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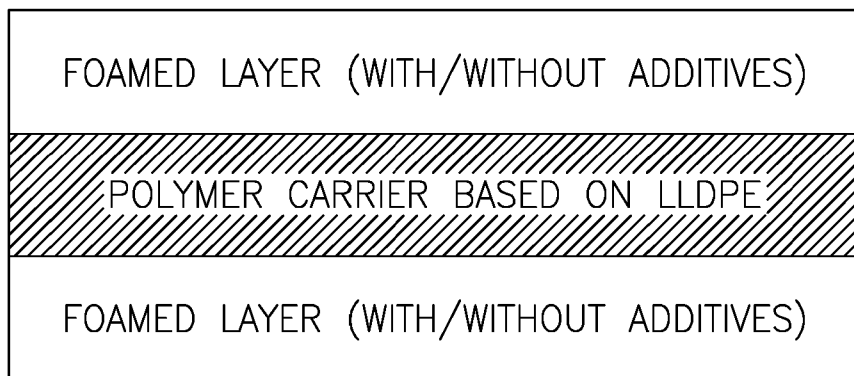
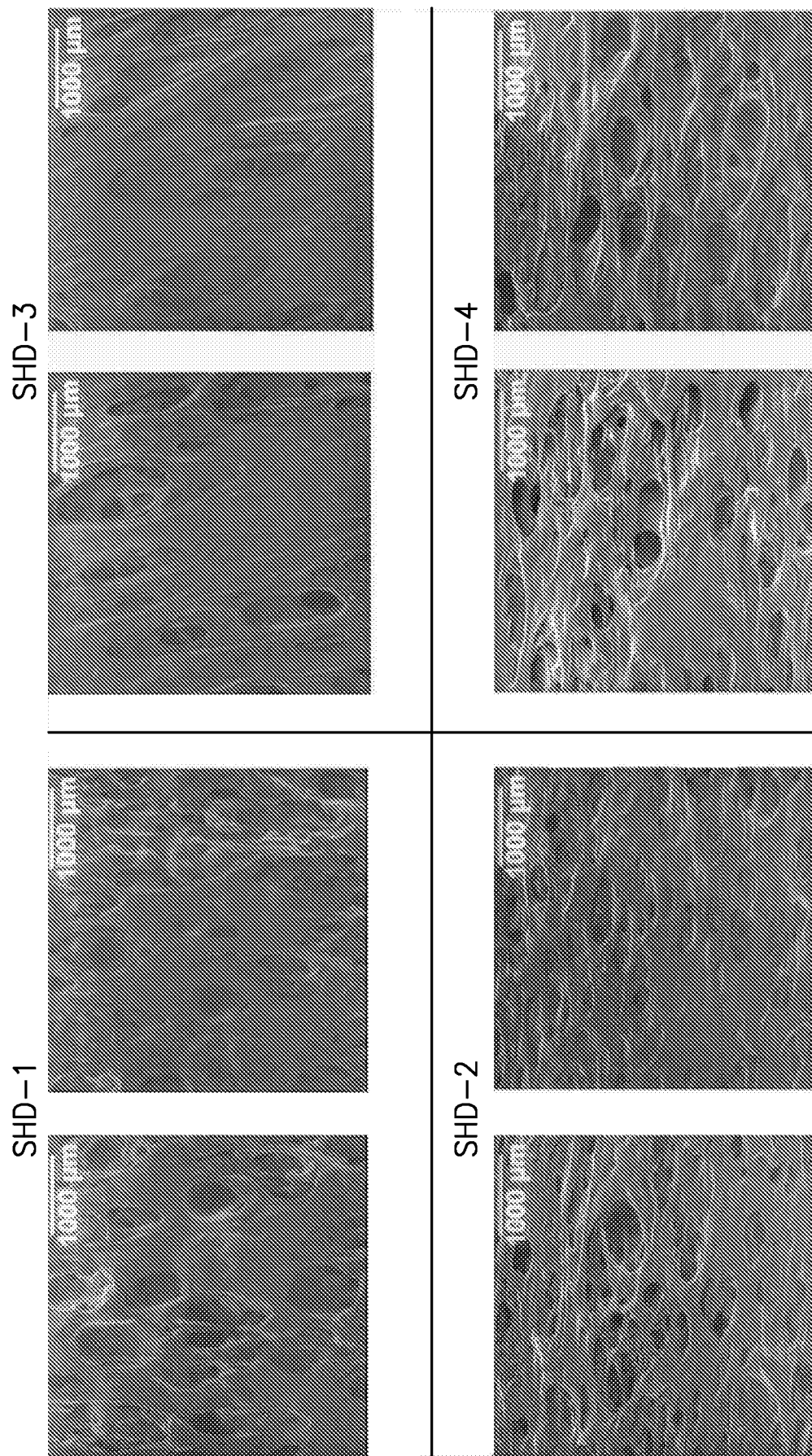


FIG.1

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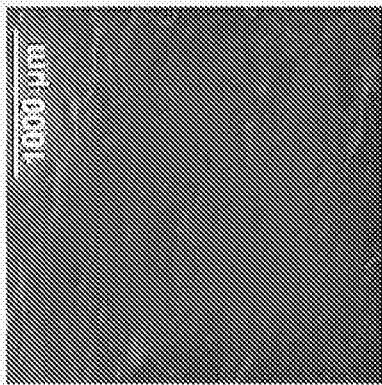


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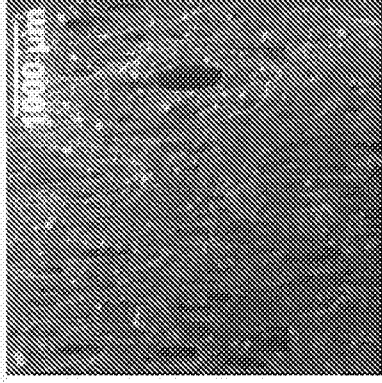
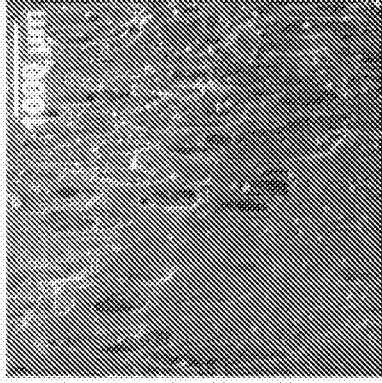
FIG.2

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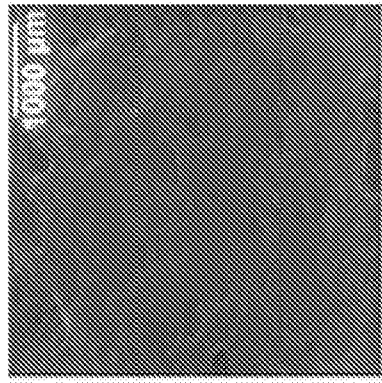
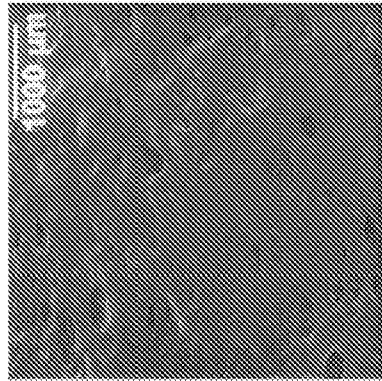
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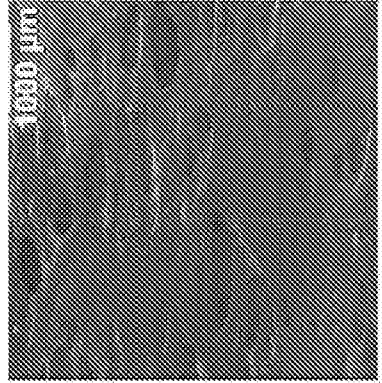
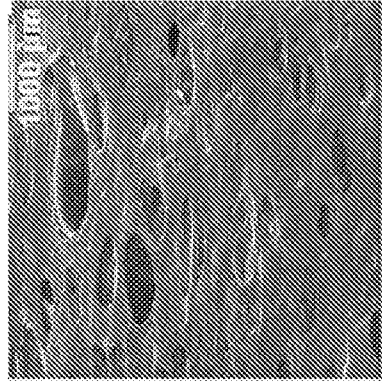
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SHD-9



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FIG.3

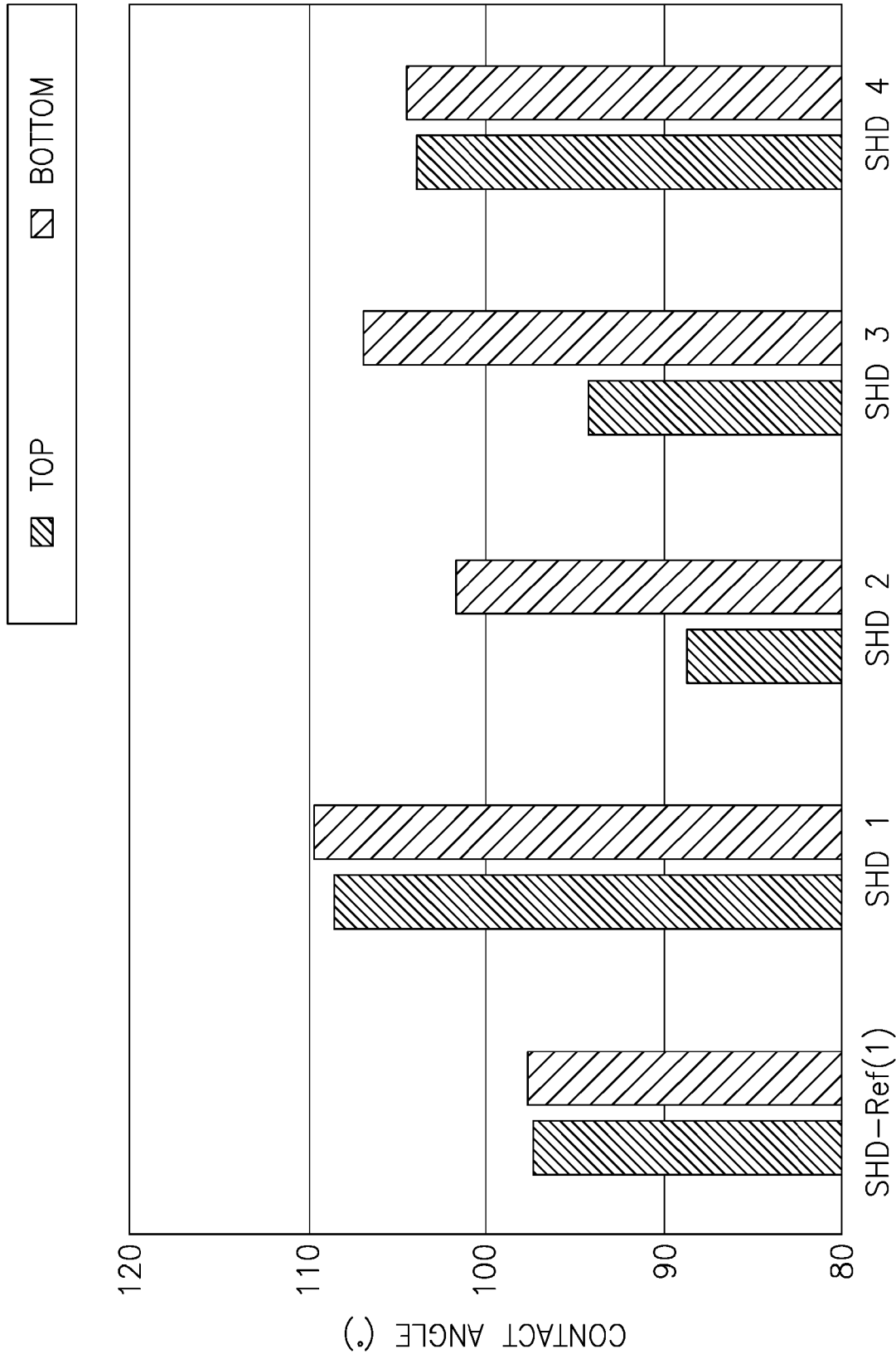


FIG.4

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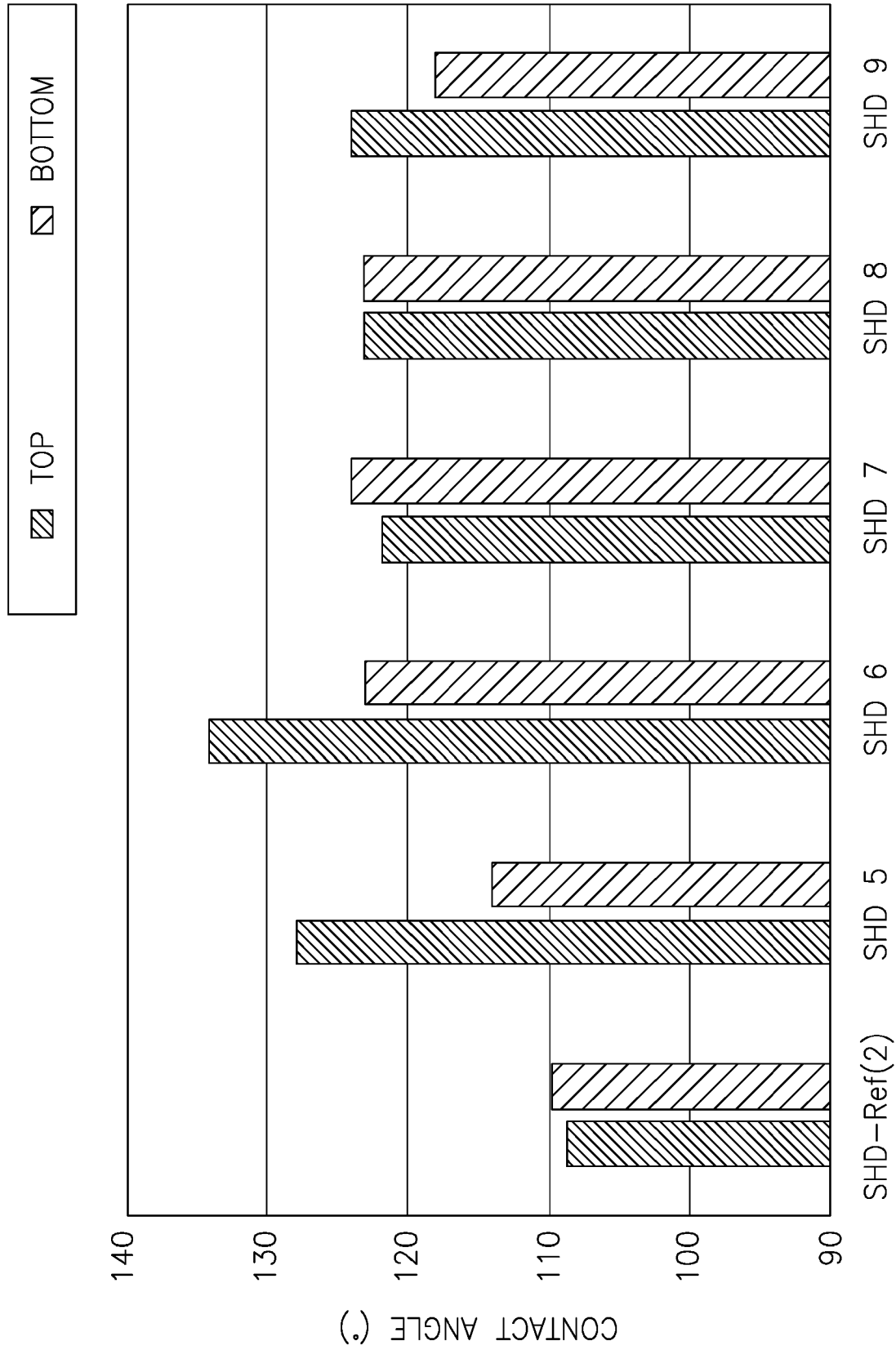


FIG.5

COMPOSITIONS AND METHODS FOR USE IN THE PREPARATION OF HYDROPHOBIC SURFACES

Technical Field

The invention belongs to the technical field of new materials, in particular to compositions for use in the preparation of hydrophobic surfaces, methods of use thereof and hydrophobic surfaces produced using such compositions and methods.

Background

Surface wettability is one of the important properties of a solid surface. The wettability of a solid surface by a liquid is quantified in terms of contact angle, which may be defined as the angle formed at the liquid-solid interface when a liquid drop is deposited on the solid surface. A solid surface having a static contact angle with water of greater than 90° is considered to be hydrophobic. When the solid surface has a contact angle with water of more than 150°, the surface is often referred to as superhydrophobic. Due to unique surface characteristics, superhydrophobic surfaces have considerable significance in both daily life and in industry.

Background art includes:

US 4,952,352; US 9,040,145; US 7,491,762; US 8,563,621;

US 2005/0064120; US 2015/0025619; WO 2016/082212;

CN 108299586; CN 107384191; CN 107652821; CN 1037159;

John T Simpson et al, 2015 Rep. Prog. Phys. 78 086501;

Arabian Journal of Chemistry (2017) 10, 368–377;

Jin P et al., R. Soc. open sci. 4: 171321;

ACS Appl. Mater. Interfaces, 2014, 6 (23), pp 21131–21140;

Gh.Barati Darband et al., Arabian Journal of Chemistry, 2018,

<https://doi.org/10.1016/j.arabjc.2018.01.013>

Shuai Wang et al. Journal of Colloid and Interface Science Volume 359, Issue 2, 15 July 2011, Pages 380-388;

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P. Zhang et al. <http://dx.doi.org/10.1016/j.energy.2015.01.061>;

Xu, et. al. (2016). RSC Advances, 6(85), 82088–82095, DOI: [10.1039/C6RA19642J](https://doi.org/10.1039/C6RA19642J) .

There is an on-going need for simple processes and materials that can be employed to provide surfaces having increased hydrophobicity, including superhydrophobic surfaces, in plastic articles or products in an efficient and controllable manner.

Summary of the Invention

The present invention is described in the appended claims. According to an aspect of some embodiments of the present invention, there is provided a blend suitable for use in preparing a polyolefin-based product having a surface with increased hydrophobicity, the blend comprising (a) between 1% and 30% of a masterbatch composition, wherein the masterbatch composition comprises (I) at least one foamable polyolefin, (II) at least one fluoropolymer, (III) and at least one blowing agent which is non-gaseous prior to activation by the application of heat; wherein said at least one blowing agent is present at a concentration of from 4% to 70% w/w of the total composition; wherein said at least one fluoropolymer comprises a fluoro elastomer; wherein said at least one foamable polyolefin and said at least one fluoropolymer together constitute a polymeric blend; and (b) between 70% and 99% by weight of a bulk foamable polyolefin.

In some embodiments, the at least one foamable polyolefin of said masterbatch composition is selected from the group consisting of polyethylene, polypropylene and a combination thereof.

In the present invention, the at least one fluoropolymer comprises a fluoro elastomer. In some embodiments, the at least one fluoropolymer comprises a fluoro homopolymer, a fluoro copolymer, or any combination thereof, optionally a fluoropolymer selected from the group consisting of polytetrafluoroethylene (PTFE), acrylic-modified PTFE; chlorofluorocarbon (CFC); hydrochlorofluorocarbon (HCFC); and combinations thereof.

In some embodiments, the at least one blowing agent is an endothermic, exothermic or combined endothermic/exothermic blowing agent. In some embodiments, the blowing agent is in the form of a solid mixture of an inorganic powder, more particularly nanoparticles of an inorganic carbonate, and an acid, such as nanoparticles of an alkaline earth metal carbonate with an average diameter of less than or equal to 0.7 microns, and an acid salt derived from weak acids, wherein the acid salts are selected from the group consisting of alkaline metal acid salts, said acid salt when liquefied being capable of reacting with said alkaline earth metal carbonate resulting in the release of carbon dioxide and forming a foamed polymer, as disclosed in U.S. Patent No. 8,563,621.

In the present invention, the at least one blowing agent is present at a concentration of from 4% to 70% w/w of the total composition.

In some embodiments, the masterbatch composition disclosed herein further comprises a nucleator (also referred to herein as a “nucleating agent”), optionally a nucleator selected

from the group consisting of β crystal nucleators, aromatic carboxylic acids and their salts, sorbitol-based nucleating agents, talcs, kaolins, clays, modified clays, nanoclays, silicates, salts of hexahydrophthalic acid, sodium benzoate, benzylidene sorbitol (DBS), montmorillonites, smectites, bentonites, nanoclays, metal salts of hexahydrophthalic acid, calcium hexahydrophthalic acid, disodium cis-endo-bicyclo (2,2,1) heptane-2-3-dicarboxylate 13-docosenamide and mixtures thereof.

In the present invention, the blend is suitable for use in preparing a polyolefin-based product having a surface with increased hydrophobicity, and the blend comprises between 1 and 30% of the masterbatch composition disclosed herein, and between 70 and 99% by weight of a bulk foamable polyolefin.

In some embodiments of the blend, the at least one bulk foamable polyolefin comprises polyethylene, polypropylene or combinations thereof.

As described herein, the fluoropolymer may be present at a concentration of from 1% (w/w) to 40% (w/w) of the total blend.

According to an aspect of some embodiments of the present invention, there is provided a polymeric film having a surface with increased hydrophobicity, the film comprising between 1 and 30% of a composition comprising at least one polyolefin, at least one fluoropolymer and at least one blowing agent residue; and between 70 and 99% by weight of a bulk polyolefin; wherein said at least one fluoropolymer comprises a fluoro elastomer; wherein said at least one polyolefin and said at least one fluoropolymer together constitute a polymeric blend, and wherein the surface of the film has increased hydrophobicity by virtue of a topography including an arrangement of surface nano and microstructures.

In some embodiments, the polymeric film has a thickness of between 3 microns and 500 microns.

According to an aspect of some embodiments of the present invention, there is provided a composite structure comprising a substrate and at least one outer layer comprising the polymeric film as disclosed herein.

In some embodiments of the composite structure, the substrate comprises a combination of LDPE and LLDPE and at least one outer layer is formed from a blend comprising at least one polyethylene and acrylic modified perfluoro polymer or fluoro-elastomer and an azodicarbonamide blowing agent.

In some embodiments, the composite structure comprises a substrate and two outer layers, each outer layer comprising the polymeric film as disclosed herein.

In some embodiments, the composite structure is prepared by co-extrusion of the substrate and the two outer layers.

In some embodiments of the composite structure, the substrate comprises low density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) and each of the two outer layers is formed from a blend of from 5% to 20% Fluoro-elastomer in LDPE, with LLDPE and a mixed exothermic/endothemic blowing agent.

In some embodiments of the composite structure, a ratio between LDPE to LLDPE in the substrate is 30:70, and/or a ratio of from 5% to 20% Fluoro-elastomer in LDPE to LLDPE in each of the two outer layers is 30:70, and/or a ratio of from 5% to 20% Fluoro-elastomer in LDPE to mixed exothermic/endothemic blowing agent in each of the two outer layers is from 95.5 to 97.3.

In some embodiments of the composite structure, a ratio of thickness between the substrate and each of the two outer layers is 100:30:30.

In some embodiments of the composite structure, at least one outer layer comprises between 0.5% (w/w) and 10% (w/w) of the composite structure.

As described herein, each of the two outer layers may be prepared from a blend comprising a mixture selected from the group consisting of:

- a) from 1-40% Fluoro-elastomer in LDPE; and from 1% to 6% (w/w) of said mixed exothermic/endothemic blowing agent;
- b) from 1% to 40% of said Fluoro-elastomer in LDPE; and 0.2% to 5% of an exothermic blowing agent;
- C) from 1% to 40% of said Fluoro-elastomer in LDPE; and 1% to 5% of an endothermic blowing agent; and
- d) from 1% to 40% of said Fluoro-elastomer in LDPE; and 0.2% to 5% of an Endothermic blowing agent, and from 0.5% to 10% of a Nucleator.

According to an aspect of some embodiments of the present invention, there is provided a method of preparing a composite structure having at least one external surface having increased hydrophobicity, the method comprising the steps of:

- i. preparing a blend as disclosed herein; and
- ii. applying the blend (diluted masterbatch) as a layer on at least one external surface of a substrate under conditions that initiate gas generation from the blowing agent, thereby forming an open cell structure on the at least one external surface, having increased hydrophobicity.

According to an aspect of some embodiments of the present invention, there is provided a method of preparing a composite structure having at least one external surface having increased hydrophobicity, the method comprising the steps of:

- i. preparing a blend as disclosed herein;
- ii. extruding the blend as a film under conditions that initiate gas generation from the blowing agent; and
- iii. applying the film as a layer on at least one external surface of a substrate, thereby forming an open cell structure on the at least one external surface, having increased hydrophobicity.

According to an aspect of some embodiments of the present invention, there is provided a method of preparing a composite structure having at least one external surface having increased hydrophobicity, the method comprising the steps of:

- i. preparing a blend as disclosed herein; and
- ii. coextruding the blend as a film together with a composition for forming a polymeric substrate, under conditions that initiate gas generation from the blowing agent, thereby forming an open cell structure on the at least one external surface, having increased hydrophobicity. In some such embodiments, the composition for forming a polymeric substrate is extruded coaxially within the blend.

In some embodiments, the method further comprises performing a cohesion peel-seal film ripping process to the layer on the at least one outer surface to expose an open cell morphology on the surface.

Brief Description of the Figures

Some embodiments of the invention are described herein with reference to the accompanying figures. The description, together with the figures, makes apparent to a person having ordinary skill in the art how some embodiments of the invention may be practiced. The figures are for the purpose of illustrative discussion and no attempt is made to show structural details of an embodiment in more detail than is necessary for a fundamental understanding of the invention. For the sake of clarity, some objects depicted in the figures are not to scale.

In the Figures:

FIG. 1 schematically represents a trilayer sheet including two outer layers in accordance with the principles of the present invention (also referred to as ABA conformation);

FIG. 2 presents electron micrograph images of representative films outside of the scope of the present invention

FIG. 3 presents electron micrograph images of representative films prepared in accordance with the principles of the present invention;

FIG. 4 is a bar graph showing contact angles of representative films outside of the scope of the present invention; and

FIG. 5 is a bar graph showing contact angles of representative films prepared in accordance with the principles of the present invention.

Detailed Description of The Invention

It has surprisingly been found that the hydrophobicity of a polyolefin-based surface can be increased by blending the polyolefin with at least one fluoropolymer and at least blowing agent which is non-gaseous prior to activation by the application of heat.

Such a composition can be used to provide a polyolefin surface wherein the micro and nano surface texture roughness, topography or morphologies, required to impart hydrophobicity can be achieved by foaming a blend comprising the composition and a bulk polyolefin.

The novel products of the invention are produced using novel though simple methods and ingredients which allow, in some embodiments, for obtaining various finely foamed morphological architectures or topographies having controlled cell size, cell density and open/closed cell ratios by controlling the foaming of this outer layer through adjustment and manipulation of process parameters and ingredients including the choice of blended fluoropolymer; foaming agent; optional nucleator; extrusion temperatures and pressures and others, where relevant. By employing controlled, apparently homogeneous, though actually immiscible, polymeric blends and foaming additives within the scope of the invention, selective foaming localized in only one dispersed phase of the polymer mix coupled with a fluoropolymer preferably having hydrophobic capacity, can be achieved and a unique arrangement of surface nano, and micro structures which impart the hydrophobic characteristic are achieved.

In some embodiments, there is provided a composite structure comprising at least one outer layer having increased hydrophobicity, the at least one outer layer formed using the blend as disclosed herein, and a polymeric substrate or core layer.

In some such embodiments, the polymeric substrate or core layer is coextruded with the blend as disclosed herein to form at least one, and preferably at least two outer layers, to manufacture a multi-layered composite structure, e.g. comprising 2, 3, 5, 7, 9 or 11 layers. In some alternative embodiments, the polymeric substrate or core layer and the at least one outer layer are extruded separately and the outer layers attached to the substrate or core layer, e.g.

by use of an adhesive or tie agent, to provide a laminated system. In further alternative embodiments, the blend as disclosed herein is applied to at least one outer surface of a pre-formed substrate or core layer under conditions that initiate gas generation from the blowing agent, such that at least one outer hydrophobic layer is formed *in situ* on the substrate.

The inventive blends of the invention and concentrated mixtures used to compound them, comprising at least one fluoropolymer; at least one foamable polyolefin polymer; and at least one blowing agent, can be used to form controllably foamed materials having at least one hydrophobic surface. Concentrated masterbatches are compounded with all required ingredients though containing a lower quantity of foamable polyolefin polymer which are intended to be diluted with further foamable polyolefin polymer to achieve the final inventive blends before manufacture. These inventive concentrated masterbatches allow for economical storage and transport, for example. Thus, process steps for the manufacture of the inventive products might include a step of dilution of concentrated masterbatch with foamable polyolefin polymer to produce such a blend as an early manufacturing process step.

As used herein, the term ‘masterbatch’ or ‘concentrated masterbatch’ refers to a composition comprising at least one foamable polyolefin, at least one fluoropolymer and at least one blowing agent which is non-gaseous prior to activation by the application of heat, wherein the composition is intended for use as an additive, for mixing together with a bulk polyolefin, to form a final blend (also referred to as a ‘diluted masterbatch’) suitable for use in the preparation of a film or layer optionally together with additional components. The term ‘masterbatch’ is also referred to herein as a ‘composition’ or ‘concentrated mixture’.

As used herein, the term “foamable polyolefin” refers to a polyolefin which is capable of foaming under suitable conditions.

As used herein, the term “bulk polyolefin” refers to a polyolefin which is mixed together with the masterbatch to provide a final blend for use in forming a film or layer, wherein the bulk polyolefin comprises between 70% and 99% (w/w) of the blend. The polyolefin of the masterbatch and the bulk polyolefin may be the same or different polyolefins.

As used herein, the term ‘substrate’ or ‘core layer’ refers to any layer on which an outer surface having increased hydrophobicity is applied. The substrate or core layer may be provided with one or more such outer surfaces. The substrate or core layer may be formed from any material. In some preferred embodiments, the substrate or core layer is a polymeric layer, preferably a polyolefin layer, in which increased hydrophobicity is desired.

As used herein, the term 'increased hydrophobicity' with regard to a surface refers to a surface having a static contact angle which is at least 10 degrees greater than that of a reference surface.

As used herein, the term 'reference surface' for a surface prepared from a blend as disclosed herein comprising a specific polyolefin refers to a surface prepared using the same polyolefin, being devoid of at least one, or both, of blowing agent which is non-gaseous prior to activation by the application of heat and a fluoropolymer.

As used herein, the term 'foaming agent' or 'blowing agent' (also known as a 'pneumatogen' or 'expanding agent') refers to a substance which is capable of producing a cellular structure via a foaming process in a material, such as a polymer, that undergoes hardening or phase transition.

The materials, compositions, structures, systems, and methods of the present invention will be described in detail by reference to various non-limiting embodiments. This description will enable one skilled in the art to make and use the invention, and it describes several embodiments, adaptations, variations, alternatives, and uses of the invention. These and other embodiments, features, and advantages of the present invention will become more apparent to those skilled in the art when taken with reference to the following detailed description of the invention and exemplified preparations.

As used in this specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly indicates otherwise. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as is commonly understood by one of ordinary skill in the art to which this invention belongs.

Unless otherwise indicated, all numbers expressing conditions, concentrations, dimensions, and so forth used in the specification and claims, are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending at least upon a specific analytical technique or measurement. The range of the term "about" is not ever intended to convey anything other than the normally encountered levels of inaccuracy of measurement encountered in analytical methodologies or methods of measurement, and in no circumstances will the range of any figure include values greater than +/- 10% of that figure within the ambit of the term about.

Although the physical characteristics of the inventive hydrophobic surface are referred to by the terms texture, morphology, roughness, or topography, these terms are to be seen as descriptive lay terms which unless specified otherwise, are interchangeable and the use of

only one or more terms rather than others is not intended to convey any distinction between the terms and nothing should read into any etymological distinctions between them.

The inventors disclose novel blends that can impart improved hydrophobic surface characteristics, in some embodiments, superhydrophobic characteristics, to polymeric products, preferably films or sheets, by creating controlled roughened surface textures, topographies and morphologies by employing blowing or foaming agents. In some embodiments, the inventive blends are used in the manufacture of multilayer polymeric thin films, based on polyethylene (PE); polypropylene (PP); Polyvinyl chloride (PVC); and mixtures thereof, more preferably, PE or PP and mixtures thereof. In some embodiments, the polyethylene is selected from the group consisting of Linear Low-Density Polyethylene (LLDPE), Low-Density Polyethylene (LDPE), Medium Density Polyethylene (MDPE) and mixtures thereof.

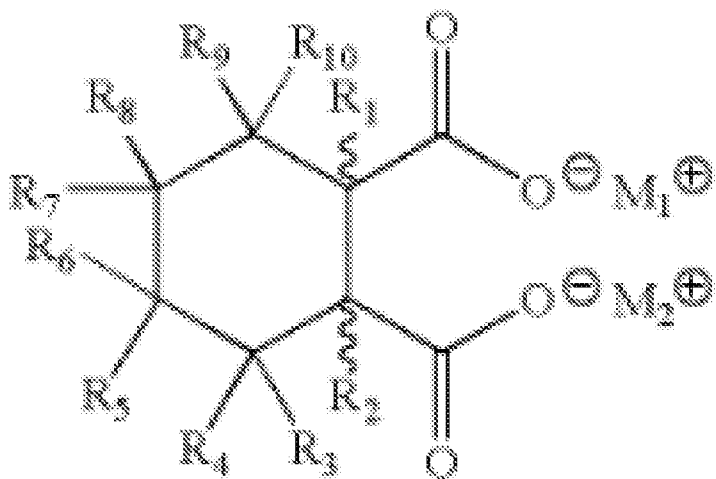
The methods and systems employed in the novel compositions, blends and resultant films or sheets involve combining blowing or foaming agents sometimes referred to as pneumatogens, with fluoro polymers, and mixtures of polymers. The inventive compositions and materials comprise foaming agents. The foaming agents may be exothermic (heat released upon foaming) or endothermic (heat absorbed during foaming) or mixed endothermic/exothermic agents.

Suitable non-limiting examples of endothermic foaming agents include sodium bicarbonate, citric acid and their derivatives, and combinations thereof, which start to evolve gas (mostly carbon dioxide (CO₂) or water vapor (H₂O)) for foaming at temperatures of at least around 120° C.

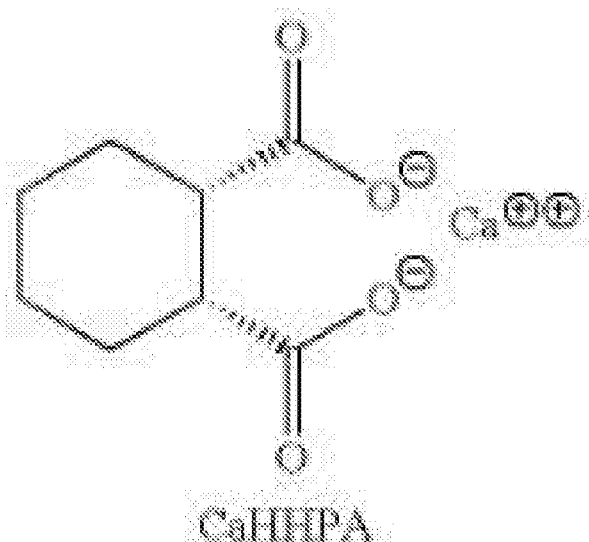
Non-limiting examples of exothermic chemical foaming agents include azodicarbonamide (ADC), 4,4'-Oxybis(benzol-sulfonylhydrazide), 5-phenyltetrazole, p-toluylenesulfonyl-semicarbazide, p-toluylenesulfonyl-hydrazide, and combinations thereof. These exothermic foaming agents become active (evolve mostly nitrogen gas for foaming) at temperatures in excess of 100° C. and release heat (exothermic), which may need to be removed by cooling or other means. It is desirable for the foaming agent to be completely decomposed and be kept in the processing mixture blend until the blend exits the die or nozzle, for example during extrusion or molding. Then, the gas should be allowed to expand in the solid phase. The gas may escape from the formed product to form open-celled structures or may remain trapped. Hydrocerol® (available from Clariant Masterbatches, Holden, Massachusetts, USA) and OnCap™ (available from PolyOne, Avon Lake, Ohio, USA) are non-limiting examples of commercially available foaming agents. One preferred type of blowing or

foaming agent is one that decomposes at elevated temperatures to release nitrogen or ammonia gas. Among these are so-called “azo” expanding agents, as well as certain hydrazide, semi-carbazides and nitroso compounds. Examples of these include azobisisobutyronitrile, azodicarbonamide, p-toluenesulfonyl hydrazide, oxybissulfohydrazide, 5-phenyl tetrazol, benzoylsulfohydroazide, p-toluoylsulfonylsemicarbazide, 4,4'-oxybis(benzenesulfonyl hydrazide) and the like. Blowing agents are also referred to as expanding agents and are available commercially under trade names such as Celogen®. Commercially available expanding agents that are useful include Celogen® 754A, 765A, 780, AZ, AZ-130, AZ1901, AZ760A, AZ5100, AZ9370, AZRV, all of which are azodicarbonamide types. Celogen®OT and TSH-C are useful sulfonylhydrazide types. Azodicarbonamide expanding agents are especially preferred. The blowing agent may comprise two or more endothermic blowing agents (such as sodium bicarbonate and citric acid) or mixtures of endothermic and exothermic blowing agents such as sodium bicarbonate, citric acid and azodicarbonamide (AZDCA) e.g a mixture of 30%NaHCO₃ + 10%citric acid+ 30%AZDCA.

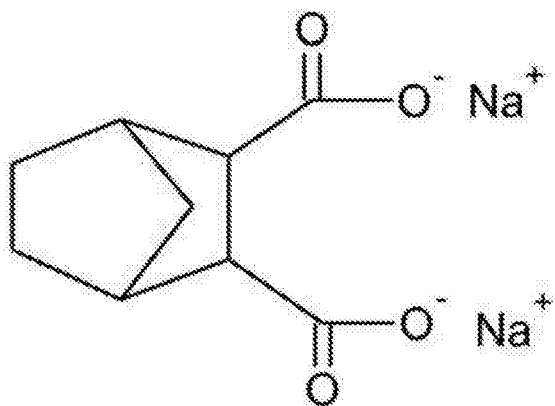
The inventive blends, and/or the compositions used for their compounding, allow for controlled processes for fabricating selectively foamed material having unique morphologies, topographies etc. In certain embodiments, the inventive blends include various nucleators. Potential nucleators can include aromatic carboxylic acids; salts e.g. sodium benzoate, sorbitol-based nucleating agents e.g. dibenzylidene sorbitol (DBS); talcs, kaolins, clays, silicates etc. not limited to, montmorillonites, smectites, bentonites, talc, and modified clays. Additional examples of nanoclays include Cloisite® NA, 10A, 15A, 25A, 30B and 93A. One exemplified type of carboxylic acid salt nucleator compounds are metal salts of hexahydrophthalic acid (“HHPA”) having a general structure:



and in particular the nucleator known as calcium hexahydrophthalic acid (calcium HHPA or Ca HHPA), a β crystal nucleator, commercially sold as HYPERFORM® HPN-20E nucleating agent by Milliken & Company of Spartanburg, S.C comprising 66 weight percent of Ca HHPA and 34 weight percent of zinc stearate. Having the following structure:



Another is HYPERFORM® HPN-68L {DISODIUM CIS-ENDO-BYCYCLO (2,2,1) HEPTANE-2-3-DICARBOXYLATE 13-DOCOSENAMIDE, (132) - SILICA WATER}.



Inventors are acutely aware that the relevant field of art is dynamic and foresee future improvements in the available nucleators and fully intend that future nucleators, heat-activated blowing agents and fluoropolymers useful in this field which provide compositions, blends and products providing the advantages of those disclosed or increased levels of hydrophobicity are already contemplated.

In some preferred embodiments, as exemplified below, coextrusion techniques are employed utilizing various blends as disclosed herein to fabricate tri-layer films, preferably symmetrical films, in ABA conformation having a substrate or core layer of 100 microns, coated with outer layers of 30 microns each. In manufacture, the layer of the films produced that comes in contact with the chilling roll equipment often employed in film manufacture, is referred to herein, as the **Bottom** layer, and the layer that is not in contact with the chilling roll, as the **Top** layer. Contact angle and slip angle is measured at five different loci on each of the Top and Bottom external surfaces. The invention will now be described by examples, which shall not be construed as limiting the scope of the invention, but merely exemplifying some though not all, preferred embodiments. The inventors also provide directions for obtaining further, as yet not exemplified embodiments.

Examples

Although the inventive blends; methods and compounded products are herein exemplified by tri-layer films or sheets, it will be clearly understood that the inventive products fabricated by the inventive methods can be single layer, bi-layer, tri-layer or multi-layer sheets or films. The sheets or films may be prepared through known techniques, including extrusion, lamination, coextrusion (such as coaxial extrusion techniques, providing coaxial products wherein the substrate or core polyolefin layer is encased within the inventive hydrophobic surface layer).

It will be immediately apparent that the inventive blends used to form hydrophobic layers in the exemplified products below, will themselves be useful to form e.g. molded or extruded monolithic structures having hydrophobic surfaces and are examples of embodiments of the invention. Similarly, for the sake of, for example, efficiency; storage and ease of transport, compositions can be supplied to manufacturers of films in the form of concentrated mixtures (masterbatches) containing a lower quantity of the foamable polyolefin polymer ingredients than required for use in the subsequent stage of preparation of the film (e.g. extrusion). These masterbatches are compounded for mixing with further foamable polyolefin polymer to achieve the final inventive blends before manufacture.

Example 1

Materials and Methods

The various raw materials and additives selected for the production of tri-layer sheets are detailed in **Table 1**. Prior to fabrication of the sheets, a number of concentrates or masterbatches were prepared using active ingredients, including fluoropolymers and different types of nucleators.

The various blends were processed by twin screw extrusion using a bench mounted 16 mm PRISM EUROLAB XL twin-screw extruder manufactured by Thermo Fisher Scientific, Germany. The extruded materials obtained were shredded and dried.

| Manufacturer | Grade name | Material type |
|-------------------|-------------------------|---|
| ExxonMobil | LDPE LD158 | LDPE |
| Dow | Dowlex (RTM) NG 5056G | LLDPE |
| Dow | Dowlex (RTM) 2607G | LLDPE |
| DuPont | PTFE 6CN | Fluoro-polymer (polytetrafluoroethylene) |
| Kafrit (RTM) | MB Fluoro-2 | Fluoro-elastomer MB (10% acrylic modified perfluoro polymer + polyethylene in LDPE) |
| | MB 1 | Blowing agent Exo/Endo mixture |
| Milliken chemical | Hyperform (RTM) HPN 20E | Nucleating agent for PE (66 wt% calcium exahydrophthalic anhydride, 34 wt% zinc stearate) |

Table 1. List of materials used.

Table 2 describes the composition of NA-HPN 20E and MB-PTFE1.

| Designation | Polyolefin | Additive |
|-------------|-----------------------------------|------------------------------------|
| NA-HPN 20E | Dowlex (RTM) 2607G [98 wt%] | Hyperform (RTM) HPN 20E [2 wt%] |
| MB-PTFE 1 | Dowlex (RTM) NG 5056G 97 [wt%] | PTFE 6CN [3 wt%] |

Table 2. Components of NA-HPN 20E and MB-PTFE1

In order to prepare the various films a cast film co-extrusion system from Randcastle Extrusion Systems, Inc. was employed, through which multilayer sheets, such as tri-layer sheets, were fabricated as illustrated.

Figure 1 represents a trilayer sheet wherein two outer layers are each prepared from a composition comprising LLDPE together with a fluoropolymer and a blowing agent, and an inner (core) layer situated between the two outer layers is prepared from LLDPE.

It should be noted that due to difficulties in fabrication of sheets containing MB-PTFE 1 as a result of large differences in the processing temperatures of the additive and polymer matrix comprising LLDPE / LDPE blends (Linear Low-Density Polyethylene/Low-Density Polyethylene), it was decided to replace MB-PTFE 1 with MB Fluoro-2 Fluoro co-polymer (Kafrit (RTM)).

The composition(s) of the films are detailed in **Tables 4** and **5**.

Table 4 describes **set #1** of experiments wherein films devoid of a fluoro co-polymer were investigated, whereas **Table 5** describes **set #2** of experiments wherein films incorporating fluoro co-polymer (fluoro homopolymer, fluoro co-polymer or Fluoro-elastomer) were investigated. **Set #1** is outside of the scope of the invention.

Tables 6 and **7** detail the processing conditions chosen for fabricating the various films of the experiments designated **Set #1** and **Set #2**.

| Sample film code | Layer no. | Polyolefin (%) | Foaming agent (%) | Nucleator (%) | Layer thickness (µm) |
|------------------|-----------|----------------|-------------------|---------------|----------------------|
| SHD-1 | 1 | NG5056G (97) | MB 1 (3) | --- | 30 |
| | 2 | LD158/NG5056 | | | 100 |
| | 3 | NG5056G (97) | MB 1 (3) | --- | 30 |
| SHD-2 | 1 | NG5056G (95) | MB 1 (95) | --- | - " - |
| | 2 | LD158/NG5056G | | | - " - |
| | 3 | NG5056G (95) | MB 1 (5) | --- | - " - |
| SHD-3 | 1 | NG5056G (94) | MB 1 (3) | NA-HPN20E | - " - |
| | 2 | LD158/NG5056G | | | - " - |
| | 3 | NG5056G (94) | MB 1 (3) | NA-HPN20E | - " - |
| SHD-4 | 1 | NG5056G (90) | MB 1 (5) | NA-HPN20E | - " - |
| | 2 | LD158/NG5056G | | | - " - |
| | 3 | NG5056G (90) | MB 1 (5) | NA-HPN20E | - " - |
| SHD-ref (1) | 1 | NG5056G (100) | --- | | - " - |
| | 2 | LD158/NG5056G | --- | | - " - |
| | 3 | NG5056G (100) | --- | | - " - |

Table 4. Composition of the various films fabricated in **set #1** of experiments – Films devoid of fluoro co-polymer. These films are outside of the scope of the invention.

| Sample film code | Layer | (%) Compound | (%) Foaming agent | (%) Nucleating agent | Layer thickness (μm) |
|------------------|-------|-----------------------|-------------------|----------------------|-----------------------------------|
| SHD-5 | 1 | PE/MB Fluoro-2* (97) | MB 1(3) | --- | 30 |
| | 2 | LD158/NG5056G (30/70) | | | 100 |
| | 3 | PE/MB Fluoro-2* (97) | MB 1(3) | --- | 30 |
| SHD-6 | 1 | PE/MB Fluoro-2* (95) | MB 1(5) | --- | - " - |
| | 2 | LD158/NG5056G (30/70) | | | - " - |
| | 3 | PE/MB Fluoro-2* (95) | MB 1(5) | --- | - " - |
| SHD-7 | 1 | PE/MB Fluoro-2* (90) | MB 1(10) | --- | - " - |
| | 2 | LD158/NG5056G (30/70) | | | - " - |
| | 3 | PE/MB Fluoro-2* (90) | MB 1(10) | --- | - " - |
| SHD-8 | 1 | PE/MB Fluoro-2* (94) | MB 1(3) | NA-HPN20E (3) | - " - |
| | 2 | LD158/NG5056G (30/70) | | | - " - |
| | 3 | PE/MB Fluoro-2* (94) | MB 1(3) | NA-HPN20E (3) | - " - |
| SHD-9 | 1 | PE/MB Fluoro-2* (90) | MB 1(5) | NA-HPN20E (5) | - " - |
| | 2 | LD158/NG5056G (30/70) | | | - " - |
| | 3 | PE/MB Fluoro-2* (90) | MB 1(5) | NA-HPN20E (5) | - " - |
| SHD-10 | 1 | PE/MB Fluoro-2* (85) | MB 1(10) | NA-HPN20E (5) | - " - |
| | 2 | LD158/NG5056G (30/70) | | | - " - |
| | 3 | PE/MB Fluoro-2* (85) | MB 1(10) | NA-HPN20E (5) | - " - |
| SHD.ref (2) | 1 | PE/MB Fluoro-2 (100) | --- | | - " - |
| | 2 | LD158/NG5056G (30/70) | --- | | - " - |
| | 3 | PE/MB Fluoro-2 (100) | --- | | - " - |

Table 5. Composition of the various films fabricated in **set #2** of experiments – Films including fluoro-co-polymer etc.

| Extruder | RPM | Temperature profile [$^{\circ}\text{C}$] | | | | | | |
|------------------|-----|--|-----|-----|-----|------------|-----|------------|
| | | Extruder | | | | Feed-Block | Die | Chill-roll |
| A | - | - | - | - | - | | | |
| B (Outer layer) | 60 | 180 | 190 | 200 | 210 | 210 | 210 | 20 |
| C (Center layer) | 100 | 180 | 190 | 200 | 210 | | | |

Table 6. Process conditions for films fabricated in **set #1** of experiments (**set #1** is outside of the scope of the invention).

| Extruder | RPM | Temperature profile [°C] | | | | | | |
|------------------|-----|--------------------------|-----|-----|-----|------------|-----|------------|
| | | Extruder | | | | Feed-Block | Die | Chill-roll |
| A | - | - | - | - | - | 215 | 215 | 20 |
| B (Outer layer) | 60 | 180 | 190 | 200 | 210 | | | |
| C (Center layer) | 100 | 180 | 190 | 200 | 210 | | | |

Table 7. Process conditions for films fabricated in **set #2** of experiments.

Regarding experiment **set #1** (outside of the scope of the invention), it should be noted that it was not possible to produce sheets or films with a foaming agent content greater than 10% due to the lack of stability of the melt flow and the appearance of large holes in the film sheet. With the addition of Fluoro co-polymer (Experiment **Set # 2**), the fabrication capability improved, and thus it was possible to fabricate films comprising high blowing agent content, concentrations greater or equal to 10%. Adding nucleators limited the possibility of producing a uniform film sheet with a high foaming agent concentration (10%), even where a fluoro co-polymer additive was present.

In order to characterize the hydrophobicity of the different sheets or surfaces that were produced, the static contact angle was measured using the optical contact angle measuring and contour analysis systems of the OCA series available from DataPhysics Instruments GmbH, Germany, at 5 different loci or points, and on both external surfaces of the film. The average contact angle over the 5 different points was calculated for each external surface of each film. The surface which is not in contact with the chill roll during the film casting is designated **Top** while the surface which is in contact with the chill roll is designated **Bottom**. In order to characterize the morphological structure of the foamed cells and the surface of the various film sheets, the surfaces were scanned using a scanning electron microscope (Aspex Explorer SEM, USA).

Results

Scanning electron micrograph (SEM) images of representative films taken at two different loci are shown in Figs. 2 and 3. Fig. 2 is outside of the scope of the invention.

A graph showing contact angles for films fabricated in **set #1** of experiments - films without fluoro co-polymer is presented in Figure 4 (outside of the scope of the invention).

A graph showing contact angles for films fabricated in **set #2** of experiments - films with fluoro co-polymer is presented in Figure 5.

Discussion of results

Experiment set #1 (outside of the scope of the invention)

- Adding 3% foaming agent (SHD-1) lead to an average contact angle increase of 10 °, relative to the reference sheet (devoid of foaming agent and fluoropolymer)
- In films with a foaming agent content higher than 3% (SHD-2 and SHD-4) it is evident that the contact angle decreases as compared to SHD-1.
- In these **set #1** films the **Bottom** surface displays higher contact angles compared to the **Top** surface.
- SEM images reveal that the foamed surfaces comprise a mixed morphology of open and closed cells.
- Addition of a nucleator (SHD-3, SHD-4) increases the size of the open cells, in addition, the cells appear to have an elongated ellipse structure, probably as a result of stretching and a decrease in the melt viscosity. During the processing of these nucleator-containing compositions, the melt viscosity was appreciably lower as compared to the composition where a nucleator was absent.
- In order to maintain the resultant morphology, careful control of the stretching ratio was needed because when the stretching ratio was too high the foam cells were seen to have been spread or squeezed over the surface, requiring re-running the experiment to achieve desired texture, morphology roughness, or topography.

Experiment set #2

- Inclusion of fluoro co-polymer lead to an average contact angle increase in all tested compositions including the reference composition (SHD-Ref 2) as compared to reference composition SHD-Ref 1.
- The most significant improvement was measured in a film prepared from a composition comprising 5% blowing agent (SHD-6), the film displaying a contact angle measured on the outer, **Top** surface of 134°, an increase of over 36 ° relative to the reference composition (SHD-Ref 1)
- Increasing the blowing agent content with or without nucleator present did not necessarily improve the contact angle achieved and a stable plateau of around 125° was attained.
- SEM images reveal the presence of fluoro co-polymer on the surface of the foamed surfaces.

- In this set of experiments too, a mixed morphology of open and closed cells is also found but the size of the open cells is relatively small compared with the first set of experiments often being an indicator of improved parameters of hydrophobicity.

Based on this example further investigation was understood as warranted in the application of this inventive concept with additional foaming/blowing agent additives and with nucleating additives to create a variety of different cell morphologies including examining the interplay between the morphology achieved and resultant contact angle of the surface. A study was additionally seen as warranted into the effect of integrating higher fluoro co-polymer content to understand the properties and morphologies that could be obtained. Investigation of higher density grades of polymers exemplified by MDPE and HDPE and investigating extrusions grades of PP homopolymer, PP-raco (Random copolymer) and systems based on PE/PP were planned.

Example 2

Based on the understanding gained in the first sets of experiments, further new compounds were developed comprising nucleators and including fluoro elastomers which were integrated into the foamed outer layers of films. In this group of experiments designated **Set #3**, the polymers of the core or substrate layer were polypropylene homopolymer and High-Density Polyethylene (HDPE) copolymer in contrast to the LLDPE/LDPE which had been used in the earlier sets of experiments. In a similar fashion the foaming concentrate chosen for this set of experiments were of an exothermic nature and specifically Kafrit (RTM) MB FM4 (EXO) [FM 00D41 LD] <http://www.kafrit.com/products?type=blowing%20agent>

Materials and Methods

The various raw materials and additives selected for the production of the tri-layer sheets are detailed in **Table 8**.

| Manufacturer | Grade Name | Material Type |
|-------------------------------|------------------------|---|
| Chevron Phillips Chemical Co. | Marlex (RTM) 5202 | High Mol. Wt. Ethylene-Hexene copolymer |
| Carmel Olefins | Capilene (RTM) E 50 E | PP Homopolymer (extrusion) |
| Carmel Olefins | Capilene (RTM) R 50 | PP Homopolymer |
| Carmel Olefins | Capilene (RTM) QC 71 E | PP Random Copolymer RC |
| ExxonMobil | LDPE LD 158 | LDPE |

| | | |
|-------------------------------------|--|--|
| Dow Plastics | Dowlex (RTM) NG5056G | LLDPE |
| Dow Plastics | Dowlex (RTM) 2607G | LLDPE |
| | MB 1 (ENDO/EXO) | Blowing Agent, Endothermic/Endothermic |
| Kafrit (RTM) | Kafrit (RTM) MB FM4 (EXO) | Blowing Agent, Exothermic |
| BYK Additives & Instrument, Germany | Cloisite® 15A (10% in HD/MDPE) | Quaternary ammonium salt modified natural montmorillonite polymer additive. [Organic Modifier: dimethyl, dihydrogenated tallow, quaternary ammonium] |
| BASF Irgaclear® XT 386 | NA-XT 386 (2% in Capilene (RTM) R-50) | 1,3,5-benzenetrisamide-based (Triamino benzene derivative) |
| BYK Additives & Instrument, Germany | Cloisite® 93A Nanoclay NA-93A (10% in Capilene (RTM) R-50) | Ternary ammonium salt modified natural montmorillonite polymer additive |
| Milliken Chemical | NA-NX8000 (10% in cPP) Millad® NX™ 10 Conc. | Triamino benzene derivative |
| Kafrit (RTM) | HD-MD/MB Fluoro-2 | 30% Fluoro-elastomer in HD/MDPE |
| Kafrit (RTM) | PP/MB Fluoro-2 | 30% Fluoro-elastomer in PP |
| Mitsubishi Chemical | (*) METABLEN (RTM) A-3000 | Acrylic-Modified PTFE |

Table 8. Polymers and Compounds in **set #3** of experiments.

* Processing aid for thermoplastics

METABLEN (RTM) is the trade name of modifiers, which have been developed originally by Mitsubishi chemical. Adding a small quantity of METABLEN (RTM) to various resins improves and increases their impact strength and processability, and further improves the characteristics, the appearance and the productivity of their final products. METABLEN (RTM) A type is acrylic-modified PTFE, which easily forms fine well-dispersed fibril in molten thermoplastic resin as network structure when kneaded under heating. With small amount of addition, it greatly improves the melt tension that is required in such processing such as vacuum molding, foam molding, blow molding and profiling by minimizing increases in melt viscosity without sacrificing the inherent properties of thermoplastics.

Table 9 describes **set #3** of experiments, tri-layer SHD film sheets in ABA conformation.

| Sample | Layer | Compound (%) | Foaming | Nucleating | Layer |
|--------|-------|--------------|---------|------------|-------|
|--------|-------|--------------|---------|------------|-------|

| Film Code | | | agent (%) | agent (%) | thickness (µm) |
|-----------|---|----------------------|-------------|-------------|----------------|
| SHD-11 | 1 | PE/MB Fluoro-2 (90) | MB FM4 (10) | - | 30 |
| | 2 | LD158/NG5056 (30/70) | | | 100 |
| | 3 | PE/MB Fluoro-2 (90) | MB FM4 (10) | - | 30 |
| SHD-12 | 1 | PE/MB Fluoro-2 (89) | MB FM4 (10) | Talc MB (1) | -- |
| | 2 | LD158/NG5056 (30/70) | | | -- |
| | 3 | PE/MB Fluoro-2 (89) | MB FM4 (10) | Talc MB (1) | -- |
| SHD-13 | 1 | PE/MB Fluoro-2 (80) | MB FM4 (10) | NA-15A (10) | -- |
| | 2 | LD158/NG5056 (30/70) | | | -- |
| | 3 | PE/MB Fluoro-2 (80) | MB FM4 (10) | NA-15A (10) | -- |
| SHD-14 | 1 | PP/MB Fluoro-2 (90) | MB FM4 (10) | - | -- |
| | 2 | LD158/NG5056 (30/70) | | | -- |
| | 3 | PP/MB Fluoro-2 (90) | MB FM4 (10) | - | -- |
| SHD-15 | 1 | PP/MB Fluoro-2 (89) | MB FM4 (10) | Talc MB (1) | -- |
| | 2 | LD158/NG5056 (30/70) | | | -- |
| | 3 | PP/MB Fluoro-2 (89) | MB FM4 (10) | Talc MB (1) | -- |
| SHD-16 | 1 | PP/MB Fluoro-2 (80) | MB FM4 (10) | NA-93A (10) | -- |
| | 2 | LD158/NG5056 (30/70) | | | -- |

| | | | | | |
|-------------------|---|-------------------------|----------------|----------------|------|
| | 3 | PP/MB Fluoro-2 (80) | MB FM4 (10) | NA-93A (10) | -''- |
| SHD-ref(3) | 1 | PE/MB Fluoro-2 (100) | - | | -''- |
| | 2 | LD158/NG5056 (30/70) | - | | -''- |
| | 3 | PE/MB Fluoro-2 (100) | - | | -''- |
| SHD-ref(4) | 1 | PP/MB Fluoro-2 (100) | - | | -''- |
| | 2 | LD158/NG5056 (30/70) | - | | -''- |
| | 3 | PP/MB Fluoro-2 (100) | - | | -''- |
| HD/MD-ref | 1 | HD/MDPE (100) | - | | -''- |
| | 2 | LD158/NG5056 (30/70) | - | | -''- |
| | 3 | HD/MDPE (100) | - | | -''- |
| PP(HP)-ref | 1 | PP/MB Fluoro-2 (100) | - | | -''- |
| | 2 | LD158/NG5056 (30/70) | - | | -''- |
| | 3 | PP/MB Fluoro-2 (100) | - | | -''- |

Table 9. Set #3 of experiments, tri-layer SHD film sheets in ABA conformation.

Results

Table 10 provides contact angle and slip angle results for the films fabricated in experiment **Set #3**.

| Sample Film Code | Contact Angle (Free Surface) | Contact Angle (Polish Surface) | Slip angle (free surface) | Slip angle (polish surface) |
|------------------|---------------------------------|-----------------------------------|------------------------------|--------------------------------|
|------------------|---------------------------------|-----------------------------------|------------------------------|--------------------------------|

| | | | | |
|--------------|-----|-----|----|----|
| SBD-11 | 138 | 138 | 66 | 65 |
| SBD-12 | 138 | 135 | 58 | 52 |
| SBD-13 | 139 | 131 | 56 | 57 |
| SBD-14 | 139 | 139 | 42 | 47 |
| SBD-15 | 134 | 136 | 58 | 58 |
| SBD-16 | 135 | 121 | 77 | 67 |
| SBD-ref (3) | 130 | 133 | 46 | 66 |
| SBD-ref (4) | 86 | 104 | 38 | 46 |
| HD-3D-ref | 90 | 98 | 34 | 31 |
| PP(BP)-ref | 97 | 98 | 32 | 30 |
| | | | | |
| SBD-5 (2.25) | 128 | 135 | 25 | 37 |
| SBD-6 (2.25) | 135 | 123 | 36 | 38 |

Table 10. Contact angle and slip angle results for the films fabricated in experiment **Set#3**.

Discussion of results

- The results obtained in experiments **set #3**, in terms of increase in hydrophobicity, expressed as the contact angles and slip angles, are arguably inferior to those achieved in Experiment **set #2**.
- It is apparent that the transition to the use of purely exothermic blowing agents did not contribute to significant improvement but arguably can be seen as producing less optimal results as compared to the films fabricated in **Set #2** where mixed exothermic/endothemic blowing agents were utilized
- It is further apparent that the positive influence of the fluoro-elastomer in certain **Set #2** compositions was expressed in a weakened form in the **Set # 3** films based on HDPE and HP-PP.

Further experimental examples will thus include mixed exothermic/endothemic foaming agents and the material to be employed will be mixtures of PP/PE and Fluoro-elastomers of the METABLEN (RTM) variety discussed above.

Example 3

Further to experiments set **#3** being completed, two additional experimental sets, **#4** and **#5**, were conducted, in which novel compounds were prepared. These preparations included nucleation additives and fluoro-elastomers, incorporated into the foamed outer layers of sheets or films wherein the principle carrier or base materials were Polypropylene-

homopolymer and high-density polyethylene (HDPE) hexene copolymer, as well as the LLDPE and LDPE previously employed in earlier examples.

Similarly, and due to the lessons learned from the results of experiments set #3, in the following experimental sets, a mixed exothermic/endothermic blowing agent additive concentrate, MB 1 was employed.

Additionally, several selected sheets or films from experimental sets # 2, #3, #4, and #5, underwent a process of opening or tearing of the foamed cells near the sheet surface, parallel to the axis of the sheet, using a cohesion peel-seal film process for the purpose of creating a simulation of open-cell morphology on the surface.

Methods and Materials

The various raw materials and additives selected for the production of the tri-layer sheets are detailed in **Table 11**. The tri-layer films in ABA conformation for fabrication in **Set #4** are presented in **Table 12**, whereas **Table 13** describes set #5 of experiments.

| Manufacturer | Grade Name | Material Type |
|-------------------------------------|--|---|
| Chevron Phillips | Marlex (RTM) 5202 | HDPE-MDPE |
| Carmel Olefins | Capilene (RTM) E 50 E | PP Homopolymer (extrusion) |
| Carmel Olefins | Capilene (RTM) R 50 | PP Homopolymer |
| Carmel Olefins | Capilene (RTM) QC 71 E | PP Random Copolymer RC |
| ExxonMobil | LDPE LD 158 | LDPE |
| Dow Plastics | Dowlex (RTM) NG5056G | LLDPE |
| Dow Plastics | Dowlex (RTM) 2607G | LLDPE |
| \ | MB 1 (ENDO/EXO) | Blowing Agent, Endothermic/Endothermic |
| Kafrit (RTM) | Kafrit (RTM) MB FM4 (EXO) | Blowing Agent, Exothermic |
| BYK Additives & Instrument, Germany | Cloisite® 15A (10% in HD/MDPE) | Quaternary ammonium salt modified natural montmorillonite polymer additive. |
| BYK Additives & Instrument, Germany | NA-XT 368 [BYK-368?] (2% in Capilene (RTM) R-50) | Polyacrylate, adsorbed on SiO ₂ |
| BYK Additives & | Cloisite® 93A Nanoclay | Ternary ammonium salt modified |

| | | |
|------------------------|---|---|
| Instrument, Germany | NA-93A (10% in Capilene (RTM) R-50) | natural montmorillonite polymer additive |
| Milliken Chemical | NA-NX8000 (10% in cPP) Millad® NX™ 10 Conc. | |
| Mitsubishi Chemical | METABLEN (RTM) A- 3800 | Acrylic-Modified PTFE |
| Kafrit (RTM) | MB Fluoro-1 | 10% Fluoro-elastomer in PP (HP) |
| Kafrit (RTM) | MB Fluoro-2 | 10% Fluoro-elastomer in LDPE |
| | HD-MD/MB Fluoro 2 | 30% MB Fluoro 2 in HD-MD |
| | PE/MB Fluoro 2 | 30% MB Fluoro 2 in LLDPE |
| | PP/MB Fluoro 1 | 30% MB Fluoro 1 in PP(HP) |
| | HD-MD/MTBN-3800 | 3% METABLEN (RTM) A-3800 in HD-MD |
| | PE/MTBN-3800 | 3% METABLEN (RTM) A-3800 in LLDPE |
| | PP/MTBN-3800 | 3% METABLEN (RTM) A-3800 in PP(HP) |

Table 11. Polymers and Compounds in set#4 of experiments.

| Sample film | Layer | Compound (%) | Foaming agent | Nucleating | Layer |
|---------------|-------|-------------------------|---------------|------------------|-------|
| SHD-17 | 1 | PP/MB Fluoro 1 (95) | MB 1 (5) | --- | 30 |
| | 2 | LD158/NG5056 (30/70) | --- | --- | 100 |
| | 3 | PP/MB Fluoro 1 (95) | MB 1 (5) | --- | 30 |
| SHD-18 | 1 | PP/MB Fluoro 1 (94) | MB 1 (5) | NA-XT 368 (1) | - " - |
| | 2 | LD158/NG5056 (30/70) | --- | --- | - " - |
| | 3 | PP/MB Fluoro 1 | MB 1 (5) | NA-XT | - " - |

| | | | | | |
|--|---|-------------------------|----------|------------------|-------|
| | | (94) | | 368 (1) | |
| SHD-19 (outside of the scope of the invention) | 1 | PP/MTBN-3800 (95) | MB 1 (5) | --- | - " - |
| | 2 | LD158/NG5056 (30/70) | --- | --- | - " - |
| | 3 | PP/MTBN-3800 (95) | MB 1 (5) | --- | - " - |
| SHD-20 (outside of the scope of the invention) | 1 | PP/MTBN-3800 (94) | MB 1 (5) | NA-XT 368 (1) | - " - |
| | 2 | LD158/NG5056 (30/70) | --- | --- | - " - |
| | 3 | PP/MTBN-3800 (94) | MB 1 (5) | NA-XT 368 (1) | - " - |
| SHD-21 (outside of the scope of the invention) | 1 | PE/MTBN-3800 (95) | MB 1 (5) | --- | - " - |
| | 2 | LD158/NG5056 (30/70) | --- | --- | - " - |
| | 3 | PE/MTBN-3800 (95) | MB 1 (5) | --- | - " - |
| SHD-22 (outside of the scope of the invention) | 1 | HD-MD/MTBN- 3800(95) | MB 1 (5) | --- | - " - |
| | 2 | LD158/NG5056 (30/70) | --- | --- | - " - |
| | 3 | HD-MD/MTBN- 3800(95) | MB 1 (5) | --- | - " - |
| SHD-ref (5) | 1 | PE/MTBN-3800 (100) | --- | --- | - " - |
| | 2 | LD158/NG5056 (30/70) | --- | --- | - " - |
| | 3 | PE/MTBN-3800 (100) | --- | --- | - " - |
| | 1 | HD-MD/MTBN- | --- | --- | - " - |

| | | | | | |
|-------------|---|-------------------------|-----|-----|-------|
| SHD-ref (6) | | 3800(95) | | | |
| | 2 | LD158/NG5056 (30/70) | --- | --- | - " - |
| | 3 | HD-MD/MTBN- 3800(95) | --- | --- | - " - |

Table 12. Set #4 of experiments, tri-layer SHD film sheets in ABA conformation.

| Sample film code | Layer | Compound (%) | HDPE-MDPE (%) | Foaming agent (%) | Layer thickness (µm) |
|--|-------|-----------------------------|------------------------|-------------------|----------------------|
| SHD-23 (outside of the scope of the invention) | 1 | Capilene (RTM) QC 71 E (60) | Marlex (RTM) 5202 (40) | --- | 30 |
| | 2 | LD158/NG5056 (30/70) | --- | --- | 100 |
| | 3 | Capilene (RTM) QC 71 E (60) | Marlex (RTM) 5202 (40) | --- | 30 |
| SHD-24 (outside of the scope of the invention) | 1 | Capilene (RTM) QC 71 E (55) | Marlex (RTM) 5202 (40) | MB 1 (5) | - " - |
| | 2 | LD158/NG5056 (30/70) | --- | --- | - " - |
| | 3 | Capilene (RTM) QC 71 E (55) | Marlex (RTM) 5202 (40) | MB 1 (5) | - " - |
| SHD-25 (outside of the scope of the invention) | 1 | PP/MB Fluoro 1 (60) | HD-MD/MB Fluoro 2 (40) | --- | - " - |
| | 2 | LD158/NG5056 (30/70) | --- | --- | - " - |
| | 3 | PP/MB Fluoro | HD-MD/MB | --- | - " - |

| | | | | | |
|---------------|---|-------------------------|---------------------------|----------|-------|
| | | 1 (60) | Fluoro 2 (40) | | |
| SHD-26 | 1 | PP/MB Fluoro 1 (55) | HD-MD/MB Fluoro 2 (40) | MB 1 (5) | - " - |
| | 2 | LD158/NG5056 (30/70) | --- | --- | - " - |
| | 3 | PP/MB Fluoro 1 (55) | HD-MD/MB Fluoro 2 (40) | MB 1 (5) | - " - |

Table 13. Set #5 of experiments, tri-layer SHD film sheets in ABA conformation.

Results

Contact angle and slip angle results for free surface and peel-seal surfaces for films fabricated are shown in **Table 14.**

| Sample film code | Contact angle (free surface) | Contact angle (peel-seal surface) | Slip angle (free surface) | Slip angle (peel-seal surface) |
|--|---------------------------------|--------------------------------------|------------------------------|-----------------------------------|
| SHD-5 (#2) | 128 | 146 | 25 | 12 |
| SHD-6 (#2) | 135 | 154 | 16 | 8 |
| SHD-12 (#3) | 118 | 137 | 53 | 26 |
| SHD-14 (#3) | 120 | 139 | 42 | 18 |
| SHD-20 (#4) (outside scope of invention) | 109 | 129 | 56 | 27 |
| SHD-22 (#4) (outside scope of invention) | 119 | 138 | 60 | 31 |
| SHD-24 (#5) (outside scope of invention) | 114 | 136 | 58 | 28 |
| SHD-26 (#5) | 110 | 131 | 67 | 42 |

15 12 21

Table 14. Contact angle and slip angle results for free surface and peel-seal surfaces for films fabricated

Discussion of results for experimental sets #4 and #5

The hydrophobic performance results obtained in the current set of experiments, and the results obtained through the opening, ripping or peeling of the near-surface foamed cells, through cohesion peel-seal, to simulate open cell morphology on the surface for selected samples indicate the following findings:

- Samples from Sets #4 and #5 did not yield better results than those obtained in sets #2 and #3
- The process of "opening or rupturing of the foam cells near the film surface, increases the hydrophobicity of the resultant films in both contact and slip angle.
- The peeling process may be useful to optimize the achievement of a surface texture of open and dense cells

In the exemplified experimental samples, the best performance so far achieved has been obtained with blends based on LLDPE/LDPE; fluoro-elastomer (Fluoro 2), employing endothermic/Endothermic blowing or foaming agents.

The inventors envision further experimental sets of compounds and blends; wherein special emphasis will be given to the creation of surfaces with open and dense cell morphologies using further blowing or foaming agent additives by which means compositions based on LLDPE/LDPE mixtures and of mixtures of PP/PE, both in combination with fluoro-elastomer will be evaluated.

Examples of foaming agents envisioned are mixtures of particles of at least one alkaline earth metal carbonate and at least one acid salt derived from weak acids e.g. alkaline metal acid salts, said acid salt when liquefied being capable of reacting with said alkaline earth metal carbonate resulting in the release of carbon dioxide for use in forming a foamed polymer.

CLAIMS

1. A blend suitable for use in preparing a polyolefin-based product having a surface with increased hydrophobicity, the blend comprising:

- (a) between 1% and 30% of a masterbatch composition,
wherein the masterbatch composition comprises
- (I) at least one foamable polyolefin, and
 - (II) at least one fluoropolymer, and
 - (III) at least one heat-activated blowing agent which is non-gaseous prior to activation by the application of heat;
- wherein said at least one blowing agent is present at a concentration of from 4% to 70% w/w of the total composition;
wherein said at least one fluoropolymer comprises a fluoro elastomer;
wherein said at least one foamable polyolefin and said at least one fluoropolymer together constitute a polymeric blend;

and

- (b) between 70% and 99% by weight of a bulk foamable polyolefin.

2. The blend of claim 1,
wherein said at least one foamable polyolefin of said masterbatch composition is selected from the group consisting of polyethylene, polypropylene and a combination thereof.

3. The blend of claim 1 or claim 2,
wherein said at least one blowing agent is an endothermic, exothermic, or combined endothermic/exothermic blowing agent.

4. The blend of any one of claims 1 to 3,
wherein said masterbatch composition further comprises a nucleator.

5. The blend of claim 4,
wherein said nucleator is selected from the group consisting of β crystal nucleators, aromatic carboxylic acids and their salts, sorbitol-based nucleating agents, talcs, kaolins, clays, modified clays, nanoclays, silicates, salts of hexahydrophthalic acid, sodium benzoate, benzylidene sorbitol (DBS), montmorillonites, smectites, bentonites, nanoclays, metal salts

of hexahydrophthalic acid, calcium hexahydrophthalic acid, disodium cis-endo-bicyclo (2,2,1) heptane-2-3-dicarboxylate 13-docosenamide and mixtures thereof.

6. The blend of any one of claims 1 to 5,
wherein said at least one bulk foamable polyolefin comprises polyethylene, polypropylene, or combinations thereof.

7. A polymeric film having a surface with increased hydrophobicity,
the film comprising between 1% and 30% of a composition comprising (I) at least one polyolefin, and (II) at least one fluoropolymer, and (III) and at least one blowing agent residue; and between 70% and 99% by weight of a bulk foamable polyolefin;
wherein said at least one fluoropolymer comprises a fluoro elastomer;
wherein said at least one polyolefin and said at least one fluoropolymer together constitute a polymeric blend, and
wherein the surface of the film has increased hydrophobicity by virtue of a topography including an arrangement of surface nano and microstructures.

8. The polymeric film of claim 7,
having a thickness of between 3 microns and 500 microns.

9. A composite structure comprising:
a substrate, and
at least one outer layer comprising the polymeric film of claim 7 or claim 8.

10. The composite structure of claim 9,
wherein said at least one polyolefin in said at least one outer layer comprises polypropylene.

11. The composite structure of claim 9 or claim 10,
wherein said substrate comprises polypropylene.

12. The composite structure of claim 9,

wherein said substrate comprises a combination of LDPE and LLDPE and said at least one outer layer is formed from a blend comprising at least one polyethylene and acrylic modified perfluoropolymer or fluoro elastomer and an azodicarbonamide blowing agent.

13. A composite structure comprising:
a substrate, and two outer layers,
wherein each outer layer comprises the polymeric film of any one of claims 9 to 12.
14. The composite structure of claim 13,
prepared by co-extrusion of said substrate and said two outer layers.
15. The composite structure of claim 13 or claim 14,
wherein said substrate comprises low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) and wherein each of said two outer layers is formed from a blend of from 5% to 20% fluoro-elastomer in LDPE, with LLDPE and a mixed exothermic/endothemic blowing agent.
16. The composite structure of claim 15,
wherein a ratio between said LDPE to said LLDPE in said substrate is 30:70.
17. The composite structure of claim 15 or claim 16,
wherein a ratio of (i) said from 5% to 20% fluoro elastomer in LDPE to (ii) said LLDPE, in said each of two outer layers, is 30:70.
18. The composite structure of any one of claims 15 to 17,
wherein a ratio of (i) said from 5% to 20% fluoro elastomer in LDPE to (ii) said mixed exothermic/endothemic blowing agent, in said each of two outer layers, is from 95:5 to 97:3.
19. The composite structure of any one of claims 13 to 18,
wherein a ratio of thickness between said substrate and each of said two outer layers is about 100:30:30.
20. The composite structure of any one of claims 13 to 19,

wherein said two outer layers comprise between about 0.5% (w/w) and about 10% (w/w) of the composite structure.

21. A method of preparing a composite structure having at least one external surface having increased hydrophobicity, said method comprising the steps of:

- i. preparing a blend according to any one of claims 1 to 6; and
- ii. applying said blend as a layer on at least one external surface of a substrate under conditions that initiate gas generation from said blowing agent,

thereby forming an open cell structure on the at least one external surface, having said increased hydrophobicity.

22. A method of preparing a composite structure having at least one external surface having increased hydrophobicity, said method comprising the steps of:

- i. preparing a blend according to any one of claims 1 to 6; and
- ii. coextruding said blend as a film together with a composition for forming a polymeric substrate, under conditions that initiate gas generation from said blowing agent,

thereby forming an open cell structure on the at least one external surface, having said increased hydrophobicity.

23. The method of claim 21 or claim 22,

further comprising performing a cohesion peel-seal film ripping process to said layer on said at least one outer surface to expose an open cell morphology on said surface.