

AN ARTIFICIAL LEATHER AND A METHOD FOR PREPARING THE SAME

FIELD OF THE INVENTION

The present disclosure relates to an artificial leather and a method for preparing the same.

INTRODUCTION

Polyolefin elastomer (POE, including olefin block copolymer (OBC)), random POE, and the like) based artificial leather is thought to be an eco-friendly and sustainable artificial leather product. Compared with incumbent polyvinyl chloride (PVC) leather, POE leather is halogen free and also free of phthalate plasticizers. Compared with another incumbent conventional polyurethane (PU) leather, no solvent (e.g. DMF, harmful) is needed during the POE leather manufacturing process. Thus, POE leather production is greener, which brings minimal water/air/soil pollution. Although PUD and solvent-free PU is becoming popular most recently, POE leather still has the advantage of easy recyclability due to its thermoplastic nature. From the point of view of performance, POE has excellent weatherability and low temperature flexibility, and no issue of hydrolysis and yellowing. Besides, POE leather can more easily meet the lightweight trend in luggage/bag, shoe and auto applications because the density of POE is much lower than PVC (by ~40%) and PU (by ~25%). It is believed that POE leather will be a promising product to replace PVC and PU leather in several applications. However, it is still difficult to develop an artificial leather based on POE, which demonstrates improved surface grain retention after embossing while delivering acceptable softness.

Therefore, there still remains a constant demand for an artificial leather which demonstrates improved surface grain retention after embossing while delivering acceptable softness.

After persistent exploration, we have surprisingly found that the soft OBC, or blending certain amount of soft OBC with soft random POE, significantly improves the surface grain retention after embossing while delivering similar softness or even higher softness compared to virgin or non-blended random POE.

SUMMARY OF THE INVENTION

In a first aspect of the present disclosure, the present disclosure provides an artificial leather comprising a multi-layer structure; the multi-layer structure comprising of a top skin layer and a bottom fabric layer, wherein the top skin layer comprises at least 10 wt% of an olefin block copolymer, based on the total weight of the top skin layer.

In a second aspect of the present disclosure, the present disclosure provides a method for preparing an artificial leather comprising a multi-layer structure; the method comprising of preparing a top skin layer and a bottom fabric layer, wherein the top skin layer comprises at least 10 wt% of an olefin block copolymer, based on the total weight of the top skin layer; and laminating the top skin layer and the bottom fabric layer together.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a photograph of an embossed leather surface.

DETAILED DESCRIPTION OF THE INVENTION

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention belongs. Also, all publications, patent applications, patents, and other references mentioned herein are incorporated by reference.

The numerical ranges disclosed herein include all values from, and including, the lower and upper value. For ranges containing explicit values (e.g., 1 or 2; or 3 to 5; or 6; or 7), any subrange between any two explicit values is included (e.g., 1 to 2; 2 to 6; 5 to 7; 3 to 7; 5 to 6; etc.). Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percentages are based on weight and all test methods are current as of the filing date of this disclosure.

As disclosed herein, the term “composition”, “formulation” or “mixture” refers to a physical blend of different components, which is obtained by mixing simply different components by a physical means. The sum of the percentages by weight of each component in a composition is 100 wt%, based on the total weight of the composition.

As disclosed herein, “and/or” means “and, or as an alternative”. All ranges include endpoints unless otherwise indicated.

The term “polymer” as used herein, refers to a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term

polymer thus, includes the term homopolymer (employed to refer to polymers prepared from only one type of monomer, with the understanding that trace amounts of impurities can be incorporated into the polymer structure), and the term interpolymer as defined hereinafter. Trace amounts of impurities, such as catalyst residues, can be incorporated into and/or within the polymer. Typically, a polymer is stabilized with very low amounts (“ppm” amounts) of one or more stabilizers.

The term “interpolymer” as used herein, refers to polymer prepared by the polymerization of at least two different types of monomers. The term interpolymer thus includes the term copolymer (employed to refer to polymers prepared from two different types of monomers) and polymers prepared from more than two different types of monomers.

“substantially free of” means the content of a certain substance is less than 1wt% , less than 0.5wt%, less than 0.2wt%, less than 0.1wt%, less than 100 ppm or 0wt% based on the total weight of the corresponding composition or layer (such as the top skin layer or the middle foam layer) comprising the stated substance.

The present disclosure provides an artificial leather comprising a multi-layer structure comprising a top skin layer and a bottom fabric layer, wherein the top skin layer comprises at least 10 wt% of an olefin block copolymer, based on the total weight of the top skin layer.

Preferably, the top skin layer is not foamed.

Preferably, the bottom fabric layer comprises a flexible, polymeric material.

Preferably, the multi-layer structure further comprises a foam layer between the top skin layer and the bottom fabric layer.

Preferably, the top skin layer is substantially free of propylene/alpha-olefin copolymer.

Top skin layer

The top skin layer comprises at least 10 wt%, preferably at least 20 wt%, preferably at least 30 wt%, at least 40 wt%, at least 50 wt%, at least 60 wt%, at least 70 wt%, at least 80 wt%, at least 90 wt%, or 100 wt% of an olefin block copolymer based on the total weight of the top skin layer. It may comprise an ethylene/ α -olefin random copolymer at a content of no greater than 90 wt %, 80 wt%, no greater than 70 wt%, no greater than 60 wt%, no greater than 50 wt%, no greater than 40 wt%, no greater than

30 wt%, no greater than 20 wt%, no greater than 10 wt%, or 0 wt %. The top skin layer can also comprise one or more optional additives such as processing aids, extenders, blocking agents, pigments and/or dyes, antioxidants, UV-stabilizers and/or absorbers, oils, flame retardants, fillers (such as talc, calcium carbonate), and the like.

Preferably, the top skin layer is substantially free of propylene/alpha-olefin copolymer.

Foam Layer

The foam layer (also called a middle foam layer) comprises at least one of (i) an olefin block copolymer, and (ii) an ethylene/ α -olefin random copolymer. The foam layer can also comprise the gas from the decomposed blowing agent or the gas originally from the decomposed blowing agent and has already been partially or totally replaced by air and any unreacted, residual blowing agent. The middle foam layer can also comprise one or more optional additives such as processing aids, extenders, blocking agents, pigments and/or dyes, antioxidants, UV-stabilizers and/or absorbers, oils, flame retardants, fillers (such as talc, calcium carbonate), and the like.

The middle foam layer can be compositionally the same as the top skin layer except for the gas and by-products attributable to the foaming process.

The middle foam layer typically comprises at least 10, or at least 20, more typically at least 40, more typically at least 50 and even more typically at least 60, weight percent (wt %) an olefin block copolymer. The maximum amount of olefin block copolymer in the middle foam layer typically does not exceed 90, more typically does not exceed 80 and even more typically does not exceed 70 wt %, based on the total weight of the foam layer.

Preferably, the middle foam layer is substantially free of propylene/alpha-olefin copolymer.

Generally, the blowing agent is incorporated into the copolymer composition which is to be foamed in amounts ranging from 0.1 to 30, preferably 1 to 20 and more preferably 2 to 10, phr. The blowing agent typically is incorporated into the melt stream under a pressure which is sufficient to inhibit its activation, that is, to inhibit foaming of the melt stream during the incorporation of the blowing agent and subsequent processing of the composition until the stream is ready to be foamed.

If present at all, the total amount of optional additives present in the foam layer typically is greater than zero, more typically at least 1 and even more typically at least

2, phr. If present at all, the total amount of optional additives in the foam layer typically does not exceed 10, more typically does not exceed 7 and even more typically does not exceed 5, phr.

If present at all, the total amount of optional filler present in the foam layer typically is greater than zero, more typically at least 5 and even more typically at least 10, weight percent (wt %). If present at all, the total amount of optional fillers in the foam layer typically does not exceed 60, more typically does not exceed 40 and even more typically does not exceed 20 wt %.

The foam layer is typically prepared by blending or compounding the individual components with one another in any conventional mixing apparatus, e.g., Banbury kneader, Brabender mixer, or any suitable extruder, under conditions and for a time that produces an at least substantially homogeneous mixture, calendering the mixture using conventional equipment and conditions to form a sheet, and then heat laminating the sheet to the top skin layer and/or bottom fabric layers using conventional lamination equipment and conditions. The foam layer is typically not subjected to foaming conditions until after it is laminated to at least one of the top skin layer or bottom fabric layers, preferably not until it is laminated to both layers (if a three- or more layer structure). The foaming conditions are such that very fine and regular cells are formed throughout the layer. Typical foaming conditions include an oven temperature of 220 °C or more and an oven residence time of 100-120 seconds. The foam expansion ratio] is based on the ratio of expanded thickness to original (non-expanded) thickness (herein referred to as the thickness ratio), and it is typically 1.5 to 4, more typically 2 to 3.

Bottom Fabric Layer

The bottom fabric layer comprises a flexible, polymeric material which can be woven, nonwoven, knitted, plained, spunbond, etc., and it can comprise of a natural and/or synthetic fiber. In one embodiment, the fabric layer is a nonwoven, polymeric, spunbond material of a weight of 100-500, more typically of 150-400 and even more typically of 200-350, grams per square meter (g/m²). Fabrics that can be used in the practice of the present disclosure include, but are not limited to, cotton, silk and various synthetics based on polyolefins (e.g., polyethylene, polypropylene, etc.), nylon, polyester, polyurethane (e.g., a spandex material), and the like. In one embodiment, the preferred fabric is prepared from polyester, polyethylene or polypropylene. The fabric

can be subjected to a pre-lamination treatment, e.g., corona surface treatment, impregnation, etc., or not, and the foam or top skin layer is ultimately heat laminated to it.

Ethylene/ α -olefin multi-block interpolymers

The term “ethylene/ α -olefin multi-block interpolymers”, also called “ethylene/ α -olefin multi-block copolymer” or “olefin block copolymer (OBC)” as used herein, refers to an interpolymers that includes ethylene and one or more copolymerizable α -olefin comonomers in polymerized form, characterized by multiple blocks or segments of two or more (preferably three or more) polymerized monomer units, the blocks or segments differing in chemical or physical properties. Specifically, this term refers to a polymer comprising two or more (preferably three or more) chemically distinct regions or segments (referred to as “blocks”) joined in a linear manner, that is, a polymer comprising chemically differentiated units which are joined (covalently bonded) end-to-end with respect to polymerized functionality, rather than in pendent or grafted fashion. The blocks differ in the amount or type of comonomer incorporated therein, the density, the amount of crystallinity, the type of crystallinity (e.g., polyethylene versus polypropylene), the crystallite size attributable to a polymer of such composition, the type or degree of tacticity (isotactic or syndiotactic), region-regularity or region-irregularity, the amount of branching, including long chain branching or hyper-branching, the homogeneity, and/or any other chemical or physical property. The block copolymers are characterized by unique distributions of both polymer polydispersity (PDI or Mw/Mn) and block length distribution, e.g., based on the effect of the use of a shuttling agent(s) in combination with catalyst systems. Non-limiting examples of the olefin block copolymers of the present disclosure, as well as the processes for preparing the same, are disclosed in U.S. Patent Nos. 7,858,706 B2, 8,198,374 B2, 8,318,864 B2, 8,609,779 B2, 8,710,143 B2, 8,785,551 B2, 9,243,090 B2, and US20230058913 which are all incorporated herein by reference in their entirety.

Ethylene/ α -olefin multi-block interpolymers are characterized by multiple blocks or segments of two or more polymerized monomer units, differing in chemical or physical properties.

In some embodiments, the multi-block copolymers can be represented by the following formula: $(AB)_n$, where n is at least 1, preferably an integer greater than 1, such as 2, 3, 4, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, or higher. Here, “A”

represents a hard block or segment, and “B” represents a soft block or segment. Preferably the A segments and the B segments are linked in a substantially linear fashion, as opposed to a substantially branched or substantially star-shaped fashion. In other embodiments, the A segments and the B segments are randomly distributed along the polymer chain. In other words, for example, the block copolymers usually do not have a structure as follows: AAA-AA-BBB-BB. In still other embodiments, the block copolymers do not usually have a third type of block or segment, which comprises different comonomer(s). In yet other embodiments, each of block A and block B has monomers or comonomers substantially randomly distributed within the block. In other words, neither block A nor block B comprises two or more sub-segments (or sub-blocks) of distinct composition, such as a tip segment, which has a substantially different composition than the rest of the block.

The olefin block copolymers, in general, are produced via a chain shuttling process, such as, for example, described in U.S. Patent 7,858,706, which is herein incorporated by reference. Some chain shuttling agents and related information are listed in Col. 16, line 39, through Col. 19, line 44. Some catalysts are described in Col. 19, line 45, through Col. 46, line 19, and some co-catalysts in Col. 46, line 20, through Col. 51 line 28. Some process features are described in Col 51, line 29, through Col. 54, line 56. See also the following: U.S. Patent 7,608,668; U.S. Patent 7,893,166; and U.S. Patent 7,947,793 as well as US Patent Publication 2010/0197880. See also U.S. Patent 9,243,173.

Preferably, ethylene comprises the majority mole fraction of the whole ethylene/ α -olefin multi-block copolymer, i.e., ethylene comprises at least 40 wt% of the whole ethylene/ α -olefin multi-block copolymer. More preferably, ethylene comprises at least 50 wt%, at least 60 wt%, at least 70 wt%, or at least 80 wt%, with the substantial remainder of the whole ethylene/ α -olefin multi-block interpolpolymer comprising the C4-C8 α -olefin comonomer, preferably, the C4-C8 α -olefin comonomer may be selected from butene, pentene, hexene, heptane, and octene, preferably 1-butene, 1-hexene, and 1-octene. In an embodiment, the ethylene/ α -olefin multi-block interpolpolymer contains from 40 wt%, 50 wt%, or 60 wt%, or 65 wt% to 80 wt%, or 85 wt%, or 90 wt% ethylene. For many ethylene/octene multi-block interpolpolymers, the composition comprises an ethylene content greater than 80 wt% of the whole ethylene/octene multi-block interpolpolymer and an octene content of from 10

wt% to 15 wt%, or from 15 wt% to 20 wt% of the whole ethylene/octene multi-block interpolymers.

The ethylene/ α -olefin multi-block copolymer includes various amounts of “hard” segments and “soft” segments. “Hard” segments are blocks of polymerized units in which ethylene is present in an amount greater than 90 wt%, or 95 wt%, or greater than 95 wt%, or greater than 98 wt%, based on the weight of the polymer, up to 100 wt%. In other words, the comonomer content (content of monomers other than ethylene) in the hard segments is less than 10 wt%, or 5 wt%, or less than 5 wt%, or less than 2 wt%, based on the weight of the polymer, and can be as low as zero. In some embodiments, the hard segments include all, or substantially all, units derived from ethylene. “Soft” segments are blocks of polymerized units in which the comonomer content (content of monomers other than ethylene) is greater than 5 wt%, or greater than 8 wt%, or greater than 10 wt%, or greater than 15 wt%, based on the weight of the polymer. In an embodiment, the comonomer content in the soft segments is greater than 20 wt%, or greater than 25 wt%, or greater than 30 wt%, or greater than 35 wt%, or greater than 40 wt%, or greater than 45 wt%, or greater than 50 wt%, or greater than 60 wt% and can be up to 100 wt%.

The soft segments can be present in an ethylene/ α -olefin multi-block interpolymers from 1 wt%, or 5 wt%, or 10 wt%, or 15 wt%, or 20 wt%, or 25 wt%, or 30 wt%, or 35 wt%, or 40 wt%, or 45 wt% to 55 wt%, or 60 wt%, or 65 wt%, or 70 wt%, or 75 wt%, or 80 wt%, or 85 wt%, or 90 wt%, or 95 wt%, or 99 wt% of the total weight of the ethylene/ α -olefin multi-block interpolymers. Conversely, the hard segments can be present in similar ranges. The soft segment weight percentage and the hard segment weight percentage can be calculated based on data obtained from DSC or NMR. Such methods and calculations are disclosed in, for example, USP 7,608,668, the disclosure of which is incorporated by reference herein in its entirety. In particular, hard and soft segment weight percentages and comonomer content may be determined as described in column 57 to column 63 of USP 7,608,668.

In an embodiment, the ethylene/ α -olefin multi-block copolymer is produced in a continuous process and possesses a polydispersity index (M_w/M_n) from 1.7 to 3.5, or from 1.8 to 3, or from 1.8 to 2.5, or from 1.8 to 2.2. When produced in a batch or semi-batch process, the ethylene/ α -olefin multi-block copolymer possesses M_w/M_n from 1.0 to 3.5, or from 1.3 to 3, or from 1.4 to 2.5, or from 1.4 to 2.

Nonlimiting examples of suitable ethylene/ α -olefin multi-block copolymer are disclosed in U.S. Patent No. 7,608,668, the entire content of which is incorporated by reference herein.

In an embodiment, the ethylene/ α -olefin multi-block copolymer consists of only (i) ethylene and (ii) a C4–C8 α -olefin.

In an embodiment, the ethylene/ α -olefin multi-block copolymer has hard segments and soft segments, is styrene-free, consists of only (i) ethylene and (ii) a C4–C8 α -olefin, and is defined as having a Mw/Mn from 1.7 to 3.5.

In an embodiment, the ethylene/ α -olefin multi-block interpolymer has a density of between about 0.850 g/cc and about 0.890 g/cc, preferably between about 0.855 g/cc and 0.880 g/cc, more preferably between about 0.858 g/cc and about 0.870 g/cc, even more preferably between about 0.860 g/cc and about 0.866 g/cc.

Preferably, the ethylene/ α -olefin multi-block interpolymer used in the present disclosure has a MI of not greater than about 30 g/10 min at 190 °C/2.16 kg, preferably a MI of not greater than about 20 g/10 min at 190 °C/2.16 kg, preferably not greater than about 18 g/10 min at 190 °C/2.16 kg, more preferably not greater than about 17 g/10 min at 190 °C/2.16 kg, more preferably not greater than about 16 g/10 min at 190 °C/2.16 kg, even more preferably not greater than about 15 g/10 min at 190 °C/2.16 kg or not greater than 12 g/10 min at 190 °C/2.16 kg. Alternatively, the ethylene/ α -olefin multi-block interpolymer used in the present disclosure has a MI from about 0.1 g/10 min at 190 °C/2.16 kg to about 20 g/10 min at 190 °C/2.16 kg, preferably about 0.5 g/10 min at 190 °C/2.16 kg to about 18 g/10 min at 190 °C/2.16 kg, more preferably about 1 g/10 min at 190 °C/2.16 kg to about 16 g/10 min at 190 °C/2.16 kg, even more preferably about 5 g/10 min at 190 °C/2.16 kg to about 15 g/10 min at 190 °C/2.16 kg.

Preferably, the ethylene/ α -olefin multi-block interpolymer used in the present disclosure has a melting point of 100-130 °C, more preferably 105-125 °C, more preferably 110-120 °C.

Suitable ethylene/ α -olefin multi-block interpolymer can be INFUSE™ from Dow, such as INFUSE™ 9107, INFUSE™ 9500, INFUSE™ 9507, INFUSE™ 9807 or OBC 1 prepared according to IE 6 of US20230058913.

Ethylene/ α -olefin random copolymer

An ethylene/ α -olefin random copolymer (also called random POE) is an ethylene/propylene random copolymer or an ethylene/C4–C8 α -olefin random

copolymer. In an embodiment, the ethylene/ α -olefin copolymer is an ethylene/C4–C8 α -olefin copolymer. The ethylene/C4–C8 α -olefin copolymer is composed of, or otherwise consists of, ethylene and one copolymerizable C4–C8 α -olefin comonomer in polymerized form. The C4–C8 α -olefin comonomer may be selected from butene, pentene, hexene, heptane, and octene, preferably 1-butene, 1-hexene, and 1-octene.

In an embodiment, the ethylene/ α -olefin random copolymer used in the present disclosure has a density of between about 0.850 g/cc and about 0.900 g/cc, preferably between about 0.855 g/cc and 0.895 g/cc, more preferably between about 0.857 g/cc and about 0.890 g/cc, even more preferably between about 0.865 g/cc and about 0.885 g/cc.

Preferably, the ethylene/ α -olefin random copolymer used in the present disclosure has a MI of not greater than about 20 g/10 min (at 190 °C/2.16 kg), preferably not greater than about 15 g/10 min at 190 °C/2.16 kg, more preferably not greater than about 10 g/10 min at 190 °C/2.16 kg, more preferably not greater than about 8 g/10 min at 190 °C/2.16 kg, even more preferably not greater than about 7 g/10 min at 190 °C/2.16 kg or not greater than 6 g/10 min at 190 °C/2.16 kg, or not greater than 5 g/10 min at 190 °C/2.16 kg. Alternatively, the ethylene/ α -olefin random copolymer used in the present disclosure has a MI from about 0.1 g/10 min at 190 °C/2.16 kg to about 20 g/10 min at 190 °C/2.16 kg, preferably about 0.2 g/10 min at 190 °C/2.16 kg to about 15 g/10 min at 190 °C/2.16 kg, more preferably about 0.3 g/10 min at 190 °C/2.16 kg to about 8 g/10 min at 190 °C/2.16 kg, even more preferably about 1 g/10 min at 190 °C/2.16 kg to about 5 g/10 min at 190 °C/2.16 kg.

Suitable ethylene/ α -olefin random copolymer can be ENGAGE™ from Dow, such as ENGAGE™ 8003, ENGAGE™ 8842, ENGAGE™ 7447, ENGAGE™ 8150, ENGAGE™ 7467 or EO 1 prepared according to Ex 1 of US11236241 B2.

Blowing Agent

Most any of the known blowing agents (also known as foaming or expansion agents) can be employed, including gaseous materials, volatile liquids and chemical agents which decompose into a gas and other byproducts. Representative blowing agents include, without limitation, nitrogen, carbon dioxide, air, methyl chloride, ethyl chloride, pentane, isopentane, perfluoromethane, chlorotrifluoromethane, dichlorodifluoromethane, trichlorofluoromethane, perfluoroethane, 1-chloro-1,1-difluoroethane, chloropentafluoroethane, dichlorotetrafluoroethane,

trichlorotrifluoroethane, perfluoropropane, chloroheptafluoropropane, dichlorohexafluoropropane, perfluorobutane, chlorononafluorobutane, perfluorocyclobutane, azodicarbonamide (ADCA), azodiisobutyronitrile, benzenesulfonhydrazide, 4,4-oxybenzene sulfonyl-semicarbazide, p-toluene sulfonyl semicarbazide, barium azodicarboxylate, N,N'-dimethyl-N,N'-dinitrosoterephthalamide, and trihydrazino triazine. Currently, ADCA is a preferred blowing agent.

Additives

The top skin and middle foam layers may contain additives including but not limited to antioxidants, curing agents, cross linking co-agents, boosters and retardants, processing aids, ultraviolet absorbers or stabilizers, antistatic agents, nucleating agents, slip agents, plasticizers, lubricants, viscosity control agents, tackifiers, anti-blocking agents, surfactants, extender oils, acid scavengers, and metal deactivators. Additives can be used in amounts ranging from 0.01 wt % or less to 10 wt % or more based on the weight of the layer.

Fillers

Examples of fillers include but are not limited to talc, clays, precipitated silica and silicates, fumed silica, calcium carbonate, ground minerals, carbon blacks with arithmetic mean particle sizes larger than 10 nanometers, and the various known flame retardants, particularly halogen-free flame retardants. Fillers can be used in amounts ranging from greater than zero to 50 wt % or more based on the weight of the layer or total composition.

The olefin block copolymer and/or an ethylene/ α -olefin random copolymer in the top skin layer and/or foam layer may be crosslinked or not by certain technology, such as E-beam curing, UV curing, peroxide curing, silane curing and the like.

Shaping and lamination

The present invention can be manufactured using the same conventional compression molding (or calendaring) and lamination processes or extrusion and lamination used for PVC-based leathers.

The multi-layer structure may comprise a bottom fabric layer and a top skin layer, the latter optionally coated with a top coating. The top skin layer is made by a compression molding, and then laminated to the bottom fabric layer. The optional PU top coating layer is then applied to the top skin layer of the multi-layer structure.

The multi-layer structure may comprise a bottom fabric layer, a middle foam layer, and a top skin layer, the latter optionally coated with a primer and the primer with a top coating. The top skin layer and middle foam layer of the artificial leather are made by a compression molding, and then laminated to one another and the bottom fabric layer in any convenient order. Foaming is typically conducted after lamination in an oven typically maintained at 220 °C or higher for 60-180 seconds. The optional primer and PU top coating layers are then applied to the top skin layer of the laminated, three-layer structure.

EXAMPLES

Some embodiments of the invention will now be described in the following Examples, wherein all parts and percentages are by weight unless otherwise specified.

The information of the raw materials used in the examples is listed in the following Table 1:

Table 1 Materials/ingredients for blending

Ingredient Type	Product Name	Chemical Description, Chemical formula, or Structure	Source
Base resin	OBC 1	HTC olefin block copolymer, density 0.86g/cm ³ , MI 5.9 g/10min (at 190 °C/2.16 kg), Shore A ~30	Prepared according to IE 6 of US20230058913
Base resin	EO 1	Random EO copolymer, density 0.857g/cm ³ , MI 5 g/10min (at 190 °C/2.16 kg), Shore A ~50	Prepared according to Ex 1 of US11236241 B2

Base resin	INFUSE™ 9507	olefin block copolymer, density 0.866 g/cm ³ , MI 5 g/10min (at 190 °C/2.16 kg), Shore A = 60	Dow
Base resin	ENGAGE™ 7447	Random EO copolymer, density 0.865g/cm ³ , MI 5 g/10min (at 190 °C/2.16 kg), Shore A = 64	Dow
Base resin	ENGAGE™ 8003	Random EO copolymer, density 0.885g/cm ³ , MI 1 g/10min (at 190 °C/2.16 kg), Shore A = 84	Dow
Base resin	ENGAGE™ 8842	Random EO copolymer, density 0.857 g/cm ³ , MI 1 g/10min (at 190 °C/2.16 kg), Shore A = 54	Dow
Base resin	INFUSE™ 9807	olefin block copolymer, density 0.866 g/cm ³ , MI 15 g/10min (at 190 °C/2.16 kg), Shore A = 55	Dow

Brabender mixing

POE resins (37 grams) and 0.185 g carbon black masterbatch with 50% carbon black were mixed in Brabender™ internal mixer at 130 °C and 50 rpm for 5 min. The compound was collected and used for the following leather preparation.

Compression molding and lamination

The compound from the Brabender™ internal mixer was compression molded into a film in a “15 cm x 15 cm x 0.3 (or 0.5) mm” mold. PTFE films were used to sandwich POE compounds from Brabender mixing. The compound was preheated at 135 °C for 3 minutes, and then degassed (repeated compression at 10 MPa and release,

for six times), followed by another 2 minutes at a pressure of 10 MPa and a temperature of 135 °C.

After cooling, the upper PTFE film was removed and a fabric (a woven fabric, 0.90 mm thick and 300 g/m²) was covered onto the POE film surface. After reheating for 5 min, a pressing was conducted by a roller to increase the adhesion between the molten POE film and fabric. After complete cooling, the lower PTFE film was removed as well and the original leather samples (with fabric and POE layer) were collected for following coating.

Application of PU top coating

The POE layer surface was firstly treated by corona (Equipment details: Nanjing Suman Electronics Co., Ltd; PLASMA GENERATOR (High performance computerized plasma and corona discharge experiment generators) to increase surface energy. Set voltage at 180V, current at 1.8A. The corona brush was moved quickly above the POE layer four times to make sure that a high surface energy (~42 dyn/cm) can be achieved.

After corona treatment, the PU top coating (95% PUD coating (Permute WF-77-307 P77062 from Stahl) + 5% curing agent (aliphatic polyisocynate, PERMUTEX® XR-48-920 from Stahl), 5 min stirring for mixing the two) was spread on the POE layer using a wire rod. The coated samples were quickly transferred into the oven at 130 °C for drying and curing for two minutes. The thickness of the resulting top coating is about 10 µm.

Embossing

The leather samples with a size of 15 cm *15 cm were firstly heated at 150 °C for 1 min. The heated samples were quickly placed onto the embossing mold with POE layer touching the mold surface with a temperature of 38 °C. A vacuum was applied for 10 seconds to emboss the grain on the mold to the leather surface. After that, the leathers were placed onto experiment bench with POE layer facing air for cooling to fix the surface grain. After completely cooled and stabilized, the surface grain was observed by naked eye under the same light conditions and also images were taken for comparison.

Test and measurement

Softness test

The test conforms to ISO 17235-2002. The diameter of metal ring is 25 mm. Three tests were conducted on a leather sample and the average of the three values was reported as the softness. For the value, the higher, the softer. The softness tester: model GT-303 is from GOTECH TESTING MACHINES CO., LTD.

Surface grain retention measurement

The surface grain difference of different samples can be observed by naked eyes under the same light conditions. In general, the POE layer thickness should be at least 0.1 mm and more preferably greater than 0.2 mm as the groove depth of the surface grain is typically less than 0.1 mm. Therefore, samples having thicknesses of 0.3 mm and 0.5 mm were both prepared to cover typical thickness range. To be more quantitative, the photographs of embossed leather surfaces were taken under the same conditions (fixed distance 30 cm from sample to camera lens, magnification times 1X, the sample light condition) for image analysis. The bump pieces which are separated by grooves (as shown in Figure 1, the surface grain consist of bumps and grooves, the bumps, like islands, are surrounded by grooves) in 2.0 cm² were counted under the same magnification times (2X) of the images for different examples. According to the number of bumps per 2.0 cm² on the leather surface, the surface grain ranking was made, as shown in Table 2.

Table 2	
Surface grain ranking	Ranking criterion description, bumps/2 cm ²
1	<60
2	60-80
3	81-100
4	101-120
5	>120

The higher the number for surface ranking, the better the surface grain retention.

Examples and Discussion

The following Table 3 and 4 showed the constitution and performance parameters of the comparative examples and inventive examples of the present disclosure.

Table 3

Examples	IE1	CE1	IE2	CE2
INFUSE™ 9507	100			
ENGAGE™ 7447		100		
OBC 1			100	
EO 1				100
Softness (0.3 mm thick POE layer)	5.2	5.2	6.1	5.8
Surface grain ranking (0.3 mm thick POE layer)	5	2	5	2
Softness (0.5 mm thick POE layer)	4.9	5.1		
Surface grain ranking (0.5 mm thick POE layer)	4	1		

Table 4

Examples	CE3	CE4	IE3
ENGAGE™ 8003	100		
ENGAGE™ 8842		100	45
INFUSE™ 9807			55
Softness (0.3 mm thick POE layer)	3.3	5.4	5.1
Surface grain ranking (0.3 mm thick POE layer)	3	2	4

Softness (0.5 mm thick POE layer)		5.9	5.5
Surface grain ranking (0.5 mm thick POE layer)		2	4

As shown in Table 3, IE1 exhibited much better surface grain retention than CE1 (for both 0.3 mm and 0.5 mm thick POE layers) and had comparable softness. IE2 showed better surface grain retention than CE2. Furthermore, IE2 had higher softness than CE2.

In CE3, a much harder random POE ENGAGE™ 8003 was used, which resulted in improved surface grain retention. That means increasing density of random POE helps. However, the trade-off is that the softness became pretty low (a much lower softness value 3.3). This result indicated that random POE could not deliver good surface grain retention and high softness (good hand-feel) at the same time.

The result of CE4 and IE3 demonstrated that blending certain amount of OBC into random POE could help achieve good surface grain retention and high softness at the same time.

Claims

1. An artificial leather comprising a multi-layer structure comprising a top skin layer and a bottom fabric layer, wherein the top skin layer comprises at least 10 wt% of an olefin block copolymer, based on the total weight of the top skin layer.
2. The artificial leather of claim 1, wherein the top skin layer comprises at least 40 wt% of an olefin block copolymer, based on the total weight of the top skin layer.
3. The artificial leather of claim 1, wherein the top skin layer comprises at least 50 wt% of an olefin block copolymer, based on the total weight of the top skin layer.
4. The artificial leather of claim 1, wherein the multi-layer structure further comprises a foam layer between the top skin layer and the bottom fabric layer.
5. The artificial leather of claim 1, wherein the bottom fabric layer comprises a flexible, polymeric material.
6. The artificial leather of claim 1, wherein the olefin block copolymer has a density of between about 0.850 g/cc and about 0.890 g/cc.
7. The artificial leather of claim 1, wherein the olefin block copolymer has a MI of not greater than about 30 g/10 min at 190 °C/2.16 kg.
8. The artificial leather of claim 1, wherein the olefin block copolymer has a melting point of 100-130 °C.
9. The artificial leather of claim 4, the foam layer comprises at least one of (i) an olefin block copolymer, and (ii) an ethylene/ α -olefin random copolymer.
10. The artificial leather of claim 1, wherein the top skin layer is substantially free of propylene/ α -olefin copolymer.
11. The artificial leather of claim 1, wherein the olefin block copolymer consists of only (i) ethylene and (ii) a C4-C8 α -olefin.
12. The artificial leather of claim 1, wherein the artificial leather has a surface grain ranking (0.3 mm thick POE layer) of 5 or greater.
13. The artificial leather of claim 1, wherein the artificial leather has a softness ranking (0.3 mm thick POE layer) of 4 or greater.
14. A method for preparing an artificial leather comprising a multi-layer structure of claims 1-13, comprising
 - preparing a top skin layer and a bottom fabric layer, wherein the top skin layer comprises at least 20 wt% of an olefin block copolymer; and
 - laminating the top skin layer and the bottom fabric layer together.