin polymer (polyolefin resin) is preferred.

[0140]

An example of the polyolefin polymer is a homopolymer (e.g., a homopolymer of a C2-C10 α -olefin, preferably a C2-C6 α -olefin). Specific examples of the homopolymer include homo-polyethylene and homo-polypropylene (hPP). In the

case of homo-polyethylene, for example, this polymer can be produced by free-radical polymerization in a high-pressure process and is typically known as a highly branched ethylene homopolymer, which is often referred to as LDPE
5 (low-density polyethylene), having a density of lower than 0.945 g/cm³, often 0.935 g/cm³ or lower, e.g., within a range from 0.900, 0.905, or 0.910 g/cm³ to 0.920, 0.925, 0.927, 0.930, 0.935, or 0.945 g/cm³. Unless otherwise described herein, the densities of all polymers are
10 determined in conformity with ASTM D1505. A sample is formed through the step C of ASTM D4703-10a and left under the conditions in ASTM D618-08 (23 ± 2°C and relative humidity 50 ± 10%) for 40 hours before testing.
[0141]

15 In another example, an ethylene monomer can be polymerized in a phase of a known gas, slurry, and/or solution (using, e.g., a catalyst such as chromium catalyst or a single site catalyst such as Ziegler-Natta and/or metallocene catalyst), each of which is well known in the
20 polymerization technique and is therefore not elaborated herein. In the case of producing a more highly linear ethylene homopolymer (e.g., using gas-phase or slurry-phase polymerization with any of the above catalysts), this is referred to as HDPE (high-density polyethylene), which
25 typically has a density of 0.945 g/cm³ or higher, e.g., within a range from 0.945 to 0.970 g/cm³.
[0142]

Examples of the polymer also include copolymers of two or more C2-C40 α-olefins, e.g., C2-C20 α-olefins, such
30 as ethylene-α-olefin copolymers and propylene-α-olefin copolymers (e.g., a propylene-ethylene copolymer and a propylene-ethylene-diene terpolymer (also known as EPDM and PEDM)). Specific examples intended herein include an ethylene copolymer and one or more C3-C20 α-olefin
35 comonomers such as a C4-C12 α-olefin comonomer (1-butene,

1-hexene, 1-octene, or a mixture of any two or more of these is preferred in a variety of embodiments). The ethylene copolymer (e.g., a copolymer of ethylene and one or more C3-C20 α -olefins) may contain an ethylene-derived unit in an amount of at least 90, 94, 95, or 96% by weight (e.g., within a range from a lower value of 80, 85, 90, 80, 85, 93, 93, 95, 96, or 97 wt% to a higher value of 94, 95, 95.5, 91, 92, 97, 94, 97.5, or 98 wt%; at least 96 wt% or 96.5 wt%), and may contain the unit in an amount within the range from any of the lower values to any of the higher values based on the total amount of the ethylene-derived unit and a comonomer-derived unit. For example, the ethylene copolymer may contain 94 or 95% by mass to 97 or 98% by mass of an ethylene-derived unit based on the total amount of the ethylene-derived unit and a comonomer-derived unit. The balance of the copolymer (based on the ethylene-derived unit and the comonomer-derived unit) consists of the comonomer-derived unit. For example, a comonomer unit (e.g., a unit derived from a C2-C20 α -olefin such as a unit derived from butene, hexene, and/or octene) may be present in an amount within a range from a lower value of 2, 2.5, 3, 3.5, 4, 4.5, 5, or 6% by mass to a higher value of 3, 4, 5, 6, 7, 8, 9, 10, 15, or 20% by mass, and the range thereof is from any of the above lower values to any intended value among the above higher values (provided that the higher value is greater than the lower value).

[0143]

Some appropriate comonomers have already been known for ethylene-based, propylene-based, or other α -olefin-based copolymers; in various embodiments, other α -olefin comonomers are intended. For example, the α -olefin comonomer may be linear or branched, and two or more comonomers may be used as appropriate. Examples of appropriate comonomers include C3-C20 linear α -olefins (e.g., butene, hexene, and octene, as described above) and

α -olefins having one or more C1-C3 alkyl branches or aryl groups. Examples include: propylene; 3-methyl-1-butene; 3,3-dimethyl-1-butene; 1-pentene; 1-pentene having one or more methyl, ethyl, or propyl substituents; 1-hexene having one or more methyl, ethyl, or propyl substituents; 1-heptene having one or more methyl, ethyl, or propyl substituents; 1-octene having one or more methyl, ethyl, or propyl substituents; 1-nonene having one or more methyl, ethyl, or propyl substituents; ethyl-, methyl- or dimethyl-substituted 1-decene; 1-dodecene; and styrene. The above list of comonomers shows mere examples and is not intended to set any limitation. In some embodiments, the comonomer includes propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, and styrene.

[0144]

In a specific embodiment, the polymer may include an ethylene copolymer or may be an ethylene copolymer (according to the above description). The ethylene copolymer can be produced by gas, slurry, or solution phase polymerization. Some particularly preferred ethylene copolymers can be produced by gas or slurry phase polymerization. Specific examples include linear low-density polyethylene (LLDPE) and a copolymer of ethylene and one or more α -olefins, which are polymerized in the presence of one or more single site catalysts, e.g., one or more Ziegler-Natta catalysts, one or more metallocene catalysts, or combination of any of these. This LLDPE may have a density within a range from a lower concentration of 0.900, 0.905, 0.907, or 0.910 g/cm³ to a higher concentration of 0.920, 0.925, 0.930, 0.935, 0.940, or 0.945 g/cm³. LLDPE is distinguishable from the aforementioned LDPE in some respects, many of which are well-known in the technical field, including the degree of branching (in many cases, there are few branches, if present) in the polymer produced. It should be noted that

LLDPE has substantially a small number of long chain branches. In a specific embodiment, the polymer of the polymer composition is or includes a metallocene-catalyzed LLDPE (mLLDPE). In other embodiments, the polymer of the
5 polymer composition is or includes a Ziegler-Natta-catalyzed LLDPE (or ZN-LLDPE).

[0145]

In some embodiments, the density of the polymer falls within a range from 0.905 to 0.945 g/cm³, e.g., from a
10 lower value of 0.905, 0.907, 0.908, 0.910, 0.911, 0.912, 0.913, 0.914, or 0.915 g/cm³ to a higher value of 0.916, 0.917, 0.918, 0.919, 0.920, 0.924, 0.926, 0.930, 0.935, 0.940, or 0.945 g/cm³, and the range thereof is from any of the above lower values to any of the above higher values
15 intended herein (e.g., from 0.910 to 0.925 or 0.935 g/cm³, e.g., from 0.912 to 0.925 or from 0.915 to 0.918 g/cm³). In other embodiments, the polymer may be a higher-density one (e.g., HDPE) having a density within a range from 0.945 g/cm³ to 0.970 g/cm³.

20 [0146]

The rheological characteristics of a polymer can have influence on the processing aid composition for forming a molded article. In common cases, a PPA composition is preferably used in a polymer having a melt index (MI or I2
25 is measured at 190°C and a 2.16 kg load in conformity with ASTM D1238) of 1.5 g/2.0 min or lower, preferably 2.5 g/3.0 min or lower, such as within a range from 0.1, 0.2, or 0.5 g/10 min to 1.0, 1.2, 5.0, 10, 2.5, 10, 4.0, or 5.0 g/10 min. In some embodiments, the polymer may commonly have a
30 melt index ratio (MIR) (MIR herein is defined as the ratio of the high-load melt index (HLMI) (determined at 190°C and a 21.6 kg load per ASTM D1238) to the melt index or as HLMI/MI) within a range from 10, 12, or 15 to 19, 20, 21, 22, 25, 27, 30, 35, 40, 45, 50, 60, 65, 70, 75, 80, 85, 90,
35 95, or 100. If necessary, this polymer may have a MI of

lower than 1.5 g/10 min, such as 1.0 g/10 min or lower (e.g., from 0.1, 0.2, or 0.5 g/10 min to 1.0; or any of 1.1, 1.2, 1.3, or 1.4, or lower than 1.5 g/10 min).

[0147]

5 The LLDPE preferably includes at least one selected from the group consisting of a Ziegler-Natta-catalyzed LLDPE and a metallocene-catalyzed LLDPE. Particularly preferred is a metallocene-catalyzed LLDPE.

[0148]

10 The thermoplastic resin (A) may have crystallinity or may have no crystallinity. The thermoplastic resin (A) having crystallinity has a melting point of preferably 80°C to 300°C, more preferably 100°C to 200°C. The thermoplastic resin (A) having no crystallinity preferably
15 has a processing temperature substantially equal to that of a thermoplastic resin (A) whose melting point range is indicated by its crystallinity.

[0149]

 The thermoplastic resin (A) preferably has a surface
20 free energy of 15.0 mN/m or more, more preferably 18.0 mN/m or more, while preferably 40.0 mN/m or less, more preferably 35.0 mN/m or less.

[0150]

 The difference in surface free energy between the
25 processing aid and the thermoplastic resin (A) is preferably 1.5 mN/m or more, more preferably 2.0 mN/m or more, still more preferably 4.0 mN/m or more, particularly preferably 5.5 mN/m or more. The difference is preferably 50 mN/m or less, more preferably 45 mN/m or less.

30 The surface free energy of the processing aid is preferably greater than the surface free energy of the thermoplastic resin (A).

[0151]

 In the masterbatch of the disclosure, the mass ratio
35 of the thermoplastic resin (A) to the processing aid

(thermoplastic resin (A):processing aid) is preferably 99:1 to 1:99. The mass ratio is more preferably 97:3 to 50:50, still more preferably 95:5 to 60:40, particularly preferably 92:8 to 70:30.

5 [0152]

The total amount of the thermoplastic resin (A) and the processing aid in the masterbatch of the disclosure is preferably 80% by mass or more, more preferably 90% by mass or more, still more preferably 95% by mass or more, particularly preferably 100% by mass.

10 [0153]

The masterbatch of the disclosure may contain a component different from the thermoplastic resin (A) and the processing aid.

15 Examples of the component different from the thermoplastic resin (A) and the processing aid include an anti-agglomerating agent; an ultraviolet absorber; a flame retarder; a reinforcing material such as glass fiber or glass powder; a stabilizer such as mineral or flaky material; a lubricant such as silicone oil or molybdenum disulfide; a pigment such as titanium dioxide or red iron oxide; a conductive agent such as carbon black; an impact resistance improver such as rubber; an antioxidant such as a hindered phenol- or phosphorus-based antioxidant; a
20 nucleating agent such as metal salt or acetal of sorbitol; and an antiblocking agent.

25 [0154]

The masterbatch of the disclosure may also be obtained by a mixing step of mixing the processing aid of the disclosure, which is prepared in advance, and the thermoplastic resin (A) fed to a mixer or the like and an ejecting step of ejecting the mixture from the mixer, for example. The disclosure also relates to a method for producing the aforementioned masterbatch including a mixing
30 step and an ejecting step.

[0155]

In the method for producing a masterbatch of the disclosure, the ejecting step may be followed by a molding step of molding the ejected matter using a molding machine,
5 for example.

[0156]

The mixing step, the ejecting step, and the molding step in the method for producing a masterbatch of the disclosure are the same as those described for the method
10 for producing a processing aid of the disclosure.

[0157]

The masterbatch of the disclosure is particularly useful as a masterbatch for improving the processibility of thermoplastic resin (particularly, polyolefin resin).

15 [0158]

<Thermoplastic resin composition>

The thermoplastic resin composition of the disclosure contains at least one of the processing aid of the disclosure or the masterbatch of the disclosure, and a
20 thermoplastic resin (B). This leads to good processibility. In particular, good extrusion processibility is achieved even in long-run molding.

[0159]

The thermoplastic resin (B) used may be the same as
25 the thermoplastic resin (A), and a preferred form thereof is also the same as that of the thermoplastic resin (A).

[0160]

The thermoplastic resin (B) preferably has a surface free energy of 15.0 mN/m or more, more preferably 18.0 mN/m
30 or more, while preferably 40.0 mN/m or less, more preferably 35.0 mN/m or less.

[0161]

The difference in surface free energy between the processing aid and the thermoplastic resin (B) is
35 preferably 1.5 mN/m or more, more preferably 2.0 mN/m or

more, still more preferably 4.0 mN/m or more, particularly preferably 5.5 mN/m or more. The difference is preferably 50 mN/m or less, more preferably 45 mN/m or less.

The surface free energy of the processing aid is preferably greater than the surface free energy of the thermoplastic resin (B).

[0162]

The thermoplastic resin composition of the disclosure contains at least one of the processing aid of the disclosure or the masterbatch of the disclosure, and preferably contains the masterbatch of the disclosure to achieve better processibility.

[0163]

In the case where the thermoplastic resin composition of the disclosure contains the masterbatch of the disclosure, the thermoplastic resin (A) and the thermoplastic resin (B) may be the same as or different from each other.

[0164]

The amount of the processing aid in the thermoplastic resin composition of the disclosure is preferably 0.001% by mass or more, more preferably 0.01% by mass or more, still more preferably 0.05% by mass or more, further preferably 0.08% by mass or more, particularly preferably 0.1% by mass or more, while preferably 5% by mass or less, more preferably 3% by mass or less, still more preferably 2% by mass or less, particularly preferably 1.0% by mass or less.

[0165]

The thermoplastic resin composition of the disclosure may contain a component different from the processing aid, the masterbatch, and the thermoplastic resin (B).

Examples of the component different from the processing aid, the masterbatch, and the thermoplastic resin (B) include an anti-agglomerating agent; an ultraviolet absorber; a flame retarder; a reinforcing

material such as glass fiber or glass powder; a stabilizer such as mineral or flaky material; a lubricant such as silicone oil or molybdenum disulfide; a pigment such as titanium dioxide or red iron oxide; a conductive agent such as carbon black; an impact resistance improver such as rubber; an antioxidant such as a hindered phenol- or phosphorus-based antioxidant; a nucleating agent such as metal salt or acetal of sorbitol; and an antiblocking agent.

10 [0166]

The thermoplastic resin composition of the disclosure may be obtained by a mixing step of mixing the masterbatch of the disclosure, which is prepared in advance, and the thermoplastic resin (B) fed to a mixer or the like and an ejecting step of ejecting the mixture from the mixer, or may be obtained by a mixing step of mixing the thermoplastic resin (B), the processing aid, and optionally the thermoplastic resin (A) fed to a mixer or the like and an ejecting step of ejecting the mixture from the mixer, for example. The disclosure also relates to a method for producing the aforementioned thermoplastic resin composition including a mixing step and an ejecting step.

15 [0167]

In the method for producing a thermoplastic resin composition of the disclosure, the ejecting step may be followed by a molding step of molding the ejected matter using a molding machine, for example.

25 [0168]

The mixing step, the ejecting step, and the molding step in the method for producing a thermoplastic resin composition of the disclosure are the same as those described for the method for producing a processing aid of the disclosure.

30 [0169]

35 <Molded article>

The molded article of the disclosure is obtainable from the thermoplastic resin composition of the disclosure and may be obtainable by, for example, a molding step of molding the thermoplastic resin composition of the disclosure.

The disclosure also relates to a method for producing a molded article including a molding step.

The thermoplastic resin composition of the disclosure is suitable for a molded article in the form of a tube, a film, or a sheet, and may be applicable to a molded article in a different form.

[0170]

The molding step is the same as that described for the method for producing a processing aid of the disclosure.

[0171]

In the molding step, the molding temperature (extruding temperature) during molding is commonly equal to or higher than the melting point of the thermoplastic resin (B) and lower than the decomposition temperature of the processing aid. To allow the processing aid to significantly exert its effects, the molding temperature preferably falls within a range of 160°C or higher and 270°C or lower.

The molding temperature may also be referred to the extrusion temperature in the case of extrusion molding.

[0172]

Examples of applications of the molded article of the disclosure include, but are not limited to, bags, coating materials, dishware such as drink containers, electric wires, cables, pipes, fibers, bottles, gasoline tanks, and other industrial molded articles.

[0173]

It should be appreciated that a variety of modifications and changes in the structure and other

details may be made to the aforementioned embodiments without departing from the spirit and scope of the claims.

EXAMPLES

5 [0174]

The disclosure is described in more detail below with reference to examples, but is not limited to these examples.

[0175]

10 The following materials were used in the examples and the comparative examples.

(Processing aid)

TPU: thermoplastic urethane elastomer (Shore A hardness: 97)

15 PBAT: polybutylene adipate terephthalate (MFR: 4 g/10 min, melting point: 115°C, mole fraction of chain ends: 0.0019 mol%)

PBS: polybutylene succinate (MFR: 22 g/10 min, melting point: 114°C, mole fraction of chain ends: 0.0020 mol%)

20 PLA: polylactic acid (MFR: 3 g/10 min, melting point: 153°C, mole fraction of chain ends: 0.0018 mol%)

EVOH-1: ethylene-vinyl alcohol copolymer (ethylene content: 48%, MFR: 6.4, melting point: 156°C, mole fraction of chain ends: 0.0019 mol%)

EVOH-2: ethylene-vinyl alcohol copolymer (ethylene content: 38%, MFR: 1.7, melting point: 171°C, mole fraction of chain ends: 0.0015 mol%)

(Thermoplastic resin (B) (matrix resin))

30 LLDPE-1: metallocene-catalyzed linear low-density polyethylene (MFR: 0.7 g/10 min, melting point: 123°C, MIR = 28.1)

(Thermoplastic resin (A) (carrier resin))

35 LLDPE-2: metallocene-catalyzed linear low-density polyethylene (MFR: 2.0 g/10 min, melting point: 121°C, MIR

= 23.6)

[0176]

<Calculation of surface free energy>

(1) For cleaning, a measurement sample dissolved in
5 an organic solvent at room temperature is dropped into a
poor solvent, and the resulting precipitate was collected.

(2) From the collected precipitate, a test piece of 3
cm in diameter × 1 mm in thickness was prepared using a
transfer molding machine under the conditions of a cylinder
10 temperature of 200°C and a pressure of 300 bsr.

(3) The resulting test piece was used to measure the
contact angle (liquid type: water, ethylene glycol), and
the surface free energy was calculated based on the
equation of the Owens-Wendt method. The results are shown
15 in Table 1.

[Table 1]

	Surface free energy (mN/m)
LLDPE-1	27.2
LLDPE-2	27.5
TPU	28.2
PBAT	32.4
PBS	33.1
PLA	36.7
EVOH-1	45.3
EVOH-2	50.9

[0177]

Comparative Examples 1 and 2, Examples 1 to 5

20 First, the carrier resin (thermoplastic resin (A))
and the processing aid were melt-kneaded in the proportions
shown in Table 1 using a twin-screw extruder (TEX25αIII
available from Japan Steel Works, Ltd.) under the
conditions including a cylinder temperature of 180°C to
25 200°C, a die temperature of 200°C, and a screw rotational
speed of 400 rpm, whereby a masterbatch (MB) was obtained.

The masterbatch obtained was then dry blended with

the matrix resin (thermoplastic resin (B)) in the proportion that ensures the concentration of the processing aid in the resulting thermoplastic resin composition remains constant (2000 ppm), and the processibility in this case was evaluated as in <Extrusion evaluation> described below. The results are shown in Table 2.

The processing aid used contained no fluorine and the processing aid therefore had a fluorine content of 0% by mass.

10 [0178]

<Extrusion evaluation>

Each material was extruded for 60 minutes through a single screw extruder (Rheomex OS available from HAAKE, L/D: 33, screw diameter: 20 mm, die diameter: 2 mm) under the conditions including a cylinder temperature of 170°C to 200°C, a die temperature of 200°C, and a shear rate of 450/sec, which was evaluated for the following items.

Before each test operation, linear low-density polyethylene containing 15% by mass of silica was fed into a hopper and the screw rotational speed was increased to 150 rpm to perform purging for about 15 minutes. The same matrix resin as one to be used for the test was then fed to perform purging for about 15 minutes. The screw rotational speed was returned to 30 rpm and extrusion was performed until the temperature stabilized. After the pressure surely returned to the initial pressure, a next experiment was performed. If the pressure did not return to the initial value, the above purging process was repeated until the pressure returned to the initial value and a next experiment was then performed.

(Melt fracture (MF) disappearance time)

The matrix resin alone was extruded until the pressure was stabilized while melt fracture occurred on the entire surface. The point of time at which the screw appeared was defined as zero, and the matrix resin was then

extruded for 60 minutes. In the examples where the processing aid or the masterbatch was used, they were fed to the hopper at the zero point. The appearance of a strand at an early stage of extrusion and the appearance of a strand at completion of extrusion were checked by visual and tactile inspection. The period of time was measured from the zero point of time described above to the point when MF disappeared. The shorter the period of time is, the better the MF disappearance time is. The cases where MF did not disappear are expressed with the symbol "-".

[0179]

[Table 2]

	Thermoplastic resin B	Composition of MB			Additive concentration (ppm) (Processing aid / (B + A + Processing aid))	Extrusion evaluation MF disappearance time (min)	Difference in surface free energy (Processing aid - Thermoplastic resin B)	Difference in surface free energy (Processing aid - Thermoplastic resin A)
		Thermoplastic resin A	Processing aid	Concentration of processing aid in MB (% by mass)				
Comparative Example 1	LLDPE-1	—	—	25	2000	—	—	—
Comparative Example 2	LLDPE-1	LLDPE-2	TPU	25	2000	—	0.98	0.66
Example 1	LLDPE-1	LLDPE-2	PBAT	25	2000	50	5.23	4.90
Example 2	LLDPE-1	LLDPE-2	PBS	25	2000	40	5.93	5.60
Example 3	LLDPE-1	LLDPE-2	PLA	25	2000	40	9.51	9.18
Example 4	LLDPE-1	LLDPE-2	EVOH-1	25	2000	20	18.08	17.76
Example 5	LLDPE-1	LLDPE-2	EVOH-2	25	2000	20	23.69	23.36

CLAIMS

Claim 1. A processing aid having a surface free energy of 28.5 mN/m or more, the processing aid being
 5 substantially free from fluorine.

Claim 2. The processing aid according to claim 1,
 wherein the processing aid has a surface free energy
 of 29.0 to 55.0 mN/m.

10

Claim 3. The processing aid according to claim 1 or
 2,

wherein the processing aid contains a structural unit
 represented by the following formula 1:

15 $-X-(CR^1R^2)_n-Y-(CR^3R^4)_m-Z-$ (formula 1)

wherein X is a single bond or a divalent group optionally
 containing a functional group;

Y and Z are each independently a group constituted by
 at least one selected from the group consisting of a single
 20 bond, $-O-$, $-C(=O)-$, $-C(=O)O-$, $-OC(=O)O-$, $-C(=NR')-$, $-$
 $C(=NR')O-$, $-OC(=NR')O-$, $-S-$, $-S(=O)-$, $-S(=O)O-$, $-OS(=O)O-$,
 $-S(=O)_2-$, $-S(=O)_2O-$, $-OS(=O)_2O-$, $-P(=O)-$, $-P(=O)O-$, $-$
 $OP(=O)O-$, $-P(=O)_2-$, $-P(=O)_2O-$, $-OP(=O)_2O-$, $-NR'-$, and $-$
 $C(OR')R'-$, wherein R's at respective occurrences are each
 25 independently a hydrogen atom or a C1-C10 hydrocarbon
 group;

R^1 , R^2 , R^3 , and R^4 are each independently a hydrogen
 atom or a C1-C10 hydrocarbon group; and

n and m are each independently an integer of 0 to 10,
 30 with at least one of X, Y, or Z being $-C(=O)-$, $-$
 $C(=O)O-$, $-OC(=O)O-$, or $-C(OR')R'-$.

Claim 4. The processing aid according to claim 3,
 wherein, in the formula 1, X is a divalent group
 35 constituted by at least one selected from the group

consisting of X^1 and X^2 ,

X^1 is a group constituted by at least one selected from the group consisting of $-C(=O)-$, $-C(=NR')-$, $-S(=O)_2-$, $-NR'-$, $-CR'R'-$, and $-C(OR')R'-$, wherein R' 's at respective
5 occurrences are each independently a hydrogen atom or a C1-C10 hydrocarbon group; and

X^2 is a C1-C12 aromatic hydrocarbon group optionally containing a substituent.

10 Claim 5. The processing aid according to claim 4,
wherein, in the formula 1, X is a divalent group containing at least one selected from the group consisting of $-C(=O)-$, $-CR'R'-$, and $-C(OR')R'-$, wherein R' 's at
respective occurrences are each independently a hydrogen
15 atom or a C1-C10 hydrocarbon group.

Claim 6. The processing aid according to any one of claims 3 to 5,

wherein, in the formula 1, Y and Z are each
20 independently a group constituted by at least one selected from the group consisting of a single bond, $-O-$, $-C(=O)-$, $-C(=O)O-$, $-C(=NR')-$, $-C(=NR')O-$, $-S-$, $-S(=O)_2-$, $-S(=O)_2O-$, $-NR'-$, and $-C(OR')R'-$, wherein R' 's at respective occurrences are each independently a hydrogen atom or a C1-C10
25 hydrocarbon group.

Claim 7. The processing aid according to claim 6,
wherein, in the formula 1, Y and Z are each
independently a group constituted by at least one selected
30 from the group consisting of a single bond, $-O-$, $-C(=O)-$,
and $-C(=O)O-$.

Claim 8. The processing aid according to any one of claims 1 to 7,

35 wherein the processing aid has a melt flow rate of

0.001 to 100 g/10 min at 190°C and a 2.16 kgf load.

Claim 9. The processing aid according to any one of claims 1 to 8,

5 wherein the processing aid includes at least one selected from the group consisting of polybutylene adipate terephthalate, polybutylene succinate, polylactic acid, and an ethylene-vinyl alcohol copolymer.

10 Claim 10. A masterbatch comprising:
the processing aid according to any one of claims 1 to 9; and
a thermoplastic resin (A).

15 Claim 11. The masterbatch according to claim 10, wherein the thermoplastic resin (A) includes a polyolefin resin.

20 Claim 12. The masterbatch according to claim 10 or 11,
wherein the thermoplastic resin (A) includes metallocene-catalyzed linear low-density polyethylene.

25 Claim 13. The masterbatch according to any one of claims 10 to 12,
wherein a difference in surface free energy between the processing aid and the thermoplastic resin (A) is 1.5 mN/m or more.

30 Claim 14. The masterbatch according to any one of claims 10 to 13,
wherein a difference in surface free energy between the processing aid and the thermoplastic resin (A) is 4.0 to 45 mN/m.

35

Claim 15. The masterbatch according to any one of claims 10 to 14,

wherein a mass ratio of the thermoplastic resin (A) to the processing aid (thermoplastic resin (A):processing aid) is 92:8 to 70:30.

Claim 16. A thermoplastic resin composition comprising:

at least one of the processing aid according to any one of claims 1 to 9 or the masterbatch according to any one of claims 10 to 15; and
a thermoplastic resin (B).

Claim 17. The thermoplastic resin composition according to claim 16,

wherein the thermoplastic resin (B) includes a polyolefin resin.

Claim 18. The thermoplastic resin composition according to claim 16 or 17,

wherein the thermoplastic resin (B) includes metallocene-catalyzed linear low-density polyethylene.

Claim 19. The thermoplastic resin composition according to any one of claims 16 to 18,

wherein a difference in surface free energy between the processing aid and the thermoplastic resin (B) is 1.5 mN/m or more.

Claim 20. The thermoplastic resin composition according to any one of claims 16 to 19,

wherein a difference in surface free energy between the processing aid and the thermoplastic resin (B) is 4.0 to 45 mN/m.

Claim 21. The thermoplastic resin composition according to any one of claims 16 to 20, wherein the processing aid is contained in an amount of 0.1 to 1.0% by mass.

5

Claim 22. A molded article comprising the thermoplastic resin composition according to any one of claims 16 to 21.

10

Claim 23. The molded article according to claim 22, wherein the molded article is in a form of a tube, a film, or a sheet.

15

Claim 24. A method for producing the processing aid according to any one of claims 1 to 9, comprising a mixing step and an ejecting step.

20

Claim 25. A method for producing the masterbatch according to any one of claims 10 to 15, comprising a mixing step and an ejecting step.

25

Claim 26. A method for producing the thermoplastic resin composition according to any one of claims 16 to 21, comprising a mixing step and an ejecting step.

Claim 27. A method for producing the molded article according to claim 22 or 23, comprising a molding step.