(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 428 331 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
16.01.2019 Bulletin 2019/03

(21) Application number: **17763153.8**

(22) Date of filing: **06.03.2017**

(51) Int Cl.:
D04H 1/4291 *(2012.01)* ***D04H 3/007*** *(2012.01)*
D04H 3/16 *(2006.01)*

(86) International application number:
PCT/JP2017/008680

(87) International publication number:
WO 2017/154813 (14.09.2017 Gazette 2017/37)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA MD

(30) Priority: **11.03.2016 JP 2016048579**

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(54) NONWOVEN FABRIC

(57) Provided is a nonwoven fabric which is formed from a resin composition and has improved antifouling properties, sound insulation properties, coefficient of friction, and texture. This nonwoven fabric is formed from a resin composition which contains (1) a thermoplastic resin and (2) a fluorine-containing copolymer, and wherein: the thermoplastic resin (1) is a polypropylene; and the fluorine-containing copolymer (2) is a copolymer which has (a) a repeating unit that is formed of a fluorine-containing monomer represented by formula $CH_2=C(-X)-C(=O)-Y-Z-Rf$ and (b) a repeating unit that is formed of a non-fluorine monomer having a hydrocarbon group with 14 or more carbon atoms, and which has a weight average molecular weight of 2,500-20,000.

Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] The present invention relates to a nonwoven fabric formed from a resin composition comprising a thermoplastic resin and a fluorine-containing copolymer.

BACKGROUND ART

[0002] Hitherto, disclosed is a technology of nonwoven fabric which adding a fluorine-containing polymer to a thermoplastic resin.

[0003] WO 01/053585A discloses a nonwoven fabric prepared by adding a lubricant comprising a vinylidene fluoride/hexafluoropropylene copolymer as processing aid to polypropylene. However, there is no surface modification effect in this nonwoven fabric comprising the fluorine-containing copolymer.

[0004] JP H09-511700A discloses a method of increasing a head-of-water pressure and an intensity to a nonwoven fabric having an average fiber diameter of at least 10 micrometers comprising a specific fluorocarbon. JP 2002-521586A discloses a method of giving water repellency and alcohol repellency to a nonwoven fabric surface by adding a fluorine-containing additive agent to a specific region. These methods have a surface modification effect, but other effects cannot be seen.

[0005] JP 2006-37085A discloses a method of mixing a fluorine-containing copolymer with a thermoplastic resin to performing a surface modification. However, only water- and oil-repellency specialized in alcohol repellency is indicated as an effect, but other effects cannot be seen.

Prior art document

Patent document

[0006]

Patent document 1: WO 01/053585 A
Patent document 2: JP H09-511700A
Patent document 3: JP 2002-521586A
Patent document 4: JP 2006-37085A

SUMMARY OF THE INVENTION

Problem to be solved by the Invention

[0007] An object of the present invention is to provide a nonwoven fabric formed from a resin composition having improved antifouling property, sound insulation property, friction coefficient and touch feeling property.

Means for Solving Problem

[0008] The present invention relates to a nonwoven fabric formed from a resin composition comprising (1) a thermoplastic resin, and (2) a fluorine-containing copolymer.

[0009] The present invention provides a nonwoven fabric formed from a resin composition comprising:

(1) a thermoplastic resin, and
(2) a fluorine-containing copolymer,

wherein the thermoplastic resin (1) is polypropylene, and
the fluorine-containing copolymer is a copolymer which comprises:

(a) a repeating unit formed from a fluorine-containing monomer represented by the formula:

$$CH_2=C(-X)-C(=O)-Y-Z-Rf$$

wherein X is a hydrogen atom, a monovalent organic group or a halogen atom,
Y is -O- or -NH-,
Z is a direct bond or an divalent organic group, and
Rf is a fluoroalkyl group having 4 to 6 carbon atoms, and

(b) a repeating unit formed from a fluorine-free monomer containing a hydrocarbon group having at least 14 carbon atoms, and

which has a weight-average molecular weight of 2,500 to 20,000.

[0010] In addition, the present invention provides a method of producing a nonwoven fabric, comprising steps of:

(i) mixing a thermoplastic resin (1) with a fluorine-containing copolymer (2) to obtain a resin composition; and
(ii) spinning a melt of the resin composition which is pressure-fed to a die by a melt blowing method, from a nozzle having a large number of arranged small holes.

Effect of the Invention

[0011] In the present invention, the resin composition (or the antifouling resin composition) can be processed into a nonwoven fabric with high processing characteristics. A melt flow rate (MFR) of the resin composition is improved. Further, processing stability at the time of preparation of the nonwoven fabric is high, and the productivity of the nonwoven fabric is high.

[0012] According to the present invention, a surface-modified nonwoven fabric is obtained. The nonwoven fabric of the present invention has excellent antifouling properties, sound insulation properties, and water-proof pressure. Furthermore, the nonwoven fabric of the present invention has excellent wiping easiness and scratch resistance. In addition, the nonwoven fabric has a good touch feeling due to a decrease in a coefficient of friction.

[0013] According to the present invention, a nonwoven fabric having a small fiber diameter and a high density can be obtained.

MODES FOR CARRYING OUT THE INVENTION

(1) Thermoplastic resin

[0014] The thermoplastic resin is polypropylene.

[0015] Examples of polypropylene are isotactic polypropylene, syndiotactic polypropylene, atactic polypropylene, and amorphous polypropylene.

[0016] The isotactic polypropylene is a highly crystalline polypropylene based on isotactic polypropylene prepared by a Ziegler-Natta catalyst or a metallocene catalyst.

[0017] The amorphous polypropylene is, for example, propylene having extremely low crystallinity prepared by using a metallocene catalyst. The amorphous polypropylene may be a mixture of polypropylene having extremely low crystallinity (for example, at least 50 wt% of a total amount of the mixture) produced by using a metallocene catalyst, with other propylene. The amorphous polypropylene is available as, for example, TAFTHREN T-3512 and T-3522 manufactured by Sumitomo Chemical Co., Ltd., and L-MODU S-400, S-600 and S-901 manufactured by Idemitsu Kosan Co., Ltd.

[0018] In the present invention, the thermoplastic resin may be one or a combination of at least two.

(2) Fluorine-containing copolymer

[0019] The fluorine-containing copolymer (2) is a copolymer having a repeating unit formed from the fluorine-containing monomer (a) and a repeating unit formed from the fluorine-free monomer (b). The fluorine-containing monomer (a) is a monomer containing a fluoroalkyl group having 4 to 6 carbon atoms. The fluorine-free monomer (b) is a monomer containing a non-cyclic or cyclic hydrocarbon group having at least 14 carbon atoms, which may contain a nitrogen, oxygen and/or sulfur atom. The fluorine-containing copolymer (2) may have a repeating unit formed from another monomer (c) other than the fluorine-containing monomer (a) and the fluorine-free monomer (b).

[0020] The fluorine-containing monomer (a) is a monomer of the formula:

$$CH_2=C(-X)-C(=O)-Y-Z-Rf$$

wherein X is a hydrogen atom, a monovalent organic group or a halogen atom,

Y is -O- or -NH-,
Z is a direct bond or an divalent organic group, and
Rf is a fluoroalkyl group having 4 to 6 carbon atoms.

[0021] X is, for example, a hydrogen atom, a methyl group, a halogen atom, a linear or branched alkyl group having 2 to 21 carbon atoms, a CFX^1X^2 group (where each of X^1 and X^2 is a hydrogen atom, a fluorine atom, a chlorine atom, a bromine atom or an iodine atom), a cyano group, a linear or branched fluoroalkyl group having 1 to 21 carbon atoms, a substituted or unsubstituted benzyl group or a substituted or unsubstituted phenyl group.

[0022] In the fluorine-containing copolymer of the present invention, X is preferably a hydrogen atom, a methyl group, a fluorine atom, or a chlorine atom. X is especially a methyl group, since antifouling property is high.

[0023] Y is preferably -O-.

[0024] Z is, for example, a direct bond,
a linear alkylene group or branched alkylene group having 1-20 carbon atoms, such as a group represented by the formula $-(CH_2)_x-$ wherein x is 1 to 10,
a group represented by the formula $-SO_2N(R^1)R^2-$ or the formula $-CON(R^1)R^2--$ wherein R^1 is an alkyl group having 1 to 10 carbon atoms and R^2 is a linear alkylene group or branched alkylene group having 1 to 10 carbon atoms,
a group represented by the formula $-CH_2CH(OR^3)CH_2-$ wherein R^3 is a hydrogen atom or an acyl group having 1 to 10 carbon atoms (for example, a formyl group or an acetyl group),
$-Ar-(CH_2)_r-$ wherein Ar is an arylene group optionally having a substituent group, and r is 0 to 10, or
a $-(CH_2)_m-SO_2-(CH_2)_n-$ group or a $-(CH_2)_m-S-(CH_2)_n-$ group wherein m is 1-10, and n is 0-10.

[0025] In the fluorine-containing copolymer of the present invention, Z is preferably a direct bond, an alkylene group having 1-20 carbon atoms, or $-SO_2N(R^1)R^2-$, particularly preferably $-(CH_2)_2-$.

[0026] The Rf group is preferably a perfluoroalkyl group, but may be a fluoroalkyl group having a hydrogen atom. The carbon number of the Rf group is preferably 4 or 6. The carbon number of the Rf group is particularly preferably 6. Examples of the Rf group include $-CF_2CF_2CF_2CF_3$, $-CF_2CF(CF_3)_2$, $-C(CF_3)_3$,$-(CF_2)_5CF_3$ and $-(CF_2)_3CF(CF_3)_2$.

[0027] Specific examples of the fluorine-containing monomer (a) include, but are not limited to, the followings:

$CH_2=C(-H)-C(=O)-O-(CH_2)_2-Rf$

$CH_2=C(-H)-C(=O)-O-C_sH_4-Rf$

$CH_2=C(-Cl)-C(=O)-O-(CH_2)_2-Rf$

$CH_2=C(-H)-C(=O)-O-(CH_2)_2N(-CH_3)SO_2-Rf$

$CH_2=C(-H)-C(=O)-O-(CH_2)_2N(-C_2H_5)SO_2-Rf$

$CH_2=C(-H)-C(=O)-O-CH_2CH(-OH)CH_2-Rf$

$CH_2=C(-H)-C(=O)-O-CH_2CH(-OCOCH_3)CH_2-Rf$

$CH_2=C(-H)-C(=O)-O-(CH_2)_2-S-Rf$

$CH_2=C(-H)-C(=O)-O-(CH_2)_2-S-(CH_2)_2-Rf$

$CH_2=C(-H)-C(=O)-O-(CH_2)_3-SO_2-Rf$

$CH_2=C(-H)-C(=O)-O-(CH_2)_2-SO_2-(CH_2)_2-Rf$

$CH_2=C(-H)-C(=O)-NH-(CH_2)_2-Rf$

$CH_2=C(-CH_3)-C(=O)-O-(CH_2)_2-Rf$

$CH_2=C(-CH_3)-C(=O)-O-C_6H_4-Rf$

$CH_2=C(-CH_3)-C(=O)-O-(CH_2)_2N(-CH_3)SO_2-Rf$

$CH_2=C(-CH_3)-C(=O)-O-(CH_2)_2N(-C_2H_5)SO_2-Rf$

$CH_2=C(-CH_3)-C(=O)-O-CH_2CH(-OH)CH_2-Rf$

$CH_2=C(-CH_3)-C(=O)-O-CH_2CH(-OCOCH_3)CH_2-Rf$

$CH_2=C(-CH_3)-C(=O)-O-(CH_2)_2-S-Rf$

$CH_2=C(-CH_3)-C(=O)-O-(CH_2)_2-S-(CH_2)_2-Rf$

$CH_2=C(-CH_3)-C(=O)-O-(CH_2)_3-SO_2-Rf$

$CH_2=C(-CH_3)-C(=O)-O-(CH_2)_2-SO_2-(CH_2)_2-Rf$

$CH_2=C(-CH_3)-C(=O)-NH-(CH_2)_2-Rf$

$CH_2=C(-F)-C(=O)-O-(CH_2)_2-S-Rf$

$CH_2=C(-F)-C(=O)-O-(CH_2)_2-S-(CH_2)_2-Rf$

$CH_2=C(-F)-C(=O)-O-(CH_2)_2-SO_2-Rf$

$CH_2=C(-F)-C(=O)-O-(CH_2)_2-SO_2-(CH_2)_2-Rf$

$CH_2=C(-F)-C(=O)-NH-(CH_2)_2-Rf$

$CH_2=C(-Cl)-C(=O)-O-(CH_2)_2-S-Rf$

$CH_2=C(-Cl)-C(=O)-O-(CH_2)_2-S-(CH_2)_2-Rf$

$CH_2=C(-Cl)-C(=O)-O-(CH_2)_2-SO_2-Rf$

$CH_2=C(-Cl)-C(=O)-O-(CH_2)_2-SO_2-(CH_2)_2-Rf$

$CH_2=C(-Cl)-C(=O)-NH-(CH_2)_2-Rf$

$CH_2=C(-CF_3)-C(=O)-O-(CH_2)_2-S-Rf$

$CH_2=C(-CF_3)-C(=O)-O-(CH_2)_2-S-(CH_2)_2-Rf$

$CH_2=C(-CF_3)-C(=O)-O-(CH_2)_2-SO_2-Rf$

$CH_2=C(-CF_3)-C(=O)-O-(CH_2)_2-SO_2-(CH_2)_2-Rf$

$CH_2=C(-CF_3)-C(=O)-NH-(CH_2)_2-Rf$

$CH_2=C(-CF_2H)-C(=O)-O-(CH_2)_2-S-Rf$

$CH_2=C(-CF_2H)-C(=O)-O-(CH_2)_2-S-(CH_2)_2-Rf$

$CH_2=C(-CF_2H)-C(=O)-O-(CH_2)_2-SO_2-Rf$

$CH_2=C(-CF_2H)-C(=O)-O-(CH_2)_2-SO_2-(CH_2)_2-Rf$

$CH_2=C(-CF_2H)-C(=O)-NH-(CH_2)_2-Rf$

$CH_2=C(-CN)-C(=O)-O-(CH_2)_2-S-Rf$

$CH_2=C(-CN)-C(=O)-O-(CH_2)_2-S-(CH_2)_2-Rf$

$CH_2=C(-CN)-C(=O)-O-(CH_2)_2-SO_2-Rf$

$CH_2=C(-CN)-C(=O)-O-(CH_2)_2-SO_2-(CH_2)_2-Rf$

$CH_2=C(-CN)-C(=O)-NH-(CH_2)_2-Rf$

$CH_2=C(-CF_2CF_3)-C(=O)-O-(CH_2)_2-S-Rf$

$CH_2=C(-CF_2CF_3)-C(=O)-O-(CH_2)_2-S-(CH_2)_2-Rf$

$CH_2=C(-CF_2CF_3)-C(=O)-O-(CH_2)_2-SO_2-Rf$

$CH_2=C(-CF_2CF_3)-C(=O)-O-(CH_2)_2-SO_2-(CH_2)_2-Rf$

$CH_2=C(-CF_2CF_3)-C(=O)-NH-(CH_2)_2-Rf$

$CH_2=C(-F)-C(=O)-O-(CH_2)_3-S-Rf$

$CH_2=C(-F)-C(=O)-O-(CH_2)_3-S-(CH_2)_2-Rf$

$CH_2=C(-F)-C(=O)-O-(CH_2)_3-SO_2-Rf$

$CH_2=C(-F)-C(=O)-O-(CH_2)_3-SO_2-(CH_2)_2-Rf$

$CH_2=C(-F)-C(=O)-NH-(CH_2)_3-Rf$

$CH_2=C(-Cl)-C(=O)-O-(CH_2)_3-S-Rf$

$CH_2=C(-Cl)-C(=O)-O-(CH_2)_3-S-(CH_2)_2-Rf$

$CH_2=C(-Cl)-C(=O)-O-(CH_2)_3-SO_2-Rf$

$CH_2=C(-Cl)-C(=O)-O-(CH_2)_3-SO_2-(CH_2)_2-Rf$

$CH_2=C(-CF_3)-C(=O)-O-(CH_2)_3-S-Rf$

$CH_2=C(-CF_3)-C(=O)-O-(CH_2)_3-S-(CH_2)_2-Rf$

$CH_2=C(-CF_3)-C(=O)-O-(CH_2)_3-SO_2-Rf$

$CH_2=C(-CF_3)-C(=O)-O-(CH_2)_3-SO_2-(CH_2)_2-Rf$

$CH_2=C(-CF_2H)-C(=O)-O-(CH_2)_3-S-Rf$

$CH_2=C(-CF_2H)-C(=O)-O-(CH_2)_3-S-(CH_2)_2-Rf$

$CH_2=C(-CF_2H)-C(=O)-O-(CH_2)_3-SO_2-Rf$

$CH_2=C(-CF_2H)-C(=O)-O-(CH_2)_3-SO_2-(CH_2)_2-Rf$

$CH_2=C(-CN)-C(=O)-O-(CH_2)_3-S-Rf$

$CH_2=C(-CN)-C(=O)-O-(CH_2)_3-S-(CH_2)_2-Rf$

$CH_2=C(-CN)-C(=O)-O-(CH_2)_3-SO_2-Rf$

$CH_2=C(-CN)-C(=O)-O-(CH_2)_3-SO_2-(CH_2)_2-Rf$

$CH_2=C(-CF_2CF_3)-C(=O)-O-(CH_2)_3-S-Rf$

$CH_2=C(-CF_2CF_3)-C(=O)-O-(CH_2)_3-S-(CH_2)_2-Rf$

$CH_2=C(-CF_2CF_3)-C(=O)-O-(CH_2)_3-SO_2-Rf$

$CH_2=C(-CF_2CF_3)-C(=O)-O-(CH_2)_2-SO_2-(CH_2)_2-Rf$

wherein Rf is a fluoroalkyl group having 4 to 6 carbon atoms.

[0028] The fluorine-containing copolymer has the repeating unit formed from the fluorine-free monomer (b) in addition to the repeating unit formed from the fluorine-containing monomer (a).

[0029] The fluorine-free monomer (b) is a monomer which contains a hydrocarbon group (a non-cyclic hydrocarbon group or a cyclic hydrocarbon group) having at least 14 carbon atoms. The lower limit of the number of carbon atoms may be 16 or 17. The upper limit of the number of carbon atoms of the hydrocarbon group may be 30, for example 25, especially 20.

[0030] The fluorine-free monomer (b) is preferably a (meth)acrylate. The fluorine-free monomer (b) is preferably a (meth)acrylate ester wherein an acryloyloxy group is bonded to a monovalent hydrocarbon group. Particularly preferably, the fluorine-free monomer (b) is an acrylate ester in which an alpha-position is a hydrogen atom.

[0031] The fluorine-free monomer (b) may be a fluorine-free non-crosslinkable monomer (b1). A specific example of the fluorine-free non-crosslinkable monomer (b1) may be a compound of the formula:

$CH_2=CA-T$

wherein A is a hydrogen atom, a methyl group, or a halogen atom other than a fluorine atom (for example, a chlorine atom, a bromine atom, and an iodine atom), T is a hydrocarbon group having 14 to 30 carbon atoms, or an organic group having 15 to 31 carbon atoms and an ester bond.

[0032] Examples of the hydrocarbon group having 14-30 carbon atoms are a linear or branched saturated or unsaturated (for example, ethylenically unsaturated) aliphatic hydrocarbon group having 14 to 30 carbon atoms, a saturated or unsaturated (for example, ethylenically unsaturated) cycloaliphatic hydrocarbon group having 14 to 30 carbon atoms, an aromatic hydrocarbon group having 14-30 carbon atoms, and an araliphatic hydrocarbon group having 14-30 carbon atoms.

[0033] Examples of the organic group having 15 to 31 carbon atoms and an ester bond are: -C(=O)-O-Q and -O-C(=O)-Q wherein Q is a linear or branched saturated or unsaturated (for example, ethylenically unsaturated) aliphatic hydrocarbon group having 14 to 30 carbon atoms, a saturated or unsaturated (for example, ethylenically unsaturated) cycloaliphatic hydrocarbon group having 14 to 30 carbon atoms, an aromatic hydrocarbon group having 14-30 carbon atoms, or an araliphatic hydrocarbon group having 14-30 carbon atoms.

[0034] The fluorine-free non-crosslinkable monomer (b1) may be a (meth)acrylate ester monomer.

[0035] Examples of the (meth)acrylate ester monomer may be a compound represented by the formula:

$CH_2=CA^{21}-C(=O)-O-A^{22}$

wherein A^{21} is a hydrogen atom, an organic group, a halogen atom other than a fluorine atom, and
A^{22} is a hydrocarbon group having 14-30 carbon atoms.

[0036] A^{21} is preferably a hydrogen atom, a methyl group or a chlorine atom.

[0037] A^{22} (hydrocarbon group) may be a non-cyclic hydrocarbon group having 14 to 30 carbon atoms and a cyclic hydrocarbon group having 14 to 30 carbon atoms. A^{22} (hydrocarbon group) is preferably a non-cyclic hydrocarbon group, particularly a chain hydrocarbon group having 14 to 30 carbon atoms.

[0038] Specific examples of the (meth)acrylate ester monomer having a non-cyclic hydrocarbon group include cetyl (meth)acrylate, stearyl (meth)acrylate and behenyl (meth)acrylate.

[0039] The fluorine-containing copolymer according to the present invention may consist of the fluorine-containing monomer (a) and the fluorine-free monomer (b) or may comprise another monomer (c) other than the fluorine-containing monomer (a) and the fluorine-free monomer (b). The other monomer (c) is preferably free from a fluorine atom. Examples of the other monomer (c) are (c1) a fluorine-free crosslinkable monomer or (c2) a halogenated olefin monomer.

[0040] The fluorine-free crosslinkable monomer (c1) is a monomer free from a fluorine atom. The fluorine-free crosslinkable monomer may be a fluorine-free compound having at least one reactive group and/or olefinic carbon-carbon double bond (preferably a (meth)acrylate group). The fluorine-free crosslinkable monomer may be a compound which has at least two olefinic carbon-carbon double bonds (preferably (meth)acrylate groups) or a compound which has at least one olefinic carbon-carbon double bond and at least one reactive group. Examples of the reactive group include a hydroxyl group, an epoxy group, a chloromethyl group, a blocked isocyanate group, an amino group, a carboxyl group and a glycidyl group.

[0041] The fluorine-free crosslinkable monomer may be a mono(meth)acrylate, di(meth)acrylate, or mono(meth)acrylamide having a reactive group. Alternatively, the fluorine-free crosslinkable monomer may be di(meth)acrylate.

[0042] Examples of the fluorine-free crosslinkable monomer include, but are not limited to, diacetone(meth)acrylamide, N-methylol(meth)acrylamide, hydroxymethyl(meth)acrylate, 2-hydroxyethyl(meth)acrylate, 2,3-dihydroxypropyl (meth)acrylate, 3-chloro-2-hydroxypropyl(meth)acrylate, 2-acetoacetoxyethyl (meth)acrylate, butadiene, isoprene, chloroprene, monochlorovinyl acetate, vinyl methacrylate, glycidyl(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, and neopentylglycol di(meth)acrylate.

[0043] The fluorine-free crosslinkable monomer may be, for example, an isocyanatoacrylate monomer. Specific examples of the isocyanatoacrylate monomer include 2-isocyanatoethyl(meth)acrylate, 3-isocyanatopropyl (meth)acrylate, 4-isocyanatobutyl(meth)acrylate, 2-butanone oxime adduct of 2-isocyanatoethyl(meth)acrylate, a pyrazole adduct of 2-isocyanatoethyl (meth)acrylate, 3,5-dimethylpyrazole adduct of 2-isocyanatoethyl(meth)acrylate, a 3-methylpyrazole adduct of 2-isocyanatoethyl(meth)acrylate, an epsilon-caprolactam adduct of 2-isocyanatoethyl(meth)acrylate, 2-butanone oxime adduct of 3-isocyanatopropyl(meth)acrylate, a pyrazole adduct of 3-isocyanatopropyl (meth)acrylate, 3,5-dimethylpyrazole adduct of 3-isocyanatopropyl(meth)acrylate, a 3-methylpyrazole adduct of 3-isocyanatopropyl(meth)acrylate, an epsilon-caprolactam adduct of 3-isocyanatopropyl(meth)acrylate, 2-butanone oxime adduct of 4-isocyanatobutyl(meth)acrylate, a pyrazole adduct of 4-isocyanatobutyl (meth)acrylate, 3,5-dimethylpyrazole adduct of 4-isocyanatobutyl(meth)acrylate, a 3-methylpyrazole adduct of 4-isocyanatobutyl(meth)acrylate, and an epsilon-caprolactam adduct of 4-isocyanatobutyl(meth)acrylate.

[0044] The halogenated olefin monomer (c2) is a monomer free from a fluorine atom.

[0045] The halogenated olefin monomer may be an olefin having 2-20 carbon atoms and substituted by 1-10 chlorine atoms, bromine atoms or iodine atoms. Preferably, the halogenated olefin monomer is a chlorinated olefin having 2-20 carbon atoms, particularly an olefin having 2-5 carbon atoms and having 1-5 chlorine atoms. Preferable examples of the halogenated olefin monomer are a vinyl halide such as vinyl chloride, vinyl bromide and vinyl iodide, and a vinylidene halide such as vinylidene chloride, vinylidene bromide and vinylidene iodide.

[0046] The term "(meth)acrylate" as used herein means an acrylate or methacrylate, and the term "(meth)acrylamide" as used herein means an acrylamide or methacrylamide.

[0047] Each of the monomers (a)-(c) may be used one alone or in a combination of at least two. The fluorine-containing copolymers (2) may be one alone or in a combination of at least two.

[0048] The fluorine-containing copolymer (2) of the present invention is preferably free from a repeating unit formed from a fluorine-free monomer containing a hydrocarbon group having at most 13 carbon atoms, for example, a (meth)acrylate ester containing a hydrocarbon group having at most 13 carbon atoms, particularly a (meth)acrylate ester containing a non-cyclic hydrocarbon group having at most 13 carbon atoms. For example, the fluorine-containing copolymer (2) of the present invention is preferably free from a repeat unit formed from lauryl acrylate. High water- and oil-repellency is obtained by being free from these repeat units.

[0049] A weight ratio of the fluorine-containing monomer (a) to the fluorine-free monomer (b) in the fluorine-containing copolymer (2) is preferably 35:65 to 70:30, more preferably 40:60 to 60:40, particularly 42.5:57.5 to 58:42. The amount of the fluorine-containing monomer (a) may be at least 25% by weight, for example, at least 35% by weight, particularly 35 to 60 % by weight, based on the fluorine-containing copolymer.

[0050] The amount of the monomer (c) may be at most 100 parts by weight, for example, 0.1 to 30 parts by weight, particularly 1 to 20 parts by weight, based on 100 parts by weight of the total of the monomer (a) and the monomer (b).

[0051] The weight-average molecular weight of the fluorine-containing polymer may be 2,500 to 20,000, preferably 3,000 to 15,000, for example, 5,000 to 12,000 in terms of polystyrene, as measured by GPC (gel permeation chromatography).

[0052] The polymer of the present invention may be a random copolymer or a block copolymer, but is generally a random copolymer.

[0053] The amount of the fluorine-containing copolymer (2) may be 0.01 to 50 parts by weight, preferably 0.1 to 20 parts by weight, particularly 0.2 to 10 parts by weight, for example, 1.0 to 8 parts by weight, more preferably 1.2 to 5.0 parts by weight, based on 100 parts by weight of the thermoplastic resin (1).

[0054] The fluorine-containing copolymer may be obtained by polymerizing by a known method using a polymerization initiator, a solvent, and optionally a chain transfer agent.

[0055] The fluorine-containing copolymer and the fluorine-free polymer in the present invention can be produced by any of conventional polymerization methods and the polymerization condition can be optionally selected. The polymerization method includes, for example, a solution polymerization, a suspension polymerization and an emulsion polymerization.

[0056] In the solution polymerization, there can be used a method of dissolving the monomer(s) into an organic solvent in the presence of a polymerization initiator, replacing the atmosphere by nitrogen, and stirring the mixture with heating at the temperature within the range from 30°C to 120°C for 1 hour to 10 hours. Examples of the polymerization initiator include azobisisobutyronitrile, benzoyl peroxide, di-tert-butyl peroxide, lauryl peroxide, cumene hydroperoxide, t-butyl peroxypivalate and diisopropyl peroxydicarbonate. The polymerization initiator may be used in the amount within the range from 0.01 to 20 parts by weight, for example, from 0.01 to 10 parts by weight, based on 100 parts by weight of total of the monomers.

[0057] The organic solvent is inert to the monomer, and dissolves the monomer, and examples of the organic solvent include an ester (for example, an ester having 2-30 carbon atoms, specifically ethyl acetate and butyl acetate), a ketone (for example, a ketone of 2-30 carbon atoms, specifically methyl ethyl ketone and diisobutyl ketone), and an alcohol (for example, an alcohol having 1-30 carbon atoms, specifically isopropyl alcohol). Specific examples of the organic solvent include acetone, chloroform, HCHC225, isopropyl alcohol, pentane, hexane, heptane, octane, cyclohexane, benzene, toluene, xylene, petroleum ether, tetrahydrofuran, 1,4-dioxane, methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, ethyl acetate, butyl acetate, 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene, tetrachlorodifluoroethane and trichlorotrifluoroethane. The organic solvent may be used in the amount within the range from 10 to 2,000 parts by weight, for example, from 50 to 1,000 parts by weight, based on 100 parts by weight of total of the monomers.

[0058] In the emulsion polymerization, there can be used a method of emulsifying monomers in water in the presence of a polymerization initiator and an emulsifying agent, replacing the atmosphere by nitrogen, and polymerizing with stirring, for example, at the temperature within the range from 50°C to 80°C for 1 hour to 10 hours. As the polymerization initiator, for example, water-soluble initiators such as benzoyl peroxide, lauroyl peroxide, t-butyl perbenzoate, 1-hydroxycyclohexyl hydroperoxide, 3-carboxypropionyl peroxide, acetyl peroxide, azobisisobutylamidine dihydrochloride, azobisisobutyronitrile, sodium peroxide, potassium persulfate and ammonium persulfate and oil-soluble initiators such as azobisisobutyronitrile, benzoyl peroxide, di-tert-butyl peroxide, lauryl peroxide, cumene hydroperoxide, t-butyl peroxypivalate and diisopropyl peroxydicarbonate can be used. The polymerization initiator may be used in the amount within the range from 0.01 to 10 parts by weight, based on 100 parts by weight of the monomers.

[0059] In order to obtain a polymer dispersion in water, which is superior in storage stability, it is preferable that the monomers are dispersed in water by using an emulsifying device capable of applying a strong shearing energy (e.g., a highpressure homogenizer and an ultrasonic homogenizer) and then polymerized. As the emulsifying agent, various emulsifying agents such as an anionic emulsifying agent, a cationic emulsifying agent and a nonionic emulsifying agent can be used in the amount within the range from 0.5 to 20 parts by weight, based on 100 parts by weight of the monomers. The anionic emulsifying agent and/or the cationic emulsifying agent and/or the nonionic emulsifying agent are preferable. When the monomers are not completely compatibilized, a compatibilizing agent capable of sufficiently compatibilizing them (e.g., a water-soluble organic solvent and a low-molecular weight monomer) is preferably added to these monomers. By the addition of the compatibilizing agent, the emulsifiability and polymerizability can be improved.

[0060] Examples of the water-soluble organic solvent include acetone, methyl ethyl ketone, ethyl acetate, propylene glycol, dipropylene glycol monomethyl ether, dipropylene glycol, tripropylene glycol and ethanol. The water-soluble organic solvent may be used in the amount within the range from 1 to 50 parts by weight, e.g., from 10 to 40 parts by weight, based on 100 parts by weight of water. Examples of the low-molecular weight monomer are methyl methacrylate, glycidyl methacrylate, 2,2,2-trifluoroethyl methacrylate. The low-molecular weight monomer may be used in the amount within the range from 1 to 50 parts by weight, e.g., from 10 to 40 parts by weight, based on 100 parts by weight of total of monomers.

[0061] A chain transfer agent may be used in the polymerization. The molecular weight of the polymer can be changed according to the amount of the chain transfer agent used. Examples of the chain transfer agent include a mercaptan group-containing compound (especially alkyl mercaptan (for example, having 1-30 carbon atoms)), such as lauryl mercaptan, thioglycol, and thioglycerol, and an inorganic salt such as sodium hypophosphite and sodium hydrogen sulfite. The amount of the chain transfer agent may be within the range from 0.01 to 10 parts by weight, for example, from 0.1 to 5 parts by weight, based on 100 parts by weight of total of the monomers.

[0062] A liquid medium is removed from a liquid (solution or dispersion) containing the fluorine-containing copolymer to obtain the fluorine-containing copolymer. For example, a dispersion of fluorine-containing copolymer (an aqueous dispersion or an organic solvent-dispersion) can be precipitated into water or an organic solvent, and dried to obtain the fluorine-containing copolymer.

[0063] The resin composition may consist of the thermoplastic resin (1) and the fluorine-containing copolymer (2), or may comprise another component. Examples of the other component include additives (that is, auxiliary agents) such as a dye, a pigment, an antistatic agent, an antioxidant, a light stabilizer, an ultraviolet light-absorbing agent, a neutralizing agent, a nucleating agent, an epoxy stabilizer, a lubricant, an antibacterial agent, a flame retardant and plasticizer.

[0064] The resin composition can be obtained by kneading (for example, melt-kneading) the thermoplastic resin (1) and the fluorine-containing copolymer (2). Generally, the thermoplastic resin (1) and the fluorine-containing copolymer (2) are heated at a temperature of 100-320°C, for example, 200-300°C to produce the nonwoven fabric. Preferably, the resin composition is heated to spin the fiber.

[0065] The method for producing the nonwoven fabric may be a wet method such as a paper-making method, and a dry method such as a melt-blown method, a spunbond method, a chemical bond method, a needle-punching method, a water punching method and a thermal bonding method. The melt-blown method and the spun-bond method are preferable, and the melt-blow method is particularly preferable.

[0066] In the melt-blow method, in general, a molten material of the resin composition pressure-fed to the die is spun from a nozzle having a large number of arranged small holes to give fibers. A discharge amount in the single hole is 0.1 to 20 g/minute, and a high-speed air amount may be 10 to 1000 Nm^3/hr/m.

[0067] Polypropylene as a base of the nonwoven fabric of the present invention may have a melt flow rate (MFR) of at least 600 g/10 min, preferably 650 to 2,500 g/10 min, more preferably 700 to 2,200 g/10 min, for example, 800 to 1,800 g/10 min. The MFR is measured under a load of 2.16 kg at a temperature of 230°C in accordance with ASTM D1238. The addition of the fluorine-containing copolymer to the polypropylene according to the present invention has the effect of giving a higher MFR. The higher MFR has the advantages that fluidity of the resin is high, and the processing performance is stabilized because of low discharge pressure during extrusion, the discharge is smooth to improve the flowability, and it is easy to narrow the diameter of the fiber. A method of thinning the fiber diameter includes a method of improving a shape of a nozzle or reducing a nozzle diameter, a method of increasing the MFR of polypropylene as the base. The addition of the fluorine-containing copolymer according to the present invention can increase the resin fluidity and can give a nonwoven fabric having a decreased fiber diameter.

[0068] An average fiber diameter of fibers in the nonwoven fabric is 0.1 to 5 micrometers, preferably 0.2 to 3 micrometers, more preferably 0.2 to 2.6 micrometers. The fiber diameter of the nonwoven fabric can be thin, since a surface-modified resin composition is used.

[0069] A basis weight of the nonwoven fabric may be 5 to 300 g/m^2, for example, 10 to 200 g/m^2. The basis weight is a value showing a weight per 1 m^2 of the nonwoven fabric prepared.

[0070] The nonwoven fabric of the present invention can be used for a clothes and health material such as operation clothes, paper diaper, sanitary napkin; a filter such as a cell filter, a dust-proof mask filter, a filter of an air cleaner and air conditioner; a separator for battery; a packaging material; a nonwoven fabric wiper; and an exterior material and interior material of automobile such as a door trim, an instrument panel, a tire house, a bumper, a floor cover, a hood cover and a roof cover; and a building material. The nonwoven fabric of the present invention is suitable for a medical use. For example, the nonwoven fabric can be used for a surgical gown, a surgical drape, a sheet, a bandage, a wiping cloth, a pillow cover, a mask, and a covering cloth.

Examples

[0071] Hereinafter, the present invention will be illustrated in detail by the following Examples, which do not limit the present invention.

[0072] In the following Examples, parts and % are parts by weight and % by weight, unless otherwise specified.

[0073] Properties were measured in the following manner.

Weight-average molecular weight of fluorine-containing polymer

[0074] A fluorine-containing polymer (0.1 g) and tetrahydrofuran (THF) (19.9 g) were mixed and then filtered by a filter after standing for one hour to prepare a THF solution of the fluorine-containing polymer. This sample was measured by a gel permeation chromatograph (GPC) set to the following device and condition. Instrument: SHODEX GPC-104 (manufactured by SHOWA DENKO K. K.) Column:

> Sample side: GPC LF-G, GPC LF604, GPC LF604, GPC KF601 and GPC KF601 (all manufactured by SHOWA DENKO K. K.) were connected in this order.
> Reference side: GPC KF600RL, GPC KF600RL, GPC KF600RH and GPC KF600RH (all manufactured by SHOWA DENKO K. K.) were connected in this order.
> Mobile phase: THF
> Mobile phase flow rate: 0.6mL/min in both sample side and reference side
> Column temperature: 40°C
> Detection unit: Differential refractometer (RI)

Basis weight

[0075] A weight and an area of a nonwoven fabric were measured to determine a weight per 1 m^2 of the nonwoven fabric.

Average fiber diameter

[0076] An electron microscope was used to prepare a picture of a nonwoven fabric taken by a magnification of 5,000x. 200 fibers were chosen at random from the fibers of the nonwoven fabric in the picture, and the diameters of the fibers were measured and an average value was calculated to give an average fiber diameter.

Antifouling property evaluation

[0077] After putting 3 g of the following test liquid on a nonwoven fabric and standing for 4 hours, the test liquid was wiped off with a cloth, and a degree of stain remaining after wiping off was visually estimated.

[0078] Test liquid:

Mustard
Ketchup
Canned coffee
Milky lotion

Evaluation method

[0079]

Excellent: Test liquid can all be wiped off to give no trace remainder.
Good: Test liquid can all be wiped off, but trace remains very slightly.
Fair: Test liquid cannot all be wiped off, and trace remains.
Bad: Test liquid cannot be wiped off at all, and trace remains distinctly.

Oleic acid repellency

[0080] 3mL of oleic acid was put on a nonwoven fabric, and time until a liquid droplet begins to sink into the nonwoven fabric was measured. The oleic acid repellency is 0 second, if the liquid droplet penetrates immediately.

Touch feeling:

[0081] A nonwoven fabric was touched by an index finger to evaluate a feel.

Evaluation method:

[0082]

Good: Slides with no feeling of catch.
Fair: Slides with slight feeling of catch.
Bad: Not slide with a feeling of catch.

Friction coefficient

[0083] A surface measuring instrument was used by using a steel ball as a friction element to measure a static friction coefficient, according to ASTM D1894.

Water-proof pressure

[0084] A water penetration test machine was used so that water adjusted to 25°C was pressurized from a back of a nonwoven fabric kept at a ring. A height (cm) of a column of water was measured at the time of three liquid droplets appearing on the surface.

Processability

[0085] Discharge pressure: A pressure applied at a tip of an extrusion machine was measured at the time of a nonwoven fabric processing. The evaluation is "unstable" if a pressure value is gradually changed in 10 seconds or less, and "stable" if a pressure value is not changed in more than 10 seconds.

[0086] Rolling-up property: When a prepared nonwoven fabric was rolled-up from a wire part, the evaluation is "unstable" if the nonwoven fabric remains on a wire without separating smoothly from the wire part, and "stable" if the nonwoven fabric is separated smoothly from the wire part.

Flowability

[0087] A pressure applied to a gear pump controlling a discharge amount of the resin from a tip of an extrusion machine was measured at the time of producing a nonwoven fabric.

Sound insulating property

[0088] A device for generating a sound by vibration was surrounded by a sound-insulated box having an opening part of a 10 cm x 10 cm, and the opening part was closed by a three-sheet pile of a nonwoven fabric. The sound was generated by the vibration, a noise meter was placed at a distance of 5 cm from the nonwoven fabric closing the opening part, to measure a degree of noise (dB).

Tensile test

[0089] A tensile test was conducted according to JIS L1913. A tensile strength, for example, was measured under the conditions of a width of a nonwoven fabric test piece of 50 mm, a distance between chucks of 200 mm and a tensile speed of 100 mm/min.

Preparative Example 1

[0090] $CH_2=C(-CH_3)-C(=O)-O-(CH_2)_2-(CF_2)_5CF_3$ (hereinafter referred to as "C6SFMA") (26.80 g), stearyl acrylate (hereinafter referred to as "StA") (40.20 g) and isopropyl alcohol (hereinafter referred to as "IPA") (100.50 g) as solvent were charged into a 300 mL flask, an internal temperature was set to be 65°C with stirring, azobisisobutyronitrile (hereinafter referred to as "AIBN") (0.82 g) was added and a mixture was kept for 10 hours. The solvent was removed to obtain a fluorine-containing copolymer.

Preparative Example 2

[0091] A fluorine-containing copolymer was obtained in the same manner as in Preparation Example 1 except that C6SFMA was 28.81 g, StA was 38.19 g, IPA was 102.51 g and AIBN was 0.47 g.

Preparative Example 3

[0092] A fluorine-containing copolymer was obtained in the same manner as in Preparation Example 1 except that C6SFMA was 30.15 g, StA was 36.85 g, IPA was 102.51 g and AIBN was 0.74 g.

Preparative Example 4

[0093] A fluorine-containing copolymer was obtained in the same manner as in Preparative Example 1 except that C6SFMA was 33.50 g, StA was 33.50 g, IPA was 101.84 g and AIBN was 0.60 g.

Preparative Example 5

[0094] A fluorine-containing copolymer was obtained in the same manner as in Preparative Example 1 except that C6SFMA was 38.86 g, StA was 28.14 g, IPA was 89.11 g and AIBN was 0.47 g.

Preparative Example 6

[0095] A fluorine-containing copolymer was obtained in the same manner as in Preparative Example 1 except that

C6SFMA was 43.55 g, StA was 23.45 g, IPA was 100.50 g and AIBN was 0.67 g.

Comparative Preparative Example 1

[0096] A fluorine-containing copolymer was obtained in the same manner as in Preparation Example 1 except that C6SFMA was 32.16 g, StA was 34.84 g, IPA was 134.00 g and AIBN was 1.34 g.

Comparative Preparative Example 2

[0097] A fluorine-containing copolymer was obtained in the same manner as in Preparation Example 1 except that IPA was 67.00 g and AIBN was 0.47 g.

Comparative Preparative Example 3

[0098] A fluorine-containing copolymer was obtained in the same manner as in Preparation Example 1 except that C6SFMA was 32.16 g, lauryl acrylate (hereinafter referred to as "LA") was 34.84 g, IPA was 93.80 g and AIBN was 0.54 g.

[0099] A monomer ratio and molecular weight of the fluorine-containing polymer obtained in Preparative Examples 1-6 and Comparative Preparative Examples 1-3 are shown in Table 1.

Table 1

	Monomer		Ratio		Molecular weight
	Fluorine-containing monomer	Fluorine-free monomer	Fluorine-containing monomer	Fluorine-free monomer	
Pre. Ex. 1	C6SFMA	StA	40	60	7000
Pre. Ex. 2	C6SFMA	StA	43	57	10000
Pre. Ex. 3	C6SFMA	StA	45	55	7000
Pre. Ex. 4	C6SFMA	StA	50	50	9000
Pre. Ex. 5	C6SFMA	StA	58	42	14000
Pre. Ex. 6	C6SFMA	StA	65	35	7000
Com. Pre. Ex. 1	C6SFMA	StA	48	52	2000
Com. Pre. Ex. 2	C6SFMA	StA	48	52	25000
Com. Pre. Ex. 3	C6SFMA	LA	48	52	9000

Examples 1 to 8

[0100] Each fluorine-containing copolymer obtained in Preparative Examples 1 to 6 was melt-mixed with polypropylene (hereinafter referred to as "PP800") having MFR of 800 at a temperature of 160°C by a twin screw extruder to give a fluorine-containing copolymer content of 20%, and the mixture was cooled with water and cut by a cutting machine to obtain pellets.

[0101] The polypropylene containing 20% of the fluorine-containing copolymer (hereinafter referred to as "fluorine-containing PP") was further mixed with PP800 in a pellet mix amount shown in Table 2, to give a target content of the fluorine-containing copolymer. This mixture was melt-mixed by a nonwoven fabric processing machine set at 240°C, and discharged on a wire part by a gear pump adjusting an amount of discharge which was set at 15 rpm equipped with a nozzle having a caliber of 0.25 mm, to obtain a nonwoven fabric. A target basis weight amount was set by changing a rolling-up speed of the wire part under the same discharge condition.

Comparative Example 1

[0102] PP800 was melt-mixed by a nonwoven fabric processing machine set at 240°C, and discharged on a wire part by a nozzle having a caliber of 0.25 mm, to obtain a nonwoven fabric having a basis weight of 30 g/m^2.

Comparative Examples 2 to 4

[0103] Each fluorine-containing copolymer of Preparative Comparative Examples 1 to 3 was melt-mixed with polypropylene (hereinafter referred to as "PP800") having MFR of 800 at a temperature of 160°C by a twin screw extruder to give a fluorine-containing copolymer content of 20%, and the mixture was cooled with water and cut by a cutting machine to obtain pellets.

[0104] A nonwoven fabric was obtained in the same manner as in Examples 1 to 8 except the above.

Example 9

[0105] A fluorine-containing copolymer of Preparative Example 3 was melt-mixed with PP800 at a temperature of 160°C by a twin screw extruder to give a fluorine-containing copolymer content of 20%, and the mixture was cooled with water and cut by a cutting machine to obtain pellets.

[0106] The polypropylene containing 20% of the fluorine-containing copolymer (hereinafter referred to as "fluorine-containing PP") was further mixed with polypropylene (hereinafter referred to as "PP1800") having MFR of 1800 in a pellet mix amount shown in Table 2, to give a target content of the fluorine-containing copolymer. This mixture was melt-mixed by a nonwoven fabric processing machine set at 240°C, and discharged on a wire part by a gear pump adjusting an amount of discharge which was set at 15 rpm equipped with a nozzle having a caliber of 0.25 mm with adjusting a rolling-up speed in the wire part, to obtain a nonwoven fabric having a basis weight of 30 g/m^2 or 5 g/m^2.

Comparative Example 5

[0107] PP1800 was melt-mixed by a nonwoven fabric processing machine set at 240°C, and discharged on a wire part by a nozzle having a caliber of 0.25 mm, to obtain a nonwoven fabric having a basis weight of 30 g/m^2.

Table 2

	PP	Fluorine-containing copolymer	Pellet mix amount (kg)		Ratio		Basis weight g/m^2
			PP	Fluorine-containing PP	PP	Fluorine-containing copolymer	
Com. Ex. 1	PP800	-	100	-	100	-	30
Ex. 1	PP800	Pre. Ex. 1	100	25	100	5	30
Ex. 2	PP800	Pre. Ex. 2	100	25	100	5	30
Ex. 3	PP800	Pre. Ex. 3	100	25	100	5	30
Ex. 4	PP800	Pre. Ex. 3	100	25	100	5	5
Ex. 5	PP800	Pre. Ex. 4	100	25	100	5	30
Ex. 6	PP800	Pre. Ex. 5	100	25	100	5	30
Ex. 7	PP800	Pre. Ex. 5	100	25	100	5	5
Ex. 8	PP800	Pre. Ex. 6	100	25	100	5	30
Com. Ex. 2	PP800	Com. Pre. Ex. 1	100	25	100	5	30
Com. Ex. 3	PP800	Com. Pre. Ex. 2	100	25	100	5	30
Com. Ex. 4	PP800	Com. Pre. Ex. 3	100	25	100	5	30
Com. Ex. 5	PP1800	-	100	-	100	-	30
Ex. 9	PP1800	Pre. Ex. 3	100	25	100	5	30

[0108] These test results are shown in Table 3.

Table 3

	Friction coefficient	Touch	Antifouling property				Oleic acid repellency. (Second)
			Mustard	Ketchup	Canned coffee	Milky lotion	
Com. Ex. 1	1.20	Bad	Bad	Bad	Bad	Bad	0
Ex. 1	1.09	Fair	Good	Good	Fair	Fair	4
Ex. 2	1.05	Good	Excellent	Fair	Good	Good	4
Ex. 3	1.03	Good	Excellent	Excellent	Good	Excellent	5
Ex. 4	1.03	Good	Excellent	Excellent	Good	Excellent	5
Ex. 5	1.03	Good	Excellent	Excellent	Good	Excellent	5
Ex. 6	1.03	Good	Excellent	Good	Good	Good	5
Ex. 7	1.03	Good	Excellent	Good	Good	Good	5
Ex. 8	1.07	Fair	Good	Good	Good	Fair	5
Com. Ex. 2	1.20	Bad	Bad	Fair	Bad	Fair	1
Com. Ex. 3	1.19	Bad	Fair	Fair	Fair	Bad	2
Com. Ex. 4	1.23	Bad	Bad	Bad	Bad	Bad	0
Com. Ex. 5	1.30	Bad	Bad	Bad	Bad	Bad	0
Ex. 9	1.06	Excellent	Excellent	Good	Fair	Excellent	5

Examples 10 to 19

[0109] Each fluorine-containing copolymer of Preparative Examples 3 and 4 was melt-mixed with PP800 at a temperature of 160°C by a twin screw extruder to give a fluorine-containing copolymer content of 20%, and the mixture was cooled with water and cut by a cutting machine to obtain pellets.

[0110] The polypropylene containing 20% of the fluorine-containing copolymer (hereinafter referred to as "fluorine-containing PP") was further mixed with PP800 in a pellet mix amount shown in Table 4, to give a target content of the fluorine-containing copolymer. This mixture was melt-mixed by a nonwoven fabric processing machine set at 240°C, and discharged on a wire part by a gear pump adjusting an amount of discharge was set at 15 rpm equipped with a nozzle having a caliber of 0.25 mm with adjusting a rolling-up speed in the wire part, to obtain a nonwoven fabric having a basis weight of 15 g/m^2.

Comparative Example 8

[0111] A nonwoven fabric was obtained in the same manner as in Comparative Example 1 except a basis weight was 15 g/m^2.

Comparative Example 9

[0112] A nonwoven fabric was obtained in the same manner as in Comparative Example 7 except a basis weight was 15 g/m^2.

Table 4

	PP	Fluorine-containing copolymer	Pellet mix amount (kg)		Ratio	
			PP	Fluorine-containing PP	PP	Fluorine-containing copolymer
Com. Ex. 6	PP800	-	100	-	100	-
Ex. 10	PP800	Pre. Ex. 3	100	2.5	100	0.5
Ex. 11	PP800	Pre. Ex. 3	100	6.0	100	1.2
Ex. 12	PP800	Pre. Ex. 3	100	15.0	100	3
Ex. 13	PP800	Pre. Ex. 3	100	25.0	100	5
Ex. 14	PP800	Pre. Ex. 3	100	40.0	100	8
Ex. 15	PP800	Pre. Ex. 6	100	2.5	100	0.5
Ex. 16	PP800	Pre. Ex. 6	100	6.0	100	1.2
Ex. 17	PP800	Pre. Ex. 6	100	15.0	100	3
Ex. 18	PP800	Pre. Ex. 6	100	25.0	100	5
Ex. 19	PP800	Pre. Ex. 6	100	40.0	100	8
Com. Ex. 7	PP1800	-	100	-	100	-
Ex. 20	PP1800	Pre. Ex. 3	100	25.0	100	5

[0113] These test results are shown in Table 5.

Table 5

	Fiber diameter (micrometer)	Workability		Sound-proofing (dB)	Water-proof pressur e	Tension test		
		Discharge pressure	Rolling-up property			Elastic modulus (MPa)	Maximu m point stress (MPa)	Maximu m point elongati on (%)
Com. Ex. 6	3.1	Unstable	Unstable	86	332	17.0	1.40	57.0
Ex. 10	2.7	Unstable	Stable	83	350	17.3	1.33	50.0
Ex. 11	2.5	Stable	Stable	80	378	18.0	1.20	43.0
Ex. 12	2.2	Stable	Stable	80	380	17.9	1.20	44.0
Ex. 13	2.2	Stable	Stable	78	390	17.7	1.25	45.7
Ex. 14	2.2	Stable	Stable	76	389	17.8	1.24	45.8
Ex. 15	2.9	Unstable	Stable	84	345	17.3	1.32	52.8
Ex. 16	2.7	Stable	Stable	82	362	17.9	1.20	44.0
Ex. 17	2.5	Stable	Stable	81	369	18.0	1.22	43.8
Ex. 18	2.5	Stable	Stable	81	371	17.9	1.23	45.1
Ex. 19	2.5	Stable	Stable	80	370	18.0	1.24	45.0
Com. Ex. 7	2.8	Unstable	Unstable	87	340	16.8	1.41	59.0
Ex. 20	1.6	Stable	Stable	78	400	18.0	1.26	46.8

Example 21 and Comparative Example 8

[0114] A nonwoven fabric was obtained in the same manner as in Example 3 and Comparative Example 1 except a basis weight was 5 g/m^2. A pellet mix amount and test results are shown in Table 6.

Table 6

	PP	Fluorine-containing copolymer	Pellet mix amount		Flowability		Basis weight (g/m^2)	Average Fiber diameter (micrometer)
			PP	Fluorine-containing PP	Gear pump (rpm)	Pressure (Mpa)		
Com. Ex. 8	PP800	-	100	-	15	1.22	5	3.1
Ex. 21	PP800	Pre. Ex. 3	100	25	15	0.87	5	2.5

[0115] In the case that a nonwoven fabric was prepared under the same conditions, when the fluorine-containing copolymer is added, a pressure was decreased. This is because the mobility of resin is improved by adding the fluorine-containing copolymer. The addition of the fluorine-containing copolymer has also the effect that the diameter of the fiber is thinner.

Example 22 and Comparative Example 9

[0116] A nonwoven fabric was obtained in the same manner as in Example 9 and Comparative Example 5 except a basis weight was 3 g/m^2. A pellet mix amount and test results are shown in Table 7.

Table 7

	PP	Fluorine-containing Copolymer	Pellet mix amount		Flowability		Basis weight (g/m^2)	Average Fiber diameter (micrometer)
			PP	Fluorine-containing PP	Gear pump (rpm)	Pressure (Mpa)		
Com. Ex. 9	PP800	-	100	-	15	0.89	3	1.1
Ex. 22	PP800	Pre. Ex. 3	100	25	15	0.52	3	0.7

Example 23 and Comparative Example 10

[0117] A nonwoven fabric was obtained in the same manner as in Example 22 and Comparative Example 9 except a nozzle diameter was 0.15 mm. A pellet mix amount and test results are shown in Table 8.

Table 8

	PP	Fluorine-containing Copolymer	Pellet mix amount		Flowability		Basis weight (g/m^2)	Average Fiber diameter (micrometer)
			PP	Fluorine-containing PP	Gear pump (rpm)	Pressure (Mpa)		
Com. Ex. 10	PP800	-	100	-	15	0.92	3	0.5
Ex. 23	PP800	Pre. Ex. 3	100	25	15	0.58	3	0.3

[0118] The fiber diameter can be thin by increasing the MFR of polypropylene used as a base, and also by decreasing the nozzle caliber. It is shown that the fiber diameter is thinner by adding the fluorine-containing copolymer according to the present invention.

INDUSTRIAL APPLICABILITY

[0119] The nonwoven fabric of the present invention can be used as, for example, a clothes and sanitary material (for example, operation clothes, a paper diaper, a sanitary napkin), a filter (for example, a battery filter, a filter of a dust-proof mask, a filter of an air-conditioner or an air purifier), a separator for batteries, a packaging material, a nonwoven fabric wiper, an automotive interior material or exterior material (for example, a door trim, an instrument panel, a tire house, a bumper, a floor cover, a bonnet cover, a roof cover), and a building material. The nonwoven fabric of the present invention is suitable for a medical use. For example, the nonwoven fabric can be used for a surgical gown, an operation drape, a sheet, a bandage, a wiping cloth, a pillow cover, a mask and a covering cloth.

Claims

1. A nonwoven fabric comprising a resin composition comprising:

    (1) a thermoplastic resin, and
    (2) a fluorine-containing copolymer,

    wherein the thermoplastic resin (1) is polypropylene, and
    the fluorine-containing copolymer (2) is a copolymer which comprises:

    (a) a repeating unit formed from a fluorine-containing monomer represented by the formula:

    $$CH_2=C(-X)-C(=O)-Y-Z-Rf$$

    wherein X is a hydrogen atom, a monovalent organic group or a halogen atom,
    Y is -O- or -NH-,
    Z is a direct bond or an divalent organic group, and
    Rf is a fluoroalkyl group having 4 to 6 carbon atoms, and

    (b) a repeating unit formed from a fluorine-free monomer containing a hydrocarbon group having at least 14 carbon atoms, and

    which has a weight-average molecular weight of 2,500 to 20,000.

2. The nonwoven fabric according to claim 1, wherein, in the fluorine-containing monomer (a), X is a methyl group and Z is a linear alkylene group or branched alkylene group having 1-20 carbon atoms.

3. The nonwoven fabric according to claim 1 or 2, wherein the fluorine-free monomer (b) is a (meth)acrylate ester in which an acryloyloxy group is bonded to a monovalent non-cyclic hydrocarbon group or cyclic hydrocarbon group having 14-30 carbon atoms.

4. The nonwoven fabric according to any one of claims 1 to 3, wherein the fluorine-free monomer (b) is an acrylate ester in which an alpha-position is a hydrogen atom.

5. The nonwoven fabric according to any one of claims 1 to 4, wherein the fluorine-containing copolymer (2) further comprises (c) a repeating unit formed from a fluorine-free crosslinkable monomer, and the amount of the monomer (c) is 0.1 to 100 parts by weight, based on 100 parts by weight of the total of the monomer (a) and the monomer (b).

6. The nonwoven fabric according to any one of claims 1 to 5, wherein the fluorine-containing copolymer (2) has a weight-average molecular weight of 3,000 to 15,000.

7. The nonwoven fabric according to any one of claims 1 to 6, wherein, in the fluorine-containing copolymer (2), a weight ratio of the fluorine-containing monomer (a) to the fluorine-free monomer (b) is 35: 65 to 70: 30 and the amount of the fluorine-containing monomer (a) is at least 25 wt%, based on the fluorine-containing copolymer.

8. The nonwoven fabric according to any one of claims 1 to 7, wherein the resin composition has a melt flow rate (MFR)

of at least 600 g/10 minutes.

9. The nonwoven fabric according to any one of claims 1 to 8, wherein a fiber in the nonwoven fabric has an average fiber diameter of 0.1 to 5 micrometers.

10. The nonwoven fabric according to any one of claims 1 to 9, wherein the amount of the fluorine-containing copolymer (2) is 0.01 to 50 parts by weight, based on 100 parts by weight of the thermoplastic resin (1).

11. A method of producing a nonwoven fabric, comprising steps of:

(i) mixing a thermoplastic resin (1) with a fluorine-containing copolymer (2) to obtain a resin composition; and
(ii) spinning fibers from a melt of the resin composition which is pressure-fed to a die by a melt blowing method, with a nozzle having a large number of arranged small holes,

wherein the thermoplastic resin (1) is polypropylene, and
the fluorine-containing copolymer (2) is a copolymer which comprises:

(a) a repeating unit formed from a fluorine-containing monomer represented by the formula:

$$CH_2=C(-X)-C(=O)-Y-Z-Rf$$

wherein X is a hydrogen atom, a monovalent organic group or a halogen atom,
Y is -O- or -NH-,
Z is a direct bond or an divalent organic group, and
Rf is a fluoroalkyl group having 4 to 6 carbon atoms, and

(b) a repeating unit formed from a fluorine-free monomer containing a hydrocarbon group having at least 14 carbon atoms, and

which has a weight-average molecular weight of 2,500 to 20,000.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/008680

A. CLASSIFICATION OF SUBJECT MATTER
D04H1/4291(2012.01)i, *D04H3/007*(2012.01)i, *D04H3/16*(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D04H1/00-18/04, D01F1/00-6/96;9/00-9/04,
C08C19/00-19/44;C08F6/00-246/00;301/00

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

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Kokai Jitsuyo Shinan Koho	1971-2017	Toroku Jitsuyo Shinan Koho	1994-2017

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	JP 03-007745 A (Sekisui Chemical Co., Ltd.), 14 January 1991 (14.01.1991), claims; page 2 (Family: none)	1-11

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

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

Date of the actual completion of the international search 24 April 2017 (24.04.17)	Date of mailing of the international search report 09 May 2017 (09.05.17)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/008680

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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