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(71) Applicant (for all designated States except US): SILVERPHASE OY [FI/FI]; Viikinkaari 6, FI-00790 Helsinki (FI).

(72) Inventors; and

(75) Inventors/Applicants (for US only): NIEMINEN, Jyri [FI/FI]; c/o SilverPhase Oy, Viikinkaari 6, FI-00790 Helsinki (FI). MÄKI, Markus [FI/FI]; c/o SilverPhase Oy, Viikinkaari 6, FI-00790 Helsinki (FI). LAÄKSONEN, Harri [FI/FI]; c/o SilverPhase Oy, Viikinkaari 6, FI-00790 Helsinki (FI). AREVA, Sami [FI/FI]; c/o SilverPhase Oy, Viikinkaari 6, FI-00790 Helsinki (FI).

(74) Agent: SEPPO LAINE OY; Itamerenkatu 3 B, FI-00180 Helsinki (FI).


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(54) Title: POLYMERIC ANTIMICROBIAL ADDITIVE

(57) Abstract: An antimicrobial copolymer composition obtained by reacting an olefinically unsaturated carboxylic acid copolymer with at least one metal ion source to form an ionomer type antimicrobial polymer composition containing at least 5 mass-% of metal ions having antimicrobial properties. The composition has low molecular weight and high antimicrobial metal content. The material is concentrated into the melt phase interfaces during melt processing and onto the surfaces of the cooled polymer and gives enhanced antimicrobial metal release.
POLYMERIC ANTIMICROBIAL ADDITIVE

Background of the Invention

Field of the Invention

The present invention relates to the field of antimicrobial polymers, more particularly it concerns ionomer type polymers and compositions, wherein said ionomer type polymer contains metals with antimicrobial properties. Moreover, the present invention relates to production methods of antimicrobial polymers and polymer additives and to articles having antimicrobial functionality through addition of antimicrobial polymer additives during production.

Description of Related Art

The development of silver based antimicrobial technologies has been in extensive progress during the recent decades. The Silver ion is known as one of the most versatile antimicrobial agents due to its powerful antimicrobial properties and low toxicity to mammalian tissues and cells. Silver possesses a broad spectrum of antimicrobial activity against Gram+ and Gram- bacteria (including antibiotic resistant strains), fungi, protozoa and viruses.

The high affinity of ionic silver towards biochemically significant chemical moieties (such as thiol, amino, carboxyl and phosphate groups) is a central feature responsible for the powerful antimicrobial activity of silver ion. The binding of silver ions to e.g. corresponding moieties of proteins in bacteria having a role in normal cell functions results in alteration of their molecular structures. Thereby, the silver ion affects many biochemical processes (cell wall synthesis, transcription, translation, electron transport and protein folding), eventually resulting in death of bacterial cell. The high affinity of silver, surprisingly, is also responsible for the fact that silver has a low toxicity in mammalian physiological systems.

Incorporation of silver and various ionic silver releasing components into different materials leads to obtaining of antimicrobial materials having activity against a broad spectrum of microbes. Silver based antimicrobial polymers and plastic products are
Increasingly developed and marketed for use in i.e. healthcare, food packaging, medical device, hygiene products and various consumer applications. Presently in the food industry silver technologies are used in packaging and storage plastics and industry objects to promote hygiene control (e.g. food contact surfaces, doorhandles), whereas in the medical field, silver is used e.g. in cathethes, dental applications and antimicrobial dressings in wound care. Antimicrobial articles, such as operation buttons, restroom seats and equipment etc. have been developed to be used in healthcare and public environments including most importantly hospitals, but also airports, transportation vehicles etc. The present consumer applications include materials in laundry machines, refrigerators, kitchenware, sportswear and applications the like wherein hygiene and/or odor control is desireable.

The chemical state of silver affects significantly its antimicrobial properties. Silver is an effective antimicrobial when it is introduced to the target microbe in its ionic form. Thus, the crucial feature in development of silver based antimicrobial materials is the capability of said material to release ionic silver into the moisture zone at the material interphase, and in more detail, the intensity and dynamics of the process. Another key challenge in constructing said materials is material efficiency, in more detail, "silver efficiency".

Silver has been incorporated into thermoplastic matrices to render them antimicrobial properties. Various techniques are described in the literature. Thus, International Patent Application PCT/US2005/032924 (E.I. DU PONT DE NERMOUS AND COMPANY) of 13 September 2005 discloses antimicrobial polymer compositions comprising at least E/X/Y copolymer, or at least ionomer of an E/X/Y copolymer, wherein E is ethylene, X is a C 3-8 alpha, beta ethylenically unsaturated carboxylic acid, and Y is a softening comonomer selected from alkyl acrylates and alkyl methacrylates. The known compositions also comprise at least one organic acid, which can be in salt form. Groups of acid X are optionally neutralized to a level of 15 to 100 mol-% with monovalent or divalent metal ions. Acid copolymers suitable for use in the invention have a weight average molecular weight (Mw) preferably greater than about 40 kD. Like Nucrel copolymers. Ionomers include ionomers obtained from ethylene (meth)acrylic acid (E/(M)AA) dipolymers having a weight average molecular weight (Mw) of from about 10 kD to about 500 kD. In the examples of the patent application, Surlyn and Himilcan ionomers and Nucrel copolymers were used, the silver salt concentrations being in the range of 0.1 to 0.5 mass-%, when melt blending was used.
Published International Patent Application WO 03/103732 A (E.I. DU PONT DE NERMOUS AND COMPANY) of 18 December 2003 discloses antimicrobial polymer articles, and polymers comprising copolymers of ethylene and unsaturated carboxylic acids like acrylic acid, methacrylic acid or 1-8 carbon alkyl acrylates methacrylates, or ionomers of ethylene/acyric acid or methacrylic acid copolymers or terpolymers. The polymers are treated with antimicrobial chitosan in aqueous acetic acid solution as a first treatment and further subjected to one or more treatments with metal salts, carboxyl containing polymer and/or chitosan.

EP Patent Application No. 0 436 725 (TOYO SEIKAN KAISHA, LTD) of 17 July 1991 discloses antibacterial polymers which contain silver and which comprise copolymers of 0.2 - 35 % ethylenically unsaturated carboxylic acids like acrylic or methacrylic acid and olefmes like ethylene. The polymers are prepared by blending the polymers with silver oxide and heating/kneading above the melting point. The polymers are used for forming packaging materials or coatings. Comparative example 7 discloses a process in which an ethylene methacrylic acid copolymer is mixed with 1 % silver acetate, heated and pressed to a film. The film is told to emit acetic acid, thus comprises an organic acid.

US Published Patent Application No. 2003/147960 A1 (LIN TUNG-LIANG ET AL) of 7 August 2003 discloses antimicrobial coatings for medical devices, like urethral stents, comprising a polymer having ionized groups and an opposite charged ionic antimicrobial agent. The antimicrobial agents include silver salts, antibiotics etc. The preferred examples show poly(ethylene co acrylic acid) as polymer and AgCl as the antimicrobial agent, which is added to the polymer as an aqueous solution, after the polymer has been transformed into an ionomer by a weak base.

Further, Published International Patent Application WO 98/14073 A (E.I. DU PONT DE NERMOUS AND COMPANY) of 9 April 1998 discloses antimicrobial films, comprising i.a. ethylene methacrylic acid copolymers or their corresponding Na, Mg, Zn, Li ionomers and sorbic, benzoic, hydroxybenzoic or propionic acid salts as an antimicrobial agents. Preferred copolymers are from Nucrel series and preferred ionomers are from the Surlyn series. The antimicrobial agents are blended with the copolymers/ionomers by melt mixing and extrusion.
US Patent No. 5 006 267 (VAUGHN E T AL) of 9 April 1991 discloses biocidal filters comprising copolymers of alpha olefines with alpha, beta ethylenically unsaturated carboxylic acids or corresponding ionomers which have been modified by reaction with biocidal agents like QUATS, bis-QUATs, polymeric QUATs etc. The biocidal copolymers/ionomer are prepared by reacting the polymers with the antimicrobial agents by milling, melt blending or contacting with aqueous solutions of the antimicrobial agents.

JP Patent Application No. 03-039363 (DU PONT MITSUI POLYCHEM CO LTD) of 7 July 1989 discloses antibacterial packaging material comprising ethylene unsaturated carboxylic acid copolymer neutralized with copper ions or silver ions or a composition consisting of the copolymer and any other thermoplastic polymer as a basic material. Copper ionomer, neutralized with copper ions is preferred. Particularly melt flow rate under 2.16 kg load 190 C degrees 0.1 to 200g/10 min are useful. Neutralization of copolymer is preferably done with extruder. Ion sources are acetates or copper hydroxide. To obtain said ionomer, copolymer can be dissolved with an organic solvent and neutralized with copper and silver salts, and then the organic solvent is eliminated. Copper and silver ions are used preferably 0.5 to 5.0 mass-% of composite. When the above composition is used in multilayer structures, effective antibacterical properties are achieved with layer thicknesses of 10 to 1000 micrometer. In examples, a copolymer of ethylene and methacrylic acid (methacrylic acid content 15 mass-%, MFR 60g/10 min), and copper(II) acetate is used. Neutralization is done with single screw extruder working at 220 C degrees. Color of above example was transparent green.

JP Patent Application No. 04-253754 (KUWABARAYASUNAGA) of 30 January 1991 discloses production of antibacterial polymers and the use thereof. Thermoplastic copolymers comprising ethylenically unsaturated carboxylic acid or anhydride are mixed with silver carbonate or silver lower carboxylate, and the obtained mixture is melt kneaded under conditions favorable for discharging a decomposition gas of the silver salt. Preferably methacrylic acid is main acid of copolymer. Preferred olefine is ethylene. Content of acid is preferably 2 to 25 mass-% of copolymer. Silver ion source preferred particle size is less than 5 micrometers. The preferred content of silver carboxylate or lower carboxylate is 0.001 to 5 mass-%. In the examples, an ethylene methacrylic acid copolymer and silver carbonate and silver acetate were used. Loading of silver ion source were 0.05 to 0.5 mass-%. 


JP Patent No. 1268610 (MITSUBISHI PETROCHEMICAL CO) of 26 October 1989 discloses a non-pollutive aquatic antifouling agent comprising an olefinic polymer having carboxyl groups at the side chains (e.g., an ethylene/alpha,beta-unsaturated carboxylic acid random or block copolymer such as ethylene/acrylic acid copolymer) is cross-linked through at least one kind of metal (e.g. silver) selected from I b group metals to provide an aquatic antifouling agent wherein the content of the metal atoms is 1 - 10 wt.%, particularly 3 - 7 wt.%. 

US Patent No. 4181786 (NITTO ELECTRIC IND CO) of 1 January 1980 discloses an antibacterial and antifungal material comprising a polymer containing carboxyl groups in an amount of at least about 0.008 milliequivalent per gram of the polymer and antibacterial and antifungal metallic ions ionically bonded to the carboxyl groups in an amount of at least about 0.0009 millimole per gram of the polymer. 

US Patent No. 4737491 (KEMIRA OY) of 12 April 1988 discloses an antimicrobial wood preservative which contains water, a copper and/or zinc complex or a copper and/or zinc complex together with a zirconium complex, dissolved in water, and an acid which stabilizes the said metals in wood. According to the invention there is used as the acid which stabilizes metals in wood an organic polymer which is soluble in water or forms micelles in water, contains acid groups, and penetrates wood at least partly. Phloroglucin derivatives of fern extract can be used in addition. 

US Published Patent Application No. 2006/0079640 of 13 April 2006 discloses an adhesive composition for dermal patches, comprising (A) a (meth)acrylic acid-base polymer having repeating units represented by formulae (1) and (2): (wherein R.sup.1 and R.sup.2 each independently represents a hydrogen atom or a methyl group and M represents NH.sub.4.sup.+ or an alkali metal) with the ratio of (1)/ (2) being in a range of 100/0 to 90/10 (by mol), (B) water, (C) a polyhydric alcohol and (D) an aluminum compound, with the content of (B) water being from 5 to 30 mass %; and a production process thereof. The adhesive composition for dermal patch of the present invention can contain a large amount of polyhydric alcohol between skeletons of the adhesive layer and forms a stable between skeletons of the adhesive layer and forms a stable base material free from syneresis of the polyhydric alcohol. Furthermore, the dermal patch using the adhesive composition for dermal patch of the present invention is excellent in the release property and adherence and has high safety.
In summary, the method of producing antimicrobial polymer compositions includes feeding substantially high molecular weight polyolefine ionomer or its acid precursor together with a silver and/or copper and/or zinc ion source to high shear, kneading, thermoplastic process like extruder, banbury mill, roll mill etc. Content of antimicrobial ion source is relatively low, 0.01 to 10 mass-%. Use of these antimicrobial polymer compositions as an effective antimicrobial additive for other polymers is limited, because of high viscosity and required relatively high loading, which is causing compatibility problems and it is decreasing mechanical properties of applications. Addition of viscous ionomers to other polymers by melt processes causes encapsulating problem i.e. antibacterial ionomer is surrounded by host polymer, causing lack of antimicrobial ion diffusion to the surface of the application.

**Summary of the Invention**

As will appear from the above review, there still remains a need to provide for more efficient antimicrobial compositions and methods for the production thereof.

As potential risks for health and environment of nanosized silver particles are under wide discussions, there is need for considerably safer silver releasing technology.

Thus, it is an aim of the present invention to provide novel compositions containing a polymer or copolymer containing metal ions and exhibiting antimicrobial properties.

Another aim of the invention is to provide a composition having properties of blooming, i.e. a tendency of antimicrobial polymer composition to accumulate at polymer phase interfaces, i.e. to form antimicrobial ionomer phase.

A still further aim of the invention is to provide antimicrobial polymer compositions which have the capability of preventing encapsulation.

These and other aims are achieved by the provision of an effective polymeric carrier for antimicrobial metal ions, capable of forming surface layers of articles, resulting in a lower need of antimicrobial ion loading i.e. an economical antimicrobial ion based fully polymeric solution.
According to the present invention, the carrier comprises a low molecular weight olefinically unsaturated carboxylic acid copolymer or polymer composition which is capable of containing at least 5 mass-%, in particular at least 10 mass-% and preferably at least 15 mass-% (suitably 20 mass-% or more) of metal ions with antimicrobial properties.

Thus, the present invention provides a polyolefin ionomer type polymer composition having a wide antimicrobial spectrum suitable for use as an antimicrobial additive for a wide range of thermoplastic polymers, with low addition levels. It has been found that ionomer compositions of the present kind are able of releasing antimicrobial ions effectively.

The antimicrobial polymer composition is suitable as an additive for thermoplastic polymer applications. The additive is compounded with host polymers, especially hydrophobic host polymers, during melt processes associated with product manufacturing.

More specifically the compositions according to the present invention are characterized by what is stated in the characterizing part of claim 1.

The method according to the present invention is characterized by what is stated in the characterizing part of claim 9.

The polymer articles according to the invention is characterized by what is stated in the characterizing parts of claims 14 and 15.

Significant advantages are obtained by the low molecular weight and high antimicrobial metal content associated with the present invention compared to prior art. The advantages include relative concentrating of said material into the melt phase interfaces during melt processing and furthermore onto the surfaces of the cooled polymer and enhanced antimicrobial metal release from the product surface.

Moreover, in comparison with the prior art, the high antimicrobial metal ion content of the additive in accordance with the invention enables decreased additive loading ratio in order to obtain required antimicrobial functionality of the product.
Further, the required low additive addition ratio enables preservation of the mechanical and melt properties of the host polymer due to low addition levels which is additionally advantageous in association with implementation of the technology into various applications.

Next, the new technology will be examined in greater detail with the aid of a detailed description and with reference to a number of working examples.

**Description of Embodiments**

In a first embodiment, the present technology provides an antimicrobial polymer or copolymer composition obtained by reacting an olefinically unsaturated carboxylic acid polymer or copolymer with at least one metal ion source to form an ionomer type antimicrobial polymer composition containing at least 15 mass-% of metal ions having antimicrobial properties.

The ionomer structure typically comprises in the repeating unit one component derived from an olefinic monomer and one component derived from an olefinically unsaturated carboxylic acid. Generally ionomers are copolymers of alpha-or beta-unsaturated carboxylic acid and an olefin.

The carboxylic acid has typically 3 to 8 carbon atoms. Thus, olefinically unsaturated carboxylic acid or their anhydrides includes such as metacrylic acid, acrylic acid, crotonic acid, itaconic acid, fumaric acid, maleic acid, maleic anhydride and itaconic anhydride. Acrylic acid and metacrylic acid are particularly preferred.

In accordance with the present invention, suitable olefins for the ionomers are, for example, ethylene, propylene, 1-butene, 1-pentene, 1-heptene, where ethylene is preferred.

In the present instance, the molecular weight of the olefinically unsaturated carboxylic acid copolymer is preferably between 500 and 8000 g/mol, in particular between 700 and 4000 g/mol.
In one embodiment, the unsaturated carboxylic acid concentration is at least 20 mass-%, in particular at least 30 mass-%, of said thermoplastic polymer composition, excluding the metal ions.

An effective copolymer composition contains acid units in amounts of from 15 to 60 mass-% of the polymer, preferably 20 to 50 mass-%. The melting range or softening range of said polymer is, in one embodiment, 50 to 100 °C, preferably 60 to 80 °C.

Preferably, the melting point of the ethylenically unsaturated carboxylic acid copolymer is below 90 °C. According to a particularly preferred embodiment, the ethylene acrylic acid copolymer has a melt index at 125 °C of at least 1000 g/min under 2.16 kg load.

As specific examples of commercially available ionomers, the following can be mentioned: A-C 5180 polyethylene acrylic acid copolymer wax by Honeywell, density 0.93 - 0.94 g/cm3, acid number 185-225 mg KOH/gm, Viscosity at 140 °C (284 °F) Brookfield 625 cps. And Primacor 5990i polyethylene acrylic acid copolymer wax by Dow Chemcals, density 0.955 g/cm3, acrylic acid content 20 mass-%, melt index 1300 g/10 min under 2.16 kg load at 190 °C.

The olefinically unsaturated carboxylic acid polymer or copolymer is reacted with at least one metal ion source, such as an ionic compound of the metal, at a temperature below the melting or softening temperature of the polymer. The temperature of the reaction is about 50 to 100 °C, preferably about 60 to 90 °C.

Examples of metal ion sources include conventional salts of mineral acids and organic acids, such as silver salts of (meth)acrylic acid and acrylic acid.

Typically, the metal ion is selected from the group of silver, copper and zinc and mixtures thereof. After the reaction, the metal ion content of the composition is 20 to 50 mass-%, preferably 20 to 35 mass-%.

In one embodiment according to the present invention, the ethylenically unsaturated carboxylic acid copolymer is partially neutralized with zinc ions or with copper ions.
The antimicrobial polymer composition is suitable as an additive for thermoplastic polymer applications. The additive can be compounded with thermoplastic host polymers, especially hydrophobic host polymers, polymer compositions, hydrophilic host polymers and polymer compositions or mixed compositions thereof.

The thermoplastic polymers can be selected from the group of polyolefins, polyesters, polyamides, polyesteramides, polyvinyls, including polyvinyl chloride, acrylic polymers, polyurethanes, polycarbonates, polyoximethylene, polyphenylene sulfide, polyphenylene oxide and polystyrene compounds, as well as mixtures of the polymers listed.

Thermoplastic co- and terpolymers are also included.

In accordance with an embodiment of the present invention, said antimicrobial additive can be used in other than thermoplastic processes and compounded or mixed with other polymers than thermoplastic host polymers, including elastomers, thermosets and composites. Thus, the additives can be used for producing compounds of thermoplastic materials, in particular having hydrophobic properties.

The thermoplastic polymeric antimicrobial additive in accordance with the present invention can also be used (independent of final applications) in melt processes associated with e.g. production of thermoplastic mono-, bi- or multilayer films, fibers and microfibers, injection molded objects, thermoplastic profiles, mono-, bi- or multilayer tubings, extrusion coated paper products etc..

Moreover, application fields and examples of potential end applications of the additive in accordance with the invention include medical and healthcare applications (e.g. sterile packaging (films, nonwovens), medical device industry packaging (films, nonwovens), medical devices, furniture parts for healthcare environments, medical tubings, other healthcare and medical textiles and nonwovens, fiber filters, wiping fabrics, trays, containers etc.) food and beverage industry applications (food packaging (films, nonwovens), tubes and tubing systems, filters industrial surfaces, process equipment, articles etc.), construction industry (e.g. construction films), agriculture (e.g. agricultural films), life sciences (labware, cleanroom materials, diagnostic instruments, fiber filters etc.) etc.. In the consumer product sector, potential end applications include e.g. textiles, sportswear, kitchenware, refrigerator interiors, cleaning equipment, preservation bags and containers, water systems etc.
Generally, the additives can be used in polymer articles in the shape of a moulded article, wherein the surface layer of the moulded article being modified by incorporation with a polymer or copolymer composition of the present kind.

**Example 1**

Antimicrobial silver ionomer was produced by reacting ethylene acrylic acid copolymer (AA20 mass-%, MFI 1300 g/10 min under 2.16 kg load at 190 °C) and silver salt of metacrylic acid by melt mixing using a twin-screw batch-type DSM mini-extruder while benzooyl peroxide was free radical initiator. The reaction was carried out at a melt temperature of 80 °C, the reaction time being 15 minutes. The obtained silver ionomer was transparent having light yellow-brown tint. The content of the silver ion was 22.3 mass-%.

**Example 2**

Antimicrobial silver ionomer was produced by reacting ethylene acrylic acid copolymer (AA20 mass-%, MFI 1300 g/10 min under 2.16 kg load at 190 °C) and silver salt of nitric acid by reacting water emulsion of ionomer precursor and 1.0 molar silver nitrate water solution under high shear homogenizator at a temperature below the melt temperature of said copolymer. Neutralization of polymer caused coagulation of silver ionomer, which was filtered and further washed with cold deionized water followed by drying under vacuum. The obtained silver ionomer was a white powder; by melting the powder at a temperature below 100 °C a transparent film having light yellow-purple tint could be formed. The silver ion content was 24.6 mass-%.

Another process applicable in the production of the polymeric antimicrobial additive according to the invention, not yet described in examples 1 and 2, comprises (i) melting down said ionomer precursor and (ii) reacting said ionomer precursor with metal salt solution (e.g. silver nitrate solution) having a temperature above the melt temperature of said ionomer precursor and (iii) mixing of said components and (iv) recovering the obtained product as a nonsoluble precipitate.
Example 3

An antimicrobial silver ionomer was produced as follows: An emulsion of ionomer precursor was produced by reacting ethylene acrylic acid copolymer (AA 26 mass-%) with 1 M potassium hydroxide solution at 95 °C under continuous mixing and followed by a period of high shear mixing. The amount of potassium hydroxide solution was set to equal the amount of the copolymer in terms of acrylic acid content of the copolymer. After formation of the emulsion, correspondingly, an equivalent amount of 1 M silver nitrate solution was added to the emulsion resulting in immediate precipitation of the silver ionomer. The aqueous mixture was objected to a period of high shear mixing. The silver ionomer thus obtained was filtered and further washed with cold deionized water. The silver ionomer appeared as a white powder, and the ionomer was pressed to a film at 30 MPa/cm² and 100 °C. A transparent film having a light yellow-purple tint was formed. Silver ion content of the ionomer was 26.4 mass-%.

Example 4

An antimicrobial silver ionomer was produced as follows: An emulsion of ionomer precursor was produced by reacting ethylene acrylic acid copolymer (AA 26 mass-%) with 1 M aqueous ammonia solution at 98 °C under continuous mixing and followed by a period of high shear mixing. The process was carried out with IKA SD41 inline homogenizer equipped with jacketed funnel reaction vessel and an agitator. The amount of aqueous ammonia solution was set to equivalent with the amount of the copolymer in terms of acrylic acid content of the copolymer. Correspondingly, an equivalent amount of 1 M silver nitrate solution was added to the emulsion resulting in immediate precipitation of the silver ionomer. The silver ionomer thus obtained was filtered and further washed with cold deionized water and it appeared as a white powder. The silver ionomer was pressed to a film at 30 MPa/cm² and 100 °C. A transparent film having a light yellow-purple tint was formed. Silver ion content of the ionomer was 26.5 mass-%.
Comparison Example 5

A silver ionomer was obtained by melt mixing at a melt temperature of 160 °C a copolymer of ethylene and methacrylic acid (MAA 15 mass-%, MFI 25 g/10 min under 2.16 kg weight at 190 °C) and a silver salt of acetic acid, using a twin-screw batch-type DSM mini-extruder. The viscosity of said silver ionomer was increased rapidly during neutralization reactions. After 15 minutes reactive mixing, a dark brown silver ionomer was formed, having a silver ion content of 8.1 mass-%.

The silver ionomers produced according to Examples 1 and 2 and Comparison Example 5 were further compounded and injection molded into test pieces in order to investigate the silver ion release performance. The materials according to following Examples 4 and 5 and Comparison Examples 6 and 7 were obtained by melt mixing, at a melt temperature of 160 °C, using a twin-screw batch-type DSM Xplore mini-extruder. The applied host polymer was a polypropylene copolymer Boreclear RB 709 CF manufactured by Borealis AG. The mixing ratios were adjusted to give a silver content of 1.0 % w/w. After the melt mixing process, the material was injection molded into half-cylinder shaped test rods (injection cylinder temperature of 150 °C).

Example 6

The material obtained in Example 1 was compounded with a polypropylene copolymer in a mixing ratio adjusted to produce injection molded test objects having a silver content of 1.0 %.

Example 7

The material obtained in Example 2 was compounded with polypropylene copolymer in a mixing ratio adjusted to produce injection molded test objects having a silver content of 1.0 %.
Comparison Example 8

The material obtained in Comparison Example 5 was compounded with polypropylene host polymer in a mixing ratio adjusted to produce injection molded test objects having a silver content of 1.0%.

Materials produced according to Examples 4 and 5 and Comparison Examples 6 and 7 were investigated in terms of silver ion release performance into deionized MQ-water. Silver-ion release analysis was carried out using the approach of serial extraction. The method is based on placing the sample objects into a known volume of test solution, which is changed at specific time points, followed by measurement of silver concentration of each solution to determine the amount of silver released during each cycle.

The tests were performed by immersing two test rods produced in association with each example into sample tubes each containing 10 of deionized MQ-water. Thereafter the sample tubes containing the test objects were sealed and placed in an orbital shaker at 37°C and 100 rpm. The deionized MQ-water was replaced after time periods of 0.5 h, 8 h, 24 h, 2 d, 3 d and 7 d. Removed immersion solution samples were stabilized with trace purum HNO₃ and kept in a fridge until silver analysis. Silver analysis of the immersion solution samples were conducted using Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS, AA-6650 Shimadzu) according to SFS standard 5074 (The Finnish Standards Association).

Table 1
Cumulative total silver release performance of materials obtained from Example 6, Example 7 and Comparative Example 8 presented in nanograms of silver released in total (ion-exchanged MQ-water).

<table>
<thead>
<tr>
<th>Time</th>
<th>E4 (µg)</th>
<th>E5 (µg)</th>
<th>CE6 (µg)</th>
<th>CE7 (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 h</td>
<td>240</td>
<td>140</td>
<td>45</td>
<td>201</td>
</tr>
<tr>
<td>1 h</td>
<td>309</td>
<td>169</td>
<td>61</td>
<td>235</td>
</tr>
<tr>
<td>2 h</td>
<td>599</td>
<td>469</td>
<td>84</td>
<td>247</td>
</tr>
<tr>
<td>4 h</td>
<td>649</td>
<td>494</td>
<td>110</td>
<td>286</td>
</tr>
<tr>
<td>8 h</td>
<td>674</td>
<td>511</td>
<td>133</td>
<td>290</td>
</tr>
<tr>
<td>24 h</td>
<td>711</td>
<td>529</td>
<td>162</td>
<td>323</td>
</tr>
<tr>
<td>2 d</td>
<td>730</td>
<td>548</td>
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<td>673</td>
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<tr>
<td>4 d</td>
<td>749</td>
<td>563</td>
<td>211</td>
<td>682</td>
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<tr>
<td>7 d</td>
<td>769</td>
<td>584</td>
<td>222</td>
<td>682</td>
</tr>
</tbody>
</table>
As can be seen by investigating the results of silver ion release analysis presented in Table 1, silver release performances of materials according to Examples 6 and 7 are radically higher when compared to the performance of comparative example 8 (CE8, prior art silver ionomer) that has a similar silver content. Moreover, as it can be noticed, the immediate release of E6 and E7 are multifold after the initial 30 minutes period. The extent of released silver in association with the examples are of at least similar or greater magnitude as measured with corresponding incorporated silver amounts using silver nanoparticles (<100 nm), which however may not be preferred as antimicrobial additives due to their risk status widely recognized in recent years.

The significantly greater silver release of the low molecular weight high silver content ionomers according to the invention refers to an ability of the material to concentrate to a certain extent at the surface portion of the injection molded sample objects. The significantly higher silver release performance leads to the fact that the present invention provides a higher antimicrobial activity with similar silver content or alternatively, enables reduced additive and silver content of the composition without losing the level of antimicrobial performance. In both cases, the mechanical properties of the host polymers are preserved better due to lower additive levels enabled by the high silver content and ability of the additive to concentrate at the polymer surface.

**Example 9 - Antimicrobial Efficacy**

The material obtained in Example 3 was compounded with polyethylene polymer (Borealis FA5223) at a mixing ratio adjusted to produce silver ionomer polyethylene having a silver content of 0.2 %. The obtained material was pressed into film at conditions of 30 MPa/cm² and 190 Celsius degrees and cut to three replicate 50x50x0.1 mm samples.

The surface antimicrobial efficacy of the samples were tested against Methicillin-resistant *Staphylococcus aureus* (MRSA strain ATCC 43300) following ISO 22 196 -standard.

The method is in brief: A suspension with a microbial count of 7.84* 10⁶ cfu/ml for MRSA was prepared from a pure culture. The suspension was pipetted (400 µl for each surface) and spread on test surfaces. The test surfaces with microbial suspension were covered with plastic foil and incubated at 36 °C for 24 hours in a humid chamber (relative humidity min.
90%). After 24 h incubation samples were placed into sterile Stomacher bags with 9.9 ml buffer solution and incubated for 5 min. The bag was shaken in a Stomacher for one minute and the solution was pipetted on a soya agar plates with proper ten-fold dilutions. The plates were incubated at 36 °C overnight. After 24-48 hrs colonies were counted and the microbicidal efficacy was determined. All the three replicate samples resulted in >41og bacterial reduction for MRSA, being equivalent to >99.99% as MRSA inactivation percentage.

While preferred embodiments have been described in the presented examples, it must be noted that various modifications and substitutions may be made thereto without losing the central idea, scope and the spirit of the invention. The description of the invention has concentrated on illustration and thus does not limit the scope of the invention.
Claims

1. An antimicrobial copolymer composition obtained by reacting an olefinically unsaturated carboxylic acid copolymer with at least one metal ion source to form an ionomer type antimicrobial polymer composition containing at least 5 mass-% of metal ions having antimicrobial properties, wherein the molecular weight of said olefinically unsaturated carboxylic acid copolymer is between 500 and 8000 g/mol, wherein the metal ion is selected from the group of silver, copper and zinc and mixtures thereof.

2. The composition according to claim 1, wherein the molecular weight of said olefinically unsaturated carboxylic acid copolymer is between 700 and 4000 g/mol.

3. The composition according to claim 1 or 2, wherein the metal ion content of composition is 10 to 50 mass-%, preferably 15 to 35 mass-%.

4. The composition according to any of the preceding claims, wherein the unsaturated carboxylic acid concentration is at least 20 mass-%, in particular at least 30 mass-%, of said thermoplastic polymer composition, excluding metal ions.

5. The composition according to any of the preceding claims, wherein the ethylenically unsaturated carboxylic acid copolymer is partially neutralized with zinc ions or with copper ions.

6. The composition according to any of the preceding claims, wherein the melting point of ethylenically unsaturated carboxylic acid copolymer is below 90 °C.

7. The composition according to any of the preceding claims, wherein the unsaturated carboxylic acid content of said polymer composition is in the range from 20 to 60 mass-% of said polymer.

8. The composition according to any of the preceding claims, wherein the olefinically unsaturated carboxylic acid copolymer is ethylene acrylic acid copolymer which has a melt index at 125 °C of at least 1000 g/min under 2.16 kg load.
9. A method of producing an antimicrobial copolymer composition comprising the step of reacting an olefinically unsaturated carboxylic acid copolymer with at least one metal ion source to form an ionomer type antimicrobial polymer composition containing at least 5 mass-%, preferably at least 10 mass-%, of metal ions having antimicrobial properties, wherein the metal ion is selected from the group of silver, copper and zinc and their mixtures, and wherein the molecular weight of said olefinically unsaturated carboxylic acid copolymer is between 500 and 8000 g/mol, in particular between 700 and 4000 g/mol.

10. The method according claim 9, wherein the olefinically unsaturated carboxylic acid copolymer with at least one metal ion source is formed in a melt process at a temperature below 100 °C.

11. The method according to claims 9 or 10, wherein the composition is manufactured by a polymer emulsion neutralization process at the melting temperature of the polymer composition.

12. The method according to any of claims 9 to 11, wherein the polymer composition is partially neutralized with ammonium ions.

13. A composition comprising a host polymer, particularly a thermoplastic host polymer, compounded with the copolymer composition according to any of the claims 1 to 8.

14. A polymer article comprising a compound of a thermoplastic material, in particular having hydrophobic properties, with a copolymer composition according to any of claims 1 to 8.

15. A polymer article in the shape of a moulded article, wherein the surface layer of the moulded article being modified by incorporation with a copolymer composition according to any of claims 1 to 8.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. A01N25/10 A01N59/16 A01N59/20 A01N25/34 C08F8/44
C08F220/06 C08F222/02 C08L23/08
ADD. C08F210/02 A01N33/12 C08L23/10 C08L23/06 C08J5/18

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A01N C08F C08L

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal , WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>X</td>
<td>US 5320 905 A (VAUGHN WALTER L [US] ET AL) 14 June 1994 (1994-06-14) claims 1-20; example 8; table 1 collumn 3, line 22 - collumn 4, line 20 -----</td>
<td>1-9, 12-15</td>
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\[X\] Further documents are listed in the continuation of Box C. \[X\] See patent family annex.

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Date of the actual completion of the international search: 30 November 2012

Date of mailing of the international search report: 10/12/2012

Name and mailing address of the ISA:
European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
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<td>WO 2006/031965 A2 (DU PONT [US]; CHEN JOHN CHU [US]; URADNISHECK JULIUS [US]) 23 March 2006 (2006-03-23) cited in the application page 39, lines 11-17; examples 1-2 page 10, line 11 - page 12, line 10 page 13, line 5 - page 16, line 6 page 21, line 14 - page 25, line 24</td>
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<td>US 4 747 954 A (VAUGHN WALTER L [US] ET AL) 31 May 1988 (1988-05-31) claims 1,5-7, 9-13, 19-23; examples 14 column 1, line 53 - column 2, line 10 column 2, line 40 - column 3, line 8</td>
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