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(54) Title: MULTILAYERED ROTOMOULDED ARTICLES COMPRISING A LAYER OF POLYESTER

(57) Abstract: A rotomoulded article comprising two or more layers A and B, wherein layer A comprises: from 50 to 100 wt% of an aliphatic polyester selected from polyhydroxyalkanoate, poly(lactic acid), polycaprolactone, copolyesters and polyesteramides, from 0 to 50 wt% of a polyolefin, from 0 to 20 wt% of a co- or ter-polymer comprising : a) 50 to 99.9 wt% of an ethylene or a styrene monomer, b) 0.1 to 50 wt% of an unsaturated anhydride-, epoxide- or carboxylic acid-containing monomer, c) 0 to 50 wt% (meth)acrylic ester monomer, and layer B comprises: from 50 to 99.4 wt% a polyolefin, which can be different from the polyolefin of layer A, from 0.5 to 50 wt% of a polyester, which can be different from the polyester of layer A, from 0.1 to 20 wt% of a co- or ter-polymer, which can be different from the co- or ter-polymer of layer A, comprising: a) 50 to 99.9 wt% of an ethylene or a styrene monomer, b) 0.1 to 50 wt% of an unsaturated anhydride-, epoxide- or carboxylic acid-containing monomer, c) 0 to 50 wt% (meth)acrylic ester monomer.



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Multilayered rotomoulded articles comprising a layer of polyester

Field of the invention

The invention pertains to multilayered rotomoulded articles having a layer of polyester.

Background of the invention

5 The process of rotational moulding, also called rotomoulding, of plastic has been known since the 1940s for the preparation of hollow plastic articles.

This process consists of adding a thermoplastic polymer into a mould, rotating the mould so that all the points of the internal surface of the mould are in contact with the polymer while heating the mould, so as to deposit the aforementioned molten polymer on the
10 internal surface of the mould. Thereafter, a stage of cooling allows the solidification of the plastic article, which is then removed from the mould.

Rotational moulding is advantageous because it avoids applying stress and strain to the plastic, which generally occurs in other transformations, for example in injection moulding. Indeed, the plastic does not undergo malaxation or compaction as in an extruder or in
15 injection moulding. Rotational moulding is particularly suitable for preparing large-sized articles, such as furniture, tanks, drums, reservoirs etc.

The most commonly used polymer in rotational moulding is polyethylene, but other polymers such as vinyl polychlorides (PVC), polyamides, polycarbonates and polypropylenes can also be used. However, alone, all of these polymers tend to shrink
20 somewhat and deform within the mould, which causes considerable withdrawal from the mould and non-uniform wall thicknesses. In addition, these polymers, used alone, are characterized either by slow coalescence, or by a raised melting point, which increases the duration of the production cycle. Polyesters, on the other hand, often lack in good thermal and mechanical properties. Thus, monolayered rotomoulded articles of polyester
25 (e.g. PLA) are not optimal. These can be reinforced by preparing multilayered articles, for example having an additional foamed layer. However, compositions for adjacent layers have to adhere to the polyester.

There thus exists a need to produce articles by multilayered rotational moulding with polyesters, which coalesce more rapidly and which make it possible to obtain articles with
30 minimal shrinkage and warpage and which have good adherence between the layers.

The object of this invention is thus to provide rotationally moulded (rotomoulded) articles comprising polyolefin having less shrinkage and/or warpage.

Another object of this invention is thus to provide rotationally moulded multilayered articles having good adherence between the layers.

Another object of this invention is to provide rotomoulded articles having a uniform wall thickness.

- 5 Another object of this invention is to provide rotomoulded articles presenting a good aspect of internal and external surfaces, without any bubbles, ripples, or other defects.

Another object of this invention is to provide rotomoulded articles with good mechanical properties, in particular improved impact strength.

- 10 Another object of this invention is to provide rotomoulded articles with good mechanical properties, in particular stiffness.

Another object of this invention is to provide rotomoulded articles with an easily paintable surface.

At least one of the objects mentioned above is carried out with the present invention.

- 15 The applicant found in a surprising way that by using a polyester, for example poly(lactic acid), optionally together with a polyolefin, for example polyethylene, the disadvantages mentioned above can be overcome.

Summary of the invention

The invention covers a rotomoulded article comprising two or more layers, wherein a layer A comprises:

- 20
- from 50 to 100 wt% of a polyester, preferably 90 to 100 wt%,
 - from 0 to 50 wt% of a polyolefin, preferably 0.1 to 25 wt%,
 - from 0 to 20 wt% of a co- or ter-polymer, preferably 0.1 to 20 wt%, comprising:
 - 25 a) 50 to 99.9 wt% of an ethylene or a styrene monomer,
 - b) 0.1 to 50 wt% of an unsaturated anhydride-, epoxide- or carboxylic acid-containing monomer, and
 - c) 0 to 50 wt%, preferably 0.1 to 30 wt%, (meth)acrylic ester monomer ,

and a layer B comprises:

- 30
- from 50 to 99.4 wt%, preferably 60 to 99 wt% of a polyolefin, which can be different from the polyolefin of layer A,
 - from 0.5 to 50 wt%, more preferably 1 to 30 wt%, of a polyester (preferably PLA), which can be different from the polyester of layer A,

- from 0.1 to 20 wt%, preferably 0.1 to 15 wt%, of a co- or ter-polymer, which can be different from the co- or ter-polymer of layer A, comprising:
 - a) 50 to 99.9 wt% of an ethylene or a styrene monomer,
 - b) 0.1 to 50 wt% of an unsaturated anhydride-, epoxide- or carboxylic acid-containing monomer, and
 - c) 0 to 50 wt% (meth)acrylic ester monomer.

Preferably, the invention covers a rotomoulded article comprising two or more layers, wherein a layer A comprises:

- from 50 to 100 wt% of an aliphatic polyester selected from polyhydroxyalkanoate, poly(lactic acid), polycaprolactone, copolyesters and polyesteramides, preferably 90 to 100 wt%,
- from 0 to 50 wt% of a polyolefin, preferably 0.1 to 25 wt%,
- from 0 to 20 wt% of a co- or ter-polymer, preferably 0.1 to 20 wt%, comprising
 - a) 50 to 99.9 wt% of an ethylene or a styrene monomer,
 - b) 0.1 to 50 wt% of an unsaturated anhydride-, epoxide- or carboxylic acid-containing monomer,
 - c) 0 to 50 wt%, preferably 0.1 to 30 wt%, (meth)acrylic ester monomer,

and a layer B comprises:

- from 50 to 99.4 wt%, preferably 60 to 99 wt% of a polyolefin, which can be different from the polyolefin of layer A,
- from 0.5 to 50 wt%, more preferably 1 to 30 wt%, of a polyester (preferably PLA), which can be different from the polyester of layer A,
- from 0.1 to 20 wt%, preferably 0.1 to 15 wt%, of a co- or ter-polymer, which can be different from the co- or ter-polymer of layer A, comprising:
 - a) 50 to 99.9 wt% of an ethylene or a styrene monomer,
 - b) 0.1 to 50 wt% of an unsaturated anhydride-, epoxide- or carboxylic acid-containing monomer,
 - c) 0 to 50 wt% (meth)acrylic ester monomer.

The article comprising layers A and B is preferably a bi- or tri-layered rotomoulded article.

The polyester is preferably an aliphatic polyester. The majority of aliphatic polyesters (e.g. polyhydroxyalkanoate (PHA), poly(lactic acid) (PLA), polycaprolactone (PCL), copolyesters, polyesteramides etc) being obtainable from renewal resources and/or being

biodegradable constitutes an additional advantage when added in combination with polyolefins, currently used alone. Preferably the aliphatic polyester is a poly(lactic acid).

The polyolefin is preferably polyethylene or polypropylene.

5 The unsaturated anhydride-, epoxide-, or carboxylic acid-containing monomer is preferably selected from maleic anhydride, or glycidyl methacrylate. Preferably, it is present from 0.2 to 30 wt% of the co- or ter-polymer.

The (meth)acrylic ester monomer is preferably selected from methyl, ethyl, n-butyl, iso-butyl, 2-ethylhexyl, or n-octyl (meth)acrylate. It is preferably present from 0.5 to 40 wt%, more preferably 1 to 30 wt%, of the terpolymer.

10 The article may comprise a further layer B comprising from 50 to 100 wt% of a polyolefin, which is preferably adjacent to layer A. The polyolefin of said layer B is preferably a polyethylene. The polyolefin can be different from the polyolefin of layer A. The polyolefin, being preferentially polyethylene, of said layer B is preferably foamed.

In a particular embodiment, the article may comprise the two layers A and B, wherein:

- 15
- layer A is the outer layer,
 - layer B is the inner layer adjacent to layer A, preferably comprising a foamed polyethylene from 50 to 100 wt%.

In a particular embodiment, the article may consist of the two layers A and B, wherein:

- 20
- layer A is the outer layer, and
 - layer B is the inner layer adjacent to layer A, preferably comprising a foamed polyethylene from 50 to 100 wt%.

The article may comprise yet a further layer C. Layer C may comprise from 50 to 100 wt% of a polyolefin, which is preferably adjacent to layer B. The polyolefin can be different from the polyolefin of layer B. The polyolefin of said layer C is preferably a polyethylene. Layer
25 C can be identical to layer B.

In a particular embodiment, the article may comprise three layers A, B and C, wherein:

- layer A is the outer layer,
- layer B is the intermediate layer adjacent to layer A and layer C, preferably comprising a foamed polyethylene from 50 to 100 wt%, and
- 30 • layer C is the inner layer, preferably comprising polyethylene from 50 to 100 wt%.

In a particular embodiment, the article may consist of the three layers A, B and C, wherein:

- layer A is the outer layer,
- layer B is the intermediate layer adjacent to layer A and layer C, preferably comprising a foamed polyethylene from 50 to 100 wt%, and
- layer C is the inner layer, preferably comprising polyethylene from 50 to 100 wt%.

5 In this case, layer C can be identical to layer B.

Such an article can be a can, a tank, car part, preferably a car door or car body.

In particular embodiments, the article comprises at least one cavity which is provided with a polyurethane (PU); preferably a polyurethane foam.

The present invention also encompasses a polyurethane filled rotomoulded article
10 comprising one or more layers wherein a layer A comprises

- from 50 to 100 wt% of a polyester, preferably 90 to 100 wt%, preferably wherein said polyester is an aliphatic polyester selected from poly(lactic acid), polyhydroxyalkanoate, polycaprolactone, copolyesters and polyesteramides; more preferably wherein said polyester is an aliphatic
15 polyester selected from poly(lactic acid), polyhydroxyalkanoate, polycaprolactone, and polyesteramides; more preferably wherein said polyester is an aliphatic polyester selected from poly(lactic acid), polycaprolactone, and polyesteramides;
- from 0 to 50 wt% of a polyolefin, preferably 0.1 to 25 wt%,
- from 0 to 20 wt% of a co- or ter-polymer, preferably 0.1 to 20 wt%,
20 comprising :
 - a) 50 to 99.9 wt% of an ethylene or a styrene monomer,
 - b) 0.1 to 50 wt% of an unsaturated anhydride-, epoxide- or carboxylic acid-containing monomer,
 - c) 0 to 50 wt%, preferably 0.1 to 30 wt%, (meth)acrylic ester monomer,

25

and a layer B comprises:

- from 50 to 99.4 wt%, preferably 60 to 99 wt% of a polyolefin, which can be different from the polyolefin of layer A,
- from 0.5 to 50 wt%, more preferably 1 to 30 wt%, of a polyester (preferably
30 PLA), which can be different from the polyester of layer A,
- from 0.1 to 20 wt%, preferably 0.1 to 15 wt%, of a co- or ter-polymer, which can be different from the co- or ter-polymer of layer A, comprising:
 - a) 50 to 99.9 wt% of an ethylene or a styrene monomer,

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- b) 0.1 to 50 wt% of an unsaturated anhydride-, epoxide- or carboxylic acid-containing monomer,
- c) 0 to 50 wt% (meth)acrylic ester monomer.

In further embodiments, such articles comprise the two layers A and B, wherein:

- 5
- layer A is the outer layer,
 - layer B is the inner layer adjacent to layer A.

Such an article can be a can, a tank, car part, preferably a car door or car body.

Brief Description of the Figures

10 Figure 1 shows the temperature cycle of a rotomoulding process to prepare a two-layered article.

Detailed Description of the Invention

1. Layer A

The rotomoulded article of the invention comprises two or more layers, namely at least layers A and B, wherein a layer A comprises:

- 15
- from 50 to 100 wt% of a polyester, preferably wherein said polyester is an aliphatic polyester selected from poly(lactic acid), polyhydroxyalkanoate, polycaprolactone, copolyesters and polyesteramides; more preferably wherein said polyester is an aliphatic polyester selected from poly(lactic acid), polyhydroxyalkanoate, polycaprolactone, and polyesteramides;
- 20
- from 0 to 50 wt% of a polyolefin,
 - from 0 to 20 wt% of a co- or ter-polymer comprising :
 - a) 50 to 99.9 wt% of an ethylene or a styrene monomer,
 - 25 b) 0.1 to 50 wt% of an unsaturated anhydride-, epoxide- or carboxylic acid-containing monomer,
 - c) 0 to 50 wt%, preferably 0.1 to 30 wt%, (meth)acrylic ester monomer,

and layer B comprises from 50 to 100 wt% of polyolefin. Preferably layer B is adjacent to layer A.

The optional polyolefin in layer A when used, can be present from 0.1 to 25 wt% of layer A, more preferably from 1 to 20 wt% of layer A.

The optional co- or ter-polymer when used, can be present from 0.1 to 20 wt% of layer A, more preferably from 0.1 to 15 wt% of layer A.

5 1.1. Polyester (e.g. PLA)

Preferably, the polyester is an aliphatic polyester, although any polyester known in the art can be used. The advantage of using an aliphatic polyester is that it is prepared from natural renewable resources. The aliphatic polyester is preferably selected from polyhydroxyalkanoate (PHA), poly(lactic acid) (PLA), polycaprolactone (PCL),
10 copolyesters and polyesteramides.

A non-limiting example of a suitable copolyester includes Tritan™ copolyester from Eastman: a copolyester based on the use of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCD) as a comonomer.

The polyester is preferably present 50,60, 65, 70, 75 or 80 up to 90, 95, 96, 97, 98, 99,
15 99.4, 99.5 or 100 wt% of layer A. In particular embodiments, the polyester is present from 70 to 95 wt% of layer A, more preferably 75 to 90 wt%. In certain embodiments, the polyester is present from 70 to 100 wt% of layer A.

Most preferably, the polyester is a poly(lactic acid) (PLA).

The poly(lactic acid) (also known as polylactide) is a thermoplastic resin derived from
20 renewable resources.

The poly(lactic acid) also includes copolymers of lactic acid. For instance, copolymers of lactic acid and trimethylene carbonate according to EP application number 11167138 and copolymers of lactic acid and urethanes according to WO 2008/037772 and PCT application number PCT/EP2011/057988. The introduction of comonomers to PLA
25 increases the ductility (i.e. decreases the brittleness) of the PLA.

Preferably, the PLA used in the rotomoulded article of the invention can be a poly-L-lactide (PLLA), a poly-D-lactide (PDLA) and/or a mixture of PLLA and PDLA. By PLLA, it is meant a polymer in which the majority of the repetitive units are monomers of L-lactide and by PDLA, a polymer in which the majority of the repetitive units are D-lactide
30 monomers. Stereocomplexes of PLLA and PDLA, as described for example in WO 2010/097463, can also be used. Preferably, the polylactide used is the PLLA.

Preferably, the PLLA or the PDLA respectively have an optical purity (called isomeric purity) of the L or D isomer, which is higher than 92 wt% of the PLA, preferably higher than 95 wt%. An optical purity from at least 99 wt% is more preferred.

The PLLA used in the invention thus includes a content of D isomer lower than 8 wt%, preferably lower than 5 wt%, more preferably lower or equal to 1 wt% of the PLLA. By analogy, the PDLA includes a content of L isomer lower than 8 wt%, preferably lower than 5 wt%, more preferably lower or equal to 1 wt% of the PDLA.

PLA (PLLA or PDLA) preferably has a number average molecular weight (Mn) ranging between 30.000 and 350.000 g/mol, more preferably between 50.000 and 175.000 g/mol, even more preferably between 70.000 and 150.000 g/mol. The number average molecular weight is measured by chromatography by gel permeation compared to a standard polystyrene in chloroform at 30°C. The ratio of the weight average molecular weight (Mw) to the Mn is generally between 1.2 and 5.0.

The process for preparing PLA is well-known by the person skilled in the art. For example it can be obtained by the process describes in documents WO1998/002480, WO 2010/081887, FR2843390, US5053522, US 5053485 or US5117008.

In an embodiment, the PLA is obtained by polymerizing lactide, in the presence of a suitable catalyst and preferably in the presence of a compound of formula (I), acting as a co-initiator and transfer agent of the polymerization,



wherein R¹ is selected from the group consisting of C₁₋₂₀alkyl, C₆₋₃₀aryl, and C₆₋₃₀arylC₁₋₂₀alkyl optionally substituted by one or more substituents selected from the group consisting of halogen, hydroxyl, and C₁₋₆alkyl. Preferably, R¹ is selected from C₃₋₁₂alkyl, C₆₋₁₀aryl, and C₆₋₁₀arylC₃₋₁₂alkyl, optionally substituted by one or more substituents, each independently selected from the group consisting of halogen, hydroxyl, and C₁₋₆alkyl; preferably, R¹ is selected from C₃₋₁₂alkyl, C₆₋₁₀aryl, and C₆₋₁₀arylC₃₋₁₂alkyl, optionally substituted by one or more substituents, each independently selected from the group consisting of halogen, hydroxyl and C₁₋₄alkyl. The alcohol can be a polyol such as diol, triol or higher functionality polyhydric alcohol. The alcohol may be derived from biomass such as for instance glycerol or propanediol or any other sugar-based alcohol such as for example erythritol. The alcohol can be used alone or in combination with another alcohol.

In an embodiment, non-limiting examples of initiators include 1-octanol, isopropanol, propanediol, trimethylolpropane, 2-butanol, 3-buten-2-ol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, 1,7-heptanediol, benzyl alcohol, 4-bromophenol, 1,4-benzenedimethanol, and (4-trifluoromethyl)benzyl alcohol; preferably, said compound of formula (I) is selected
5 from 1-octanol, isopropanol, and 1,4-butanediol.

The PLA structure can be of the following types in terms of chain termination:

R-OH and R-COOH, with R being the PLA chain, obtainable when using monoalcohol as co-initiator,

HO-R-OH and HOOC-R-COOH obtainable when using diol as co-initiator,

10 or multiple OH (e.g. 5), obtainable when using triol or higher functionality polyhydric alcohol as co-initiator,

Preferably, the PLA used in layer A has R-OH and R-COOH, chain termination, and was obtained using a monoalcohol as co-initiator.

15 Preferably, the PLA used in the layer A of the invention has a crystallinity index (CI), as measured by XRD, of at least 5%. Preferably the crystallinity index of the PLA is at most 60%.

Preferably, the PLA used in the process of the invention is in the form of particles with an average particle size between 20 μm and 2000 μm . However between 50 and 1000 μm is preferred and even more preferred is the average particle size of between 100 and 800
20 μm . In the present invention, by particles one understands "grains", which can be spherical, and/or ovoid forms, or can be of any other shapes or forms. The size corresponds to the longest dimension of these particles. In the case of spherical particles, the size corresponds to the diameter of these particles. The particles of PLA can be obtained by extrusion of the PLA exiting the polymerization reactor through a die with die
25 gaps having corresponding dimensions.

The PLA defined in the present invention can be in the form of micropellets or powders. The particles of PLA can be also obtained by grinding/milling pellets of PLA whose dimension is higher than 2000 μm , for example pellets whose dimension lies between 4000 μm and 5000 μm . Such pellets of PLA can be obtained after polymerization per
30 extrusion while passing the PLA through a die whose openings have corresponding dimension. In this case, the grinding of PLA pellets can be carried out by various types of grinders, such as for example a grinder with a disc, a mill, or an electromagnetic grinder, for example with a piston. Grinding can be done at room temperature or cryogenically, i.e.

carried out at a temperature ranging between -10 and -200°C, preferentially between -20 and -100°C. Cryogenic grinding allows in particular to avoid yellowing of the articles obtained and to obtain a highly grinded powder flow. Cryogenic grinding also makes it possible to produce a powder without filaments, this being particularly adapted to the rotomoulding application. Grinding can be carried out under inert atmosphere, i.e. in the absence of oxygen; for example under nitrogen.

After grinding, it is possible to measure and/or modify the granulometry of the PLA by using rotating sieves. To determine the granulometry of the PLA one can use a method of sieving, for example, by using sieves of different mesh sizes, or with a laser i.e. a Malvern Mastersizer.

In the present invention, one defines the PLA whose average particle size lies between 20 µm and 2000 µm which was obtained from grinding PLA pellets with initial dimensions greater than 2000 µm "PLA powder". The PLA used in the process of the invention can be either in the form of powder, or in the form of micropellets, or in the form of a mixture of powder and micropellets. The powder or micropellets of PLA can be used as they are without the addition of other compounds or they can be mixed with various compounds, loads, agents and/or additives.

Many methods of mixing PLA with such additives can be used in the process of the invention: mixing the additives with PLA in the melt or adding the additives directly to the mould with the PLA powder or micropellets. They can also be mixed with the powder after grinding or with the micropellets before introduction into the rotational mould. They can also be introduced into the PLA still in the molten state obtained directly after polymerization. Some of these additives can even be added during the polymerization of the PLA. One can also consider the addition of these additives to PLA pellets having a dimension higher than 2.000 µm before grinding. The powder and micropellets of PLA can thus include antioxidants, and light and heat stabilizers, as well as anti-UV agents.

For example, suitable antioxidants include compounds containing phenol functional groups which are sterically hindered in simple or oligomeric form such as Irganox® MD1024 from BASF. One can also use antioxidants called "secondaries" such as compounds containing phosphite functional groups such as Ultrinox® 626 from Chemtura.

When one of these additives is present, its concentration in the PLA lies between 0.05 wt% and 5 wt% compared.

Fillers, impact resistance modifiers and other additives can also be included.

Fillers are preferentially selected from the group of fibrous compositions such as glass fibres, metal fibres, carbon fibres, minerals such as clays, kaolin, or nanoparticles such as carbon nanotubes, and powders such as talc.

5 Other additives which can be used include, for example, fire retardants, lubricants, plasticizers, anti-static agents, pigments, dyes, surfactants. Among plasticizers, one can in particular select those of the family of citrates, in particular citrate esters like citrate of terbutylene (TBC) or butyrate esters like tri-ethylene glycol di 2-ethyl hexylbutyrate or their mixtures. Preferably, TBC is used.

10 The polyester, in particular PLA, is then blended either in dry form or in the melt with the polyolefin, to create the composition required for layer A.

In another embodiment of layer A, the PLA pellets, optional polyolefin and optional co- or ter-polymer are compounded together according to any known compounding method in the art, e.g. mixer, like a Banbury mixer, or an extruder, preferably a twin screw extruder. The extrusion is generally carried out at a temperature below 230°C.

15 1.2. Optional polyolefin of layer A (e.g. polyethylene)

The polyolefin is optionally present preferably from 0.1, 0.5, 1, 2, 5, 10, 15, or 20 up to 25, 30, 35, 40, 45 or 50 wt% of layer A. In particular, preferably from 0.1 to 25 wt% of layer A, more preferably 1 to 20 wt%.

20 The polyolefin can be selected from polyethylene, polypropylene, polybutene or polyhexene.

Preferably, the polyolefin is polyethylene. With polyethylene herein it is meant a polyethylene comprising at least 50 wt% of ethylene monomers. The polyethylene may comprise up to 50 wt% of alpha-olefin comonomers selected from alpha-olefins having from 3 to 12 carbon atoms. Preferably, the comonomer is selected from propylene, n-butene, iso-butene, n-pentene, iso-pentene, n-butene or iso-butene.

The polyethylene can be prepared with a Ziegler-Natta catalyst or a single-site catalyst, such as a metallocene, according to any known polymerization process in the art.

30 Preferably, the polyethylene is prepared with a single-site catalyst, in particular with a metallocene catalyst. This induces a narrow molecular weight distribution, regular comonomer insertion, and uniform comonomer distribution. This means such a polyethylene preferably has a narrow molecular weight distribution of from 1 to 5 (measured by GPC) and a narrow comonomer distribution index (CDBI) i.e. at least 50%, preferably at least 60%, more preferably at least 75%, measured by TREF (temperature

rising elution fractionation). Any metallocene known in the art can be used to prepare the polyethylene. In one embodiment, the metallocene can be an unbridged metallocene, for example, selected from the group comprising bis(iso-butylcyclopentadienyl) zirconium dichloride, bis(pentamethylcyclopentadienyl) zirconium dichloride, bis(tetrahydroindenyl) zirconium dichloride, bis(indenyl) zirconium dichloride, bis(1,3-dimethylcyclopentadienyl) zirconium dichloride, bis(methylcyclopentadienyl) zirconium dichloride, bis(n-butylcyclopentadienyl) zirconium dichloride, and bis(cyclopentadienyl) zirconium dichloride; and preferably selected from the group comprising bis(cyclopentadienyl) zirconium dichloride, bis(tetrahydroindenyl) zirconium dichloride, bis(indenyl) zirconium dichloride, and bis(1-methyl-3-butyl-cyclopentadienyl)zirconium dichloride. In another embodiment, the metallocene can be a bridged metallocene, for example, selected from the group comprising ethylene bis(4,5,6,7-tetrahydro-1-indenyl) zirconium dichloride, ethylene bis(1-indenyl) zirconium dichloride, dimethylsilylene bis(2-methyl-4-phenyl-inden-1-yl) zirconium dichloride, dimethylsilylene bis(2-methyl-1H-cyclopenta[a]naphthalen-3-yl) zirconium dichloride, cyclohexylmethylsilylene bis[4-(4-tert-butylphenyl)-2-methyl-inden-1-yl] zirconium dichloride, dimethylsilylene bis[4-(4-tert-butylphenyl)-2-(cyclohexylmethyl)inden-1-yl] zirconium dichloride. Bridged bis(tetrahydroindenyl) metallocenes are preferred, in particular ethylene bis(4,5,6,7-tetrahydro-1-indenyl) zirconium dichloride.

The polyethylene preferably has a density of at least 0.900 g/cm^3 , more preferably at least 0.910 g/cm^3 , even more preferably of at least 0.920 g/cm^3 and most preferably of at least 0.930 g/cm^3 . It is of at most 0.965 g/cm^3 , preferably of at most 0.960 g/cm^3 . Most preferably, the polyethylene has a density of 0.932 to 0.945 g/cm^3 . The density is measured following the method of standard test ISO 1183 at 23°C .

The polyethylene preferably has a melt index MI2 of at least 1 dg/min, preferably of at least 1.5 dg/min, more preferably of at least 2 dg/min. It is preferably at most 25 dg/min, more preferably at most 20 dg/min. Most preferably, the polyethylene has an MI2 of 1 dg/min to 10 dg/min. The melt flow index MI2 is measured following the method of standard test ISO 1133 condition D at a temperature of 190°C and a load of 2.16 kg.

Most preferably the polyethylene is prepared with an ethylene bis(4,5,6,7-tetrahydro-1-indenyl) zirconium dichloride metallocene, wherein the polyethylene has a density of 0.930 to 0.950 g/cm^3 and a melt index MI2 of 1 to 10 dg/min.

The polyolefin of layer A may contain additives, in particular additives suitable for rotational moulding, such as, by way of example, processing aids, mould-release agents, anti-slip agents, primary and secondary antioxidants, light stabilizers, anti-UV agents, acid scavengers, flame retardants, fillers, nanocomposites, lubricants, antistatic additives,

nucleating/clarifying agents, antibacterial agents, plasticizers, colorants/pigments/dyes and mixtures thereof. Preferably the polyolefin comprises an anti-UV agent. Illustrative pigments or colorants include titanium dioxide, carbon black, cobalt aluminum oxides such as cobalt blue, and chromium oxides such as chromium oxide green. Pigments such as ultramarine blue, phthalocyanine blue and iron oxide red are also suitable. Specific examples of additives include lubricants and mould-release agents such as calcium stearate, zinc stearate, SHT, antioxidants such as Irgafos 168™, Irganox 1010™, and Irganox 1076™, anti-slip agents such as erucamide, light stabilizers such as Cyasorb THT 4611 and 4802, tinuvin 622™ and tinuvin 326™, and nucleating agents such as Milliken HPN20E™, or Milliken Hyperform® HPR-803i.

An overview of the additives that can be used in the injection-moulded articles of the present invention may be found in *Plastics Additives Handbook*, ed. H. Zweifel, 5th edition, 2001, Hanser Publishers.

In a preferred embodiment of layer A, the PLA pellets, optional polyolefin and optional co- or ter-polymer are compounded together according to any known compounding method in the art, e.g. mixer, like a Banbury mixer, or an extruder, like a twin screw extruder. The extrusion is generally carried out at a temperature below 230°C.

1.3. Optional Co- or Ter-polymer (compatibilising agent)

The optional co- or ter-polymer comprises ethylene or styrene monomer, an unsaturated anhydride-, epoxide- or carboxylic acid-containing monomer and optionally a (meth)acrylic ester monomer. When present, the co- or ter-polymer acts as a compatibilizer between the polar polyester and any polyolefin. It also acts as a chain modifier.

If present the co-or ter-polymer is preferably present from 0.1 to 20 wt%, more preferably from 0.1 to 15 wt%, even more preferably from 0.5 to 10 wt%, most preferably from 1 to 5 wt% of layer A.

Preferably, the optional co- or ter-polymer comprises:

- a) 50 to 99.9 wt% of ethylene or styrene monomer, preferably 50 to 99.8 wt% ,
- b) 0.1 to 50 wt% of an unsaturated anhydride-, epoxide- or carboxylic acid-containing monomer,
- c) 0 to 50 wt% of a (meth)acrylic ester monomer,

the total sum of components being 100 wt%.

In the embodiment of the co-polymer, it comprises preferably:

- a) 50 to 99.9 wt% of ethylene or styrene monomer, preferably 50 to 99 wt%,
- b) 0.1 to 50 wt% of an unsaturated anhydride-, epoxide- or carboxylic acid-containing monomer, preferably 1 to 50 wt% ,

5

the total sum of components being 100 wt%.

In the embodiment of the ter-polymer, it comprises preferably:

- a) 50 to 99.8 wt% of ethylene or styrene monomer,
- b) 0.1 to 50 wt% of an unsaturated anhydride-, epoxide- or carboxylic acid-containing monomer,
- c) 0.1 to 50 wt% of a (meth)acrylic ester monomer,

10

the total sum of components being 100 wt%.

In all embodiments of the co- or ter-polymer, the ethylene or styrene monomer (a) is present from 50 to 99.9 wt%, preferably from 50 to 99.8 wt%, more preferably from 60 to 99.5 wt%, even more preferably from 65 to 99 wt%, most preferably from 70 to 98 wt%. In the embodiment of the copolymer, the ethylene or styrene monomer can be present from 90 to 98 wt%.

15

In all embodiments of the co- or ter-polymer, the unsaturated monomer (b) is preferably selected from an unsaturated anhydride- or epoxide-containing monomer. More preferably, the unsaturated monomer (b) is selected from a glycidyl (meth)acrylate or maleic anhydride. The unsaturated monomer (b) is preferably present from 0.1 to 40 wt%, more preferably from 0.2 to 30 wt%, even more preferably from 0.3 to 20 wt%, yet even more preferably from 0.3 to 15 wt% and most preferably from 0.3 to 10 wt% of the co- or ter-polymer.

20

The (meth)acrylic ester monomer (c), if present, is preferably selected from those acrylates which have between 1 and 10 carbon atoms such as for example methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, iso-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, or n-octyl (meth)acrylate. If present, it preferably makes up 0.1 to 50 wt% of the terpolymer, preferably 0.5 to 40 wt%, more preferably 1 to 30 wt%, even more preferably 2 to 25 wt% and most preferably 5 to 25 wt% of the terpolymer.

25

30

The copolymers of ethylene or styrene monomer and of a glycidyl (meth)acrylate or maleic anhydride can contain from 50 to 99 wt% of ethylene or styrene monomer and from

1 to 50 wt% of a glycidyl (meth)acrylate or maleic anhydride, preferably from 90 to 98 wt% of ethylene or styrene monomer and from 2 to 10 wt% of a glycidyl (meth)acrylate or maleic anhydride, the total sum of components being 100 wt%.

The terpolymers of ethylene or styrene monomer, of a glycidyl (meth)acrylate or maleic anhydride and of a (meth)acrylic ester monomer can contain from 50 to 98.8 wt% of ethylene or styrene monomer, from 0.2 to 10 wt% of a glycidyl (meth)acrylate or maleic anhydride and from 1 to 50 wt% of a (meth)acrylic ester monomer, the total sum of components being 100% of the terpolymer. Preferably the terpolymer can contain from 55 to 97.7 wt% of ethylene or styrene monomer, from 0.3 to 8% of a glycidyl (meth)acrylate or maleic anhydride, and from 2 to 35% of (meth)acrylic ester monomer, the total sum of components being 100% of the terpolymer.

Still more preferably, the co- or ter-polymer is selected among copolymers of ethylene and glycidyl methacrylate and terpolymers of ethylene or styrene, acrylic ester monomers and glycidyl methacrylate or maleic anhydride. Among those one can use for example the copolymer of ethylene and glycidyl methacrylate sold under the trademark Lotader®AX 8840 by Arkema France, the terpolymer of ethylene, ethylacrylate and maleic anhydride sold under the denomination Lotader®4700 by Arkema France, as well as the terpolymer of styrene monomer, acrylic esters and glycidyl methacrylate sold under the trademark Joncryn® by BASF.

In the most preferred embodiment, the co- or ter-polymer is selected from a terpolymer of ethylene or styrene monomer, acrylic esters and glycidyl methacrylate. Preferably, the acrylic ester is methylacrylate. An example of such a terpolymer is Lotader®AX8900 sold by Arkema France comprising 68 wt% of ethylene monomer, 8 wt% of glycidylmethacrylate and 24 wt% methyl acrylate.

The co- or terpolymer, is then blended either in dry form or in the melt with the polyolefin, in particular a polyethylene, and the polyester, in particular PLA, to create the composition required for layer A.

The co- or terpolymer and the polyester can be added one by one to the polyolefin and mixed after each addition or they can be added together and mixed together once.

In a preferred embodiment of layer A, the PLA pellets, polyolefin and optional co- or terpolymer are compounded together according to any known compounding method in the art, e.g. mixer, like a Banbury mixer, or an extruder, preferably a twin screw extruder. The extrusion is generally carried out at a temperature below 230°C.

The composition for layer A can be in powder or micropellet form suitable for rotational moulding.

2. Layer B

Layer B comprises

- 5 • from 50 to 99.4 wt%, preferably 60 to 99 wt% of a polyolefin, which can be different from the polyolefin of layer A,
- from 0.5 to 50 wt%, more preferably 1 to 30 wt%, most preferably 5 to 30 wt%, of a polyester (preferably PLA), which can be different from the polyester of layer A,
- 10 • from 0.1 to 20 wt%, preferably 0.1 to 15 wt%, of a co- or ter-polymer, which can be different from the co- or ter-polymer of layer A, comprising:
 - a) 50 to 99.9 wt% of an ethylene or a styrene monomer ,
 - b) 0.1 to 50 wt% of an unsaturated anhydride-, epoxide- or carboxylic acid-containing monomer,
 - 15 c) 0 to 50 wt% (meth)acrylic ester monomer.

2.1. Polyolefin of layer B

Layer B is preferably adjacent to layer A.

The polyolefin is present from 50, 60 or 70 up to 100 wt% of layer B, or up to 99.8, 99, 97.5, 97, or 95 wt% of layer B.

- 20 The polyolefin can be the same as or different from the polyolefin optionally present in layer A.

The polyolefin can be selected from polyethylene, polypropylene, polybutene or polyhexene.

- 25 Preferably, the polyolefin is polyethylene. The description of polyethylene present in layer A applies *mutatis mutandis* to the polyethylene in layer B, which can be the same as or different from any polyethylene present in layer A.

- 30 The composition for layer B can be in powder or micropellet form, suitable for rotational moulding. When optional chemical blowing agent is present and micropellets are used, the polyolefin and chemical blowing agent are preferably compounded together instead of dry blended.

2.2. The Polyester and the Co- and ter-polymer of layer B

The description of the polyester (section 1.1 above) and the co- or ter-polymer (section 1.3 above) present in layer A applies *mutatis mutandis* to layer B. The optional polyester (preferably PLA) and the optional co- or ter-polymer can be the same as or different from
5 those present in layer A. In particular embodiments, layer B comprises 5 to 30 wt% PLA.

Thus, layer B can be the same as or different from layer A.

2.3. The optionally foamed layer B – chemical blowing agents

Optionally, layer B is a foamed polyolefin layer. In order to foam polyolefin a chemical blowing agent can be included into layer B, which causes the polyolefin to foam under the
10 appropriate conditions in the presence of a blowing gas in the mould during rotational moulding. The chemical blowing step generally fulfils several requirements:

- the decomposition temperature range of the blowing agent is compatible with the processing temperature of the polyolefin;
- the liberation of the blowing gas occurs within a defined temperature range of
15 about 10 °C and is controllable during the process;
- the decomposition is not autocatalysed in order to avoid overheating;
- the blowing gas is chemically inert, such as preferably nitrogen, carbon dioxide and water;
- the chemical blowing agent is homogeneously and easily incorporated in and
20 compatible with polyethylene.

During the foaming process, at elevated temperatures, chemical blowing agents undergo chemical reactions that liberate gas, typically N₂, CO, CO₂ and NH₃ and water.

The chemical agents that can be used in the present invention can function according to three main processes:

25 Irreversible reaction: $AB \rightarrow C + \text{gas}$. They can be selected from the group consisting of azo compounds, hydrazine derivatives, semicarbazides, tetrazoles and nitroso compounds.

Equilibrium reactions: $AB \rightleftharpoons C + \text{gas}$. They can be selected from the group consisting of bicarbonates and carbonates.

30 Combination of compounds that liberate gases as a result of their chemical interactions: $A + BG \rightarrow AB + \text{gas}$.

The chemical blowing agents can be:

Exothermic, such as for example azodicarbonamide (AZ) or 4,4'-oxy-bis(benzenesulfonylhydrazide) (OB); or

Endothermic, such as for example sodium bicarbonate (SB).

5 Suitable chemical blowing agents include:

Organic chemical blowing agents:

Azo compounds such as for example azodicarbonamide decompose at a temperature range of from 160 to 215 °C and liberate about 220 ml/g of gas, mostly N₂, CO, CO₂, NH₃ and water.

10 Hydrazides such as for example or 4,4'-oxy-bis(benzenesulfonylhydrazide) (from example Genitron®OB from LANXESS). It decomposes at a temperature range of from 140 to 160 °C and liberates 120 to 140 ml/g of gas, mostly N₂ and H₂O. This type of agent is particularly preferred as it is exothermic and releases only neutral gases.

15 Other examples include modified azodicarbonamide, i.e., azodicarbonamide modified with zinc oxide, calcium carbonate or the like to lower the decomposition temperature, 5-phenyltetrazole, dinitrosopentamethylene tetramine, azobisisobutyronitrile, diazoaminobenzene, oxybis(benzenesulfonylhydrazide) and the like.

20 *Inorganic chemical blowing agents:*

Carbonates such as for example sodium bicarbonate NaHCO₃. It decomposes at a temperature range of from 150 to 230 °C and liberates 140 to 230 ml/g of gas, mostly CO₂ and H₂O.

25 Other examples include sodium borohydride, ammonium carbonate, and modified sodium bicarbonate, i.e. sodium bicarbonate modified with a proton donor such as citric acid, and the like.

The amount of blowing agent added to the polyolefin is of at least 0.2 wt% based on the total weight of layer B, preferably of at least 1 wt%. It is of at most 5 wt%, preferably of at most 3 wt%. The most preferred amount is of about 2.5 wt%. The chemical blowing agent
30 totally decomposes upon foaming.

2.4. Preparing the optionally foamed polyolefin layer B

The foamed polyolefin layer is prepared by standard techniques with one or more chemical blowing agent(s). The chemical blowing agent is incorporated into the polyolefin to form a blend. The blend may be prepared by extruding the polyolefin either with a masterbatch comprising the chemical blowing agent or directly with the blowing agent. In both cases, the extrusion temperature must be kept above the melt temperature of the polyolefin but below the decomposition temperature range of the chemical blowing agent(s). The melt is passed through a suitable die, such as used with a pelletizer, to obtain the pelletized resin.

Alternatively, and preferably, the polyolefin is dry blended with the chemical blowing agent(s) and introduced directly into the mould during the rotomoulding cycle. Dry blending is favoured over compounding the chemical blowing agent with the polyolefin, because the mixing has to be carried out below the decomposition temperature of the chemical blowing agent.

While it is not necessary, additives which function to control or modify foam cell size or foam density or modify/control the activator temperature or rate of decomposition of the chemical blowing agent may also be included in the polyolefin. Useful additives of this type include calcium carbonate, titanium dioxide, zinc oxide, talc, calcium stearate, nanocomposites and the like. When present, the amount of these additives typically ranges from about 0.01 to about 1 percent by weight, based on the weight of the foamed polyolefin layer.

The preferred density of the foamed layer is between 100 to 200 kg/m³.

The preferred thickness of the foamed layer is from 10 to 500 mm, preferably 100 to 200 mm, according to the desired use of the rotomoulded article.

3. Optional Layer C

3.1. Polyolefin

Layer C is preferably adjacent to layer B. In a particular embodiment, layer C is adjacent to layer B, which is adjacent to layer A. Layer A is preferably the outer lay in this case, layer B in the intermediate layer and layer C the inner layer. Layer C can be the same as or different from layer A.

Layer C can comprise a polyolefin. The polyolefin is preferably present from 50, 60 or 70 up to 100 wt% of layer C, or up to 99.8, 99, 97.5, 97, or 95 wt% of layer B.

The polyolefin can be the same as or different from the polyolefin present in layer B.

The polyolefin can be selected from polyethylene, polypropylene, polybutene or polyhexene.

Preferably, the polyolefin is polyethylene. The description of polyethylene optionally present in layer A applies *mutatis mutandis* to the polyethylene in layer C, which can be
5 the same as or different from any polyethylene present in layer A.

The composition for layer C can be in powder or micropellet form, suitable for rotational moulding.

3.2. Further optional components

In another embodiment, particularly when layer C is the inner, layer C may also comprise
10 other components besides the polyolefin. For example, it may comprise:

- from 50 to 99.5 wt%, preferably 60 to 99.4 wt%, of the polyolefin, which can be different from the polyolefin of layer A,
- from 0 to 50 wt%, preferably 0.5 to 50 wt%, more preferably 0.5 to 30 wt% ,
15 of a polyester (preferably PLA), which can be different from the polyester of layer A,
- from 0 to 20 wt%, preferably 0.1 to 15 wt%, of a co- or ter-polymer, which can be different from the co- or ter-polymer of layer A, comprising:
 - a. 50 to 99.9 wt% of an ethylene or a styrene monomer,
 - b. 0.1 to 50 wt% of an unsaturated anhydride-, epoxide- or
20 carboxylic acid-containing monomer,
 - c. 0 to 50 wt% (meth)acrylic ester monomer.

The description of the polyester (section 1.1 above) and the co- or ter-polymer (section 1.3 above) present in layer A applies *mutatis mutandis* to layer C. The optional polyester (preferably PLA) and the optional co- or ter-polymer can be the same as or different from
25 those present in layer A. Layer C can be the same as or different from layer B.

4. The rotomoulding process

The rotomoulded article according to the invention comprises at least one layer, namely layer A. The article can be a mono-layered article only having layer A, or it can be a bi-layered or tri-layered rotomoulded article.

According to the invention, the article may further comprise a layer B, preferably adjacent
30 to layer A. In addition, a third layer, layer C, is present, preferably adjacent to layer B.

The rotational moulding is a process well-known to the person skilled in the art. The various processes of rotational moulding usually comprise the following stages:

- a) loading of the mould,
- b) rotation of the mould,
- 5 c) heating of the mould,
- d) cooling and
- e) release from the mould.

The mould can be made of any material known in the art for such a purpose. For example, the mould can be an aluminum mould or a Teflon mould. Teflon moulds are preferred to
10 avoid any sticking to the mould due to the decreased shrinkage and warpage according to the article of the invention.

The rotation of the mould is generally carried out around two perpendicular axes.

The quantity of powder and/or of micropellets introduced into the mould depends on the size of the article and on the desired wall thickness.

15 The heating step (c) of the mould occurs simultaneously with the rotation of the mould in step (b).

In one embodiment, the heating step can be carried out in an oven or by electric heating elements. In another preferred embodiment heating can be carried out with a mould heated by an oil-filled heating jacket, as in for example, the Leonardo® rotomoulding
20 machine from Persico®. The heating temperature of the oven, electric heating elements or oil can vary from 150 to 350°C. One generally uses a temperature of at least of 10°C higher, preferentially at least of 20°C higher, more preferentially at least of 30°C higher compared to the melting point of the layer that one wishes to mould. A heating temperature ranging from 180 and 270°C is preferably used. In another embodiment,
25 heating can also be carried out by microwaves.

The duration of the moulding varies according to dimensions and the thickness of rotomoulded article, it can be range from 5 to 600 minutes.

The duration and the time of cooling step depends on the installation, on the dimensions of the article to be moulded and of the type of article which one wishes to obtain. As
30 mentioned previously, it is possible to cool the mould and/or the article contained in the mould. To cool the mould from the outside, one can use air at room temperature, water between 5 and 25°C or oil between 5 and 80°C. To cool the article from the inside of the

mould, one can inject air and/or inert gas such as nitrogen and/or spray water (like a mist) within the interior of the mould, for example at a temperature of 25°C. The time of cooling generally varies between 5 and 500 minutes depending on the thickness of the rotomoulded article and the process used for cooling. When the article has a thickness of
5 more than 10 mm, the mould should preferably be cooled from both the inside of the mould and the outside, preferably using air or inert gas such as nitrogen or a spray of water (mist).

According to a mode of realization, the cooling of the mould and/or article obtained are done in just one step until a temperature ranging between room temperature and a
10 temperature lower than 100°C is obtained. According to this mode of realization, cooling in this way results in a crystalline rotomoulded object.

Thereafter, the article is released from the mould. Release of the article from the mould is generally carried out when the article has sufficient rigidity. The release from the mould is generally done at a temperature lower than 100°C.

15 According to another mode of realization, the cooling of the mould and/or article obtained are done in just one step until a temperature ranging between room temperature and a temperature lower than 100°C is obtained.

According to another mode of realization, the cooling of the mould and/or article comprises the following steps:

- 20
- i. cooling until a temperature ranging between 100°C and 150°C, preferably between 100°C and 130°C, is reached,
 - ii. maintaining this temperature for 1 to 60 minutes,
 - iii. cooling again until a temperature ranging between the room temperature and a temperature lower than 100°C is reached.

25 According to this mode of realization, cooling in this way results in a crystalline rotomoulded object which is characterized by a melting point. The object obtained by this process thus presents properties of improved thermal resistance compared to a process wherein cooling is carried out fast and is done in only one stage.

30 Thereafter, the article is released from the mould. Release of the article from the mould is generally carried out when the article has sufficient rigidity.

If the moulded object obtained is amorphous, the release from the mould is done at a temperature ranging between the room temperature and 60°C, preferentially in lower part of 60°C, more preferentially with 55°C.

If the moulded object obtained is crystalline, the release from the mould is generally done at a temperature lower than 100°C.

The rotational moulding can be carried out under inert gas in the absence of oxygen. In order to do so, one can for example add into the mould a compound which liberates
5 carbon dioxide, such as dry ice. This can be for example together with the powder or pellets of the different components. Dry ice generates carbon dioxide during the heating and rotating steps of the moulding process. One can also purge the mould with an inert gas, such as nitrogen, by injecting nitrogen after closing the mould.

The walls of the articles can comprise one or more successive layers, at least having layer
10 A as claimed. It is thus possible to manufacture articles with walls comprising for examples two or three layers e.g. optionally having a layer B and layer C. In one embodiment, layer B can be foamed.

In a particular embodiment, layer A is the outer layer, layer B is the intermediate layer and layer C is the inner layer. In this particular embodiment, layer C may further comprise a
15 polyester and optionally a co- or terpolymer according to the same definitions as in layer A. Layer C can be same as or different from layer A.

In another embodiment, layer A is the intermediate layer adjacent to layers B and C, wherein layers B and C are either the outer or inner layers respectively. Layers B and C can be same or different in this embodiment.

20 There are several known methods to manufacture multilayered rotomoulded articles: by manual introduction of material during the rotomoulding cycle, or by the use of a drop-box, or by a one-shot system wherein each layer has a different melting temperature and are introduced into the mould together.

Manual addition involves moving the mould from the oven, removing a vent tube or plug
25 that creates an opening in the part and adding more material using a funnel or wand. This operation must be repeated for each additional layer.

A drop-box typically contains the material for a particular layer and it is an insulated container that holds material until it is released at the appropriate time during the cycle. The signal for release of material is usually transmitted as a pressure pulse via the airline
30 through the arm of the machine. The insulation is kept cool to prevent the material inside the box from melting.

In either of these two methods, there are two factors to consider, which are in fact known to the skilled person in multilayered rotomoulding applications:

- i. the temperature at which the subsequent layer is added for determining the wall thickness of the previous skin formed and how well the two layers may be bound together;
- ii. the time elapsed before addition of the subsequent layer of material to avoid sag.

5 It is possible to control these by lowering the melt index of the first layer and/or by reducing the injection temperature of the next layer, and/or by cooling the mould slightly before injection of the next layer.

The cycle time necessary to produce multilayer rotomoulded articles depends upon the number of layers and upon the mass injected for each layer.

10 The present invention also discloses a method for rotomoulding the articles according to the invention for one or more layers comprising the steps of (in no particular order) according to the process known to the skilled person:

a) feeding the composition for layer A) into a mould;

b) placing the filled mould in pre-heated oven;

15 c) rotating the filled mould about two perpendicular axes;

d) optionally feeding the composition for layer B, optionally with a chemical blowing agent and blowing gas to prepare a foamed layer B, followed by repeating steps (b) and (c);

20 e) optionally feeding the composition for layer C), followed by repeating steps (b) and (c);

f) optionally feeding desired additional layers, each addition followed by repeating steps (b) and (c),

g) cooling and retrieving the rotomoulded article.

Preferably, the process is carried out in the order described.

25 Alternatively, the optional chemical blowing agent for creating a foamed layer B can be introduced during the rotomoulding cycle by a Teflon tube.

The first key point in the process is the time at which the temperature inside the mould reaches the melting temperature of the composition for layer A. Composition for layer B (if adjacent to layer A) comprising polyolefin (and optionally a chemical blowing agent) is

30 injected as soon as or just before that first melting temperature is reached. The

composition for layer B is preferably injected at an internal air temperature situated between 125 and 160°C.

The second key point in the process is the time at which the temperature inside the mould reaches the melting temperature of composition for layer B. Composition for layer C is injected as soon as or just before that second melting temperature is reached. The composition for layer C is injected at an internal air temperature situated between 125 and 160°C. The internal air temperature must be compatible with the temperature and is preferably of at most 170°C during the whole cycle time.

The articles obtained by rotational moulding are generally hollow parts without any welding lines, such as for tanks, drums, containers, vats, jerrycans, cans, cisterns, boxes, bumpers, furniture (bath tubs), car parts such as car doors, car bodies and car seats, nautical and aquatic equipment, buoys, floats, boards, planks and joints. The rotomoulded article is preferably selected from the group comprising car parts. Among the car parts, one can for example quote the car body and car door and interior components such as the instrument panel and door handles.

These articles can have one or more openings and/or inserts of plastic or metal and/or "kiss offs" which are reinforcing junctions or bridges between two surfaces within the article.

Articles obtained by the rotational moulding process according to the invention do not have a point of weakness. They show homogeneous characteristics, such as for example a uniform thickness of the walls as well as a good surface aspects both internally and internally and externally, without any deformation, bubble or other defects. In addition, the compositions for use in the present process do not present any sagging behavior during the rotomoulding process.

In particular, the articles obtained have a very little shrinkage and warpage. In addition, the presence of the co- or terpolymer (compatibilising agent) increases the impact strength of the article.

In another embodiment, when layer A is the outer layer the outer surface of the article can be painted. This is done very easily because of the high surface tension.

30 **5. Filling with polyurethane**

The articles obtained by rotational moulding are generally hollow parts without any welding lines. Being hollow the rotomoulded articles according the present invention typically comprise one or more cavities. In an embodiment, enhanced insulation properties

or structural properties can be obtained by filling these cavities with a polyurethane (PU), such as a polyurethane foam.

The inventors surprisingly found that for the rotomoulded articles according to the present invention the adherence between the article inner wall and a PU foam is excellent.

- 5 Accordingly, in particular embodiments, the present rotomoulded articles comprise at least one cavity which comprises, preferably which is filled with, a polyurethane, such as a polyurethane foam.

PU foams can greatly enhance the structural and insulating properties of the rotomoulded article, without adding much weight to the article.

- 10 The PU foam may be a rigid, semi-rigid, or soft PU foam. Rigid PU foams are preferred to enhance the structural properties of the rotomoulded article. The softness and elastic properties of the polyurethane foams depend on the choice of the polyol and isocyanate monomers, as the polyol monomers typically provide soft domains, and the isocyanate monomers form harder domains.

- 15 The type of PU polymer comprised by the PU foam is not critical to the present invention. The PU polymer may be made by introduction into the rotomoulded article of a PU forming composition as described below.

The filling with PU foam can be obtained by introducing a PU forming composition into one or more cavities of the rotomoulded article.

- 20 In general, such a PU forming composition comprises :

at least one isocyanate compound, hereinafter also referred to as "isocyanate monomer"; and

at least one polyol, hereinafter also referred to as "polyol monomer".

- 25 Suitable isocyanate monomers include polyisocyanates, such as diisocyanates and/or triisocyanates. The polyisocyanates may be aliphatic, araliphatic and/or aromatic polyisocyanates, typically of the type $R^2-(NCO)_x$ with x being at least 2 and R^2 being an aromatic, aliphatic or combined aromatic/aliphatic group. Examples of R^2 are diphenylmethane, toluene, dicyclohexylmethane, hexamethylene, or groups providing a similar polyisocyanate.

- 30 Non-limiting examples of suitable polyisocyanates are diphenylmethane diisocyanate (MDI) – type isocyanates in the form of its 2,4'-, 2,2'- and 4,4'-isomers and mixtures thereof (also referred to as pure MDI), the mixtures of diphenylmethane diisocyanates

(MDI) and oligomers thereof (known in the art as "crude" or polymeric MDI), and reaction products of polyisocyanates (e.g. polyisocyanates as set out above), with components containing isocyanate-reactive hydrogen atoms forming polymeric polyisocyanates or so-called prepolymers. Other examples are tolylene diisocyanate (also known as toluene diisocyanate, and referred to as TDI), such as 2,4 TDI and 2,6 TDI in any suitable isomer mixture, hexamethylene diisocyanate (HMDI or HDI), isophorone diisocyanate (IPDI), butylene diisocyanate, trimethylhexamethylene diisocyanate, di(isocyanatocyclohexyl)methane, e.g. 4,4'-diisocyanatodicyclohexylmethane (H12MDI), isocyanatomethyl-1,8-octane diisocyanate and tetramethylxylene diisocyanate (TMXDI), 1,5-naphthalenediisocyanate (NDI), p-phenylenediisocyanate (PPDI), 1,4-cyclohexanediisocyanate (CDI), tolidine diisocyanate (TODI), any suitable mixture of these polyisocyanates, and any suitable mixture of one or more of these polyisocyanates with MDI-type polyisocyanates.

The polyurethane is generally prepared by reacting an isocyanate monomer with one or more polyol monomers. Suitable polyol monomers include a hydroxyl terminated polyester (polyester polyols), a hydroxyl terminated polyether (polyether polyols), a hydroxyl terminated polycarbonate, or a mixture thereof. In particular embodiments, the polyol monomers comprise one or more monomers selected from the group consisting of a polyether diol, a polyether triol, a polyester diol, and a polyester triol.

The polyester polyols may be generally a linear polyester, and may have an average molecular weight (M_n) of from about 500 to 10000. The molecular weight may be determined by assay of the terminal functional groups and is related to the number average molecular weight. The polymers can be produced by (1) an esterification reaction of one or more glycols with one or more dicarboxylic acids or anhydrides or (2) by transesterification reaction, i.e. the reaction of one or more glycols with esters of dicarboxylic acids. Mole ratios generally in excess of more than one mole of glycol to acid are preferred so as to obtain linear chains having a preponderance of terminal hydroxyl groups. Suitable polyester intermediates also include various lactones such as polycaprolactone typically made from caprolactone and a bifunctional initiator such as diethylene glycol. The dicarboxylic acids of the desired polyester can be aliphatic, cycloaliphatic, aromatic, or combinations thereof. Suitable dicarboxylic acids which can be used alone or in mixtures generally have a total of from 4 to 15 carbon atoms and include: succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, dodecanedioic, isophthalic, terephthalic, cyclohexane dicarboxylic, and the like. Anhydrides of the above dicarboxylic acids such as phthalic anhydride, tetrahydrophthalic anhydride, or the like, can also be

used. The glycols which are reacted to form a desirable polyester intermediate can be aliphatic, aromatic, or combinations thereof, and have a total of from 2 to 12 carbon atoms, and include ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol, 1,4-cyclohexanedimethanol, decamethylene glycol, dodecamethylene glycol, and the like.

Polyether polyols may be derived from a diol or polyol having a total of from 2 to 15 carbon atoms, preferably an alkyl diol or glycol which is reacted with an ether comprising an alkylene oxide having from 2 to 6 carbon atoms, typically ethylene oxide or propylene oxide or mixtures thereof. For example, hydroxyl functional polyether can be produced by first reacting propylene glycol with propylene oxide followed by subsequent reaction with ethylene oxide. Primary hydroxyl groups resulting from ethylene oxide are more reactive than secondary hydroxyl groups and thus are preferred. Useful commercial polyether polyols include poly(ethylene glycol) comprising ethylene oxide reacted with ethylene glycol, poly(propylene glycol) comprising propylene oxide reacted with propylene glycol, poly(tetramethyl glycol) (PTMG) comprising water reacted with tetrahydrofuran (THF). Polyether polyols further include polyamide adducts of an alkylene oxide and can include, for example, ethylenediamine adduct comprising the reaction product of ethylenediamine and propylene oxide, diethylenetriamine adduct comprising the reaction product of diethylenetriamine with propylene oxide, and similar polyamide type polyether polyols. Copolyethers can also be utilized in the current invention. Typical copolyethers include the reaction product of glycerol and ethylene oxide or glycerol and propylene oxide.

Hydroxyl terminated polycarbonate intermediates can be prepared by reacting a glycol with a carbonate. US 4131731 is hereby incorporated by reference for its disclosure of hydroxyl terminated polycarbonates and their preparation. Such polycarbonates are linear and have terminal hydroxyl groups with essential exclusion of other terminal groups. The essential reactants are glycols and carbonates. Suitable glycols are selected from cycloaliphatic and aliphatic diols containing 4 to 40, and preferably 4 to 12 carbon atoms, and from polyoxyalkylene glycols containing 2 to 20 alkoxy groups per molecule with each alkoxy group containing 2 to 4 carbon atoms. Diols suitable for use in the present invention include aliphatic diols containing 4 to 12 carbon atoms such as butanediol-1,4, pentanediol-1,4, neopentyl glycol, hexanediol-1,6, 2,2,4-trimethylhexanediol-1,6, decanediol-1,10, hydrogenated dilinoleylglycol, hydrogenated diolelylglycol; and cycloaliphatic diols such as cyclohexanediol-1,3, dimethylolcyclohexane-1,4, cyclohexanediol-1,4, dimethylolcyclohexane-1,3, 1,4-endomethylene-2-hydroxy-5-hydroxymethyl cyclohexane, and polyalkylene glycols. The diols used in the reaction may

be a single diol or a mixture of diols depending on the properties desired in the finished product.

Non-limiting examples of suitable carbonates for use herein include ethylene carbonate, trimethylene carbonate, tetramethylene carbonate, 1,2-propylene carbonate, 1,2-butylene carbonate, 2,3-butylene carbonate, 1,2-ethylene carbonate, 1,3-pentylene carbonate, 1,4-pentylene carbonate, 2,3-pentylene carbonate and 2,4-pentylene carbonate.

Also suitable herein are dialkylcarbonates, cycloaliphatic carbonates, and diarylcarbonates. The dialkylcarbonates can contain 2 to 5 carbon atoms in each alkyl group and specific examples thereof are diethylcarbonate and dipropylcarbonate. Cycloaliphatic carbonates, especially dicycloaliphatic carbonates, can contain 4 to 7 carbon atoms in each cyclic structure, and there can be one or two of such structures. When one group is cycloaliphatic, the other can be either alkyl or aryl. On the other hand, if one group is aryl, the other can be alkyl or cycloaliphatic. Preferred examples of diarylcarbonates, which can contain 6 to 20 carbon atoms in each aryl group, are diphenylcarbonate, ditolylcarbonate and dinaphthylcarbonate.

The reaction is carried out by reacting a glycol with a carbonate, preferably an alkylene carbonate in the molar range of 10:1 to 1:10, but preferably 3:1 to 1:3 at a temperature of 100°C to 300°C and at a pressure in the range of 0.1 to 300 mm Hg in the presence or absence of an ester interchange catalyst, while removing low boiling glycols by distillation.

In particular embodiments, the PU forming composition can comprise one or more polyether diols or triols. The choice of polyol monomer may depend on the required specifications of the rotomoulded, PU filled article. For example, polyethers typically provide a better microbial and fungal resistance, are easier to process (due to the lower viscosity), and have a lower cost, compared to polyesters. On the other hand, polyesters may provide a better wear resistance; load bearing properties; heat aging properties; reactivity; and oxygen, ozone and UV stability. Polyesters may further swell less in oils, grease and solvents.

The PU forming composition may further comprise one or more chain extenders, all of which are well known to those skilled in the art. Non-limiting examples of suitable chain extenders are lower aliphatic or short chain glycols having from about 2 to about 10 carbon atoms and include, for instance, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,3-butanediol, 1,5-pentanediol, 1,4-cyclohexanedimethanol, hydroquinone di(hydroxyethyl)ether, neopentylglycol, and the like.

In particular embodiments, the PU formulation can comprise one or more catalysts, for example selected from the group consisting of a tertiary amine, such as bis-(2-dimethylaminoethyl)ether, N-ethylmorpholine, triethylenediamine, dimethylcyclohexylamine, or dimethylethanolamine; and an organotin compound, such as

5 dibutyltin dilaurate, dioctyltin mercaptide, or dibutyltin oxide.

In certain embodiments, the PU forming composition may comprises one or more mineral fillers such as certain oxides, carbonates, silicates, borates, stannates, mixed oxide hydroxides, oxide hydroxide carbonates, hydroxide silicates, or hydroxide borates, or a mixture of these substances. By way of example, use may be made of calcium oxide,

10 aluminum oxide, manganese oxide, tin oxide, boehmite, dihydrotalcite, hydrocalumite, or calcium carbonate.

In certain embodiments, the PU forming composition may comprise one or more foam stabilizers. Foam stabilizers are substances which promote the formation of a regular cell structure during foaming. Non-limiting examples of foam stabilizers are silicone-

15 comprising foam stabilizers such as siloxane-oxalkylene copolymers or other organopolysiloxanes, alkoxylation products of fatty alcohols, oxo alcohols, fatty amines, alkylphenols, dialkylphenols, alkylcresols, alkylresorcinol, naphthol, alkyl-naphthol, naphthylamine, aniline, alkylaniline, toluidine, bisphenol A, alkylated bisphenol A, and polyvinyl alcohol.

20 The PU forming composition can further comprise one or more solvents, as known by the person skilled in the art.

The polyurethane is generally made from the abovementioned polyol monomer, preferably polyether, which is further reacted with an isocyanate monomer, preferably a diisocyanate, along with one or more additives selected from a chain extender, a catalyst, a foam

25 stabilizer, a filler, a dye, a pigment, a flame retarder, an antioxidant, a fungicide, and a biocide.

Foams can be made by using chemical or inert blowing agents while conducting above reactions, or by using a gas in order to create a froth during these reactions. A particularly suitable chemical blowing agent is water. Water can react with isocyanate functional

30 groups, thereby releasing carbon dioxide, which can act as blowing gas. Accordingly, in particular embodiments, the PU forming composition comprises water.

The amount of blowing agent present in the PU forming mixture influences the density of the PU foam formed by the PU forming composition.

6. Coating of the rotomoulded article

The inventors have found that the rotomoulded articles of the invention are easy to coat or paint. Surprisingly, the inventors further found that the rotomoulded articles can be coated as soon as the articles are demoulded, without any surface treatment.

- 5 The rotomoulded articles described herein may be coated for various purposes, for example for aesthetic reasons, for providing fire-retardant properties, for providing hydrophilic or hydrophobic properties, for protecting the surface against UV-light, scratching, heat, etc.

10 In particular embodiments, the rotomoulded article described herein is painted. Suitable paints which provide good results include polyurethane-based paints, epoxy based paints, and nitrocellulose-based paints, acrylic paints, and alkyd paints. In preferred embodiments, the paint is selected from the group consisting of polyurethane-based paints, epoxy based paints, and nitrocellulose-based paints. The adherence of the paint was tested via a cross-cut test according to NF EN ISO 2409.

- 15 In particular embodiments, the article is painted or coated with a flame-retardant substance, for example a flame-retardant paint or varnish. In particular embodiments, the articles may comprise a flame-retardant coating, wherein said coating preferably comprises one or more intumescent substances, i.e. substances that swell as a result of heat exposure, thus increasing in volume and decreasing in density, thereby providing a
20 passive fire protection. Examples of intumescent substances include sodium silicates and materials which comprise a significant amount of hydrates.

In certain embodiments, the rotomoulded article is coated with a topcoat. Non-limiting examples of topcoat materials include a polyester resin, an amino resin, or isophthalic pre-accelerated unsaturated polyester such as Polycor iso PA F from CCP composite, or
25 combinations thereof. Such articles may be car parts, boat parts, or the like.

The coatings described herein may be applied by any suitable coating technique, including but not limited to spray coating, and dip coating.

EXAMPLES

30 The following examples illustrate the invention, but by no means intend to limit the scope of the invention.

Analytical methods

1. Determination of the optical purity of the PLA

In the examples which follow, the determination of the optical or isomeric purity of the PLA is done by the enzymatic method. The principle of the method is the following: The ions Lactate and D-Lactate are oxidized in pyruvate respectively by the enzymes L-lactate dehydrogenase and D-lactate dehydrogenase using the nicotinamide adenine dinucleotide (NAD) as the coenzyme. To force the reaction in the direction of pyruvate formation, it is necessary to trap this compound by reaction with hydrazine. The optical density increase to 340 Nm is proportional to the quantity of L-lactate or D-lactate present in the sample.

The samples of PLA were prepared by mixing 25 ml of sodium hydroxide (1mol/L) with 0.6 g of PLA. The solution was refluxed for 8 hours and then cooled. The solution was then neutralized to pH 7 using a hydrochloric acid solution (1mol/L), then sufficient deionized water was added to obtain 200 ml of solution.

The samples were then analyzed on a Vital Scientific Selectra Junior analyzer used for the determination of L isomer of the poly-L-lactide, the box entitled "L-lactic acid 5260" marketed by the company Scil was used and for the determination in D isomer of the poly-D-lactide, the box entitled "L-lactic acid 5240" marketed by the company Scil was used. During the analysis, a reactive blank and a calibration solution called "Scil 5460" were used.

2. Determination of the molecular weight of the PLA

In the examples which follow, the measurement of the molecular weight is carried out at 30°C by using a liquid chromatograph WATERS 610. A solution of the polymer in chloroform at a concentration of 1mg/mL was prepared. 100 µl of this solution is injected, through a filter having pores of 0.2 µm in diameter, in the column of the chromatograph at 30°C. The molecular weight is given on the basis of the retention time in the column. One sample is carried out as the reference using standard polystyrene samples and a universal calibration curve.

3. Determination of the shrinkage/warpage of the moulded object

The measurement of the rotomoulded article compared to the mould itself is done by three-dimensional analysis according to the method described in international patent application published WO 2008/151988.

The average withdrawal measured on the moulded object is expressed in % compared to the internal volume of the mould.

4. Determination of the aspect of the walls of the moulded object

The aspects of the interior and exterior walls, uniformity, presence of bubbles, ripples etc were visually evaluated.

5. Determination of the regularity thickness of the walls of the moulded object

- 5 The regularity thickness of the walls is determined by tomography, technique well-known by the man of Art.

Example 1Resins used in the example

The resins identified hereafter were used:

10 PLA

- Resin 1** As the polyester a PLA was used, namely a poly-L-lactide (PLA HIGH PURITY from Futerro®) in the form of powder obtained after grinding pellets of PLLA having an optical purity of at least 99% w/w, a water content of maximum 250 ppm, free lactide content of maximum 0.1 % w/w and a number average molecular weight Mn of approximately 100,000 (using a polystyrene reference). The average particle size of the particles of the powder after grinding is of 300 µm.

Physical Properties of the PLA HIGH PURITY from Futerro®:

- Specific Gravity at 25°C of 1.24 measured according to ISO 1183.
- Melt density at 230°C of 1.08-1.12.
- 20 • Melt index measured at 190°C under a load of 2.16 kg of 10-30 g/10min measured according to ISO 1133.
- Melt index measured at 210°C under a load of 2.16 kg of 30-60 g/10min measured according to ISO 1133.
- Haze at 2mm thickness of less than 5%, measured according to ISO 14782.
- 25 • Transmittance at 2mm thickness of greater than 90%, measured according to ISO 14782/
- Glass transition temperature of 52-60°C measured according to ISO 11357.
- Crystalline melt temperature of 145-175°C also measured according to ISO 11357.
- The tensile modulus is around 4000 MPa measured according to ISO527.

Terpolymer

Resin 2: Lotader 8890®(sold by Arkema®) was used as the terpolymer. LOTADER® AX8890 is a random terpolymer of ethylene, acrylic ester and glycidyl methacrylate, polymerized under high-pressure in an autoclave process.

5 Physical properties of Lotader 8890® as sold:

- Melt index measured at 190°C under a load of 2.16 kg of 6 g/10min measured according to ISO 1133
- Methyl acrylate content of 24 wt% as measured by FTIR
- Glycidyl methacrylate content of 8 wt% as measured by FTIR
- 10 • Ethylene monomer of 68 wt% as measured by FTIR
- Density (at 23°C) of 0.94 g/cm³ measured according to ISO 1183
- Melting point at 65 °C measured according to ISO 11357-3
- Young's modulus of 8 MPa measured according to ASTM D 638 Type IV

15 The following are given as physical properties measured on compression moulded samples:

- Vicat softening point (1 kg) of 87 °C measured according to ISO 306
- Flexural modulus of less than 30 MPa measured according to ISO 178
- Elongation at break of 1100 % measured according to ASTM 638 Type IV
- Tensile strength at break of 4 MPa measured according to ASTM D 638 type IV
- 20 • Hardness Shore D (at 1s) of 18 measured according to ASTM D 2240
- Hardness Shore A (at 1s) of 64 measured according to ASTM D 2240

Resin 3: Lotader 8840®(sold by Arkema®) was used as the copolymer compatibilising agent. LOTADER® AX8840 is a random copolymer of ethylene and glycidyl methacrylate, polymerized under high-pressure in an autoclave process.

25 Physical properties of Lotader® as sold:

- Melt index measured at 190°C under a load of 2.16 kg of 5 g/10min measured according to ISO 1133
- Glycidyl methacrylate content of 8 wt% as measured by FTIR
- Ethylene monomer of 92 wt% as measured by FTIR

- Density (at 23°C) of 0.94 g/cm³ measured according to ISO 1183
- Melting point at 106 °C measured according to ISO 11357-3

The following are given as physical properties measured on compression moulded samples:

- 5 • Vicat softening point (at 10N) of 87 °C measured according to ISO 306
- Tensile modulus of 104 MPa measured according to ISO 527-2
- Flexural modulus of 85 MPa measured according to ISO 178
- Elongation at break of 400 % measured according to ISO 527-2
- Tensile strength at break of 8 MPa measured according to ISO 527-2
- 10 • Hardness Shore D (at 1s) (1) 50 - measured according to ISO 868

Polyolefin

As the polyolefin for layer B, the following polyethylenes were used.

Resin 4: M3581UV® from Total Petrochemicals

The white polyethylene powders were obtained after grinding the polyethylene pellets.

- 15 The polyethylene having a density of 0.935 g/cm³ (ISO 1183) and melt index MI2 of 6 g/10 min (ISO 1133 condition D under a load of 2.16 kg at 190°C). The average particle size of the powder after grinding is of 300 µm. The polyethylene was prepared with ethylene bis(tetrahydroindenyl) zirconium dichloride catalyst. The tensile modulus is around 800 MPa measured according to ISO527.

20 Composition 1a for Layer A

- **Resin 1:** PLA HIGH PURITY from Futerro® 77.5 % wt
- Red master batch (red pigment) : 4% wt
- CaCO₃ : 10% wt
- MB Transmar® : 0.4 % wt
- 25 – Irganox 1076 ®(from Ciba) : 0.1 %wt
- **Resin 2:** Lotader AX 8900® (from Arkema) : 8% wt

Composition 1b for Layer A

- **Resin 1:** PLA HIGH PURITY from Futerro® 85.9 % wt
- Red master batch (red pigment) : 4% wt

- CaCO₃ : 10% wt
- MB Transmar® : 0.4 % wt
- Irganox 1076 ®(from Ciba) : 0.1 %wt

Composition 2 for preparing Layer B

- 5 Composition was obtained by compounding and forming to micropellets of 300 µm in average particle size the following:
- **Resin 4:** 86 wt%
 - **Resin 1:** PLA high Purity Futerro® = 10 wt%
 - Green Master batch color (pigment Gympap® GM11725) = 2 wt%
- 10 - **Resin 3:** Lotader 8840® (Arkema®) = 2 wt%

Machine and Mould Configuration

A carousel oven machine was used, wherein the process with following conditions were present:

- Oven set temp for all trials 270°C
- 15
- Aluminium moulds
 - External air cooling only. Air was used at room temperature (between 20 to 25°C)
 - A dropbox used for all additional layers to form the multilayered articles

Manufacture of 2-layered bottles by rotational moulding

These were manufactured according to TP-SEAL® technology.

- 20 The two layers consist of an outer "skin" layer (layer A according to the invention) prepared with **Composition 1a or 1b**, and an inner foamed polyethylene layer (layer B according to the invention) prepared with **Composition 2**.

A bottle was manufactured by rotational moulding. The parameters of the cycle are the following:

- 25
- Heating of the oven to a temperature of 270°C
 - PIAT 1 (peak internal air temperature): 140°C
 - PIAT 2: 180°C (except for bottle 4 at 165°C)
 - rotational ratio: 4/1

- Cooling of the mould from the outside from 180°C at a rate of 3°C / minute using air at room temperature

- Removed from the oven at 160°C

Bottles of different compositions were rotomoulded, namely:

5 Bottle 1: according to the invention

- Outer Layer A: 350g of **Composition 1a** (used straight out of the bag without drying)
- Inner foamed layer B: 600g of **Composition 2** dry blended with 3wt% of Genitron OB® chemical blowing agent (18g) in a top blender for 5 minutes (dropped into
10 the mould during the cycle at 180°C)

Bottle 2: according to the invention

- Outer Layer A: 350g of **Composition 1a** (dried first at 50°C for 19h in a fan-assisted oven)
- Inner foamed layer B: 600g of **Composition 2** dry blended with 3wt% of Genitron
15 OB® chemical blowing agent (18g) in a top blender for 5 minutes (dropped into the mould during the cycle at 180°C)

Bottle 3: according to the invention

- Outer Layer A: 350g of **Composition 1b** (dried first at 50°C for 19h in a fan-assisted oven)
- Inner foamed layer B: 600g of **Composition 2** dry blended with 3wt% of Genitron
20 OB® chemical blowing agent (18g) in a top blender for 5 minutes (dropped into the mould during the cycle at 180°C)

Bottle 4: according to the invention

- Outer Layer A: 350g of **Composition 1b** (dried first at 50°C for 19h in a fan-assisted oven, then removed from the oven 6h before moulding)
- Inner foamed layer B: 600g of **Composition 2** dry blended with 2wt% of Genitron
25 OB® chemical blowing agent (12g) in a top blender for 5 minutes (dropped into mould during cycle at 165°C)

Bottle 5: according to the invention

- Outer Layer A: 350g of **Composition 1a** (used straight out of the bag without
30 drying)

- Inner foamed layer B: 600g of **Composition 2** dry blended with 2wt% of Genitron OB® chemical blowing agent (12g) in a top blender for 5 minutes (dropped into mould during cycle at 180°C)

The internal and external surface aspects of the walls were examined. The surface of the bottles according to the invention were shinier and smoother than the bottle of the prior art. All bottles showed good adherence of the foamed layer to the outer layer of PLA. Furthermore, the outer layer of PLA was easily paintable.

Example 2

Manufacture of 2-layered car part by rotational moulding:

10 Layer A: Polyester: outer layer was made of resin 6.

Resin 6: NatureWorks® PLA polymer 6201D

As the polyester a PLA was used, namely a poly-L-lactide (NatureWorks® PLA polymer 6201D) in the form of powder obtained after grinding pellets of PLLA.

Physical Properties of the PLA :

- 15 • Specific Gravity at 25°C of 1.24 measured according to D792.
- Melt density at 230°C of 1.08.
- Melt index measured at 210°C under a load of 2.16 kg of 15-30 g/10min measured according to D1238.
- Glass transition temperature of 55-60°C measured according to D3417.
- 20 • Crystalline melt temperature of 160-170°C also measured according to D3418.

Layer B: inside layer composition 2 as described in example 1:

Composition 2 was obtained as described in example 1 by compounding and forming to micropellets of 300 µm in average particle size the following:

- **Resin 4 of example 1:** 86 wt%
- 25 – **Resin 1 of example 1:** PLA high Purity Futerro® = 10 wt%
- Green Master batch color (pigment Gymap® GM11725) = 2 wt%
- **Resin 3 of example 1:** Lotader 8840® (Arkema®) = 2 wt%

Machine and Mould Configuration

A carousel oven machine was used. The following steps and conditions were used:

- Adding resin 6 in the mould
- Heating of the oven to a temperature of 270°C
- Heating the PLA up to 180°C (PIAT 1) :
- Dropping composition 2 into the mould
- 5 - Heating composition 2 up to 200°C
- Cooling of the mould to 120°C ($\pm 10^\circ\text{C}$)
- Maintaining 20 min at 120°C (crystallization « plateau »)
- Cooling to 100-100°C, and
- Demoulding the part at 100-110°C.

10 Figure 1 shows the temperature cycle of the rotomoulding process.

The internal and external surface aspects of the walls were examined.

The warpage of the articles with respect to the mould were analyzed (see WO 2008/151988). The rotomoulded car part and the mould have been scanned. No warpage was observed. High stiffness of the part was observed. There was a very good bond
15 between the two layers and the part was easy to demould. The PLA layer was crystallized.
The article was easily painted on the outside, and the paint showed good adherence.

CLAIMS

1. A rotomoulded article comprising at least two layers A and B, wherein layer A comprises:

- from 50 to 100 wt% of an aliphatic polyester selected from polyhydroxyalkanoate, poly(lactic acid), polycaprolactone, copolyesters and polyesteramides,
- from 0 to 50 wt% of a polyolefin,
- from 0 to 20 wt% of a co- or ter-polymer comprising
 - a) 50 to 99.9 wt% of ethylene or styrene monomer,
 - b) 0.1 to 50 wt% of an unsaturated anhydride-, epoxide- or carboxylic acid-containing monomer,
 - c) 0 to 50 wt% of a (meth)acrylic ester monomer,

and the layer B comprises:

- from 50 to 99.4 wt% a polyolefin, which can be different from the polyolefin of layer A,
- from 0.5 to 50 wt% of a polyester, which can be different from the polyester of layer A,
- from 0.1 to 20 wt% of a co- or ter-polymer, which can be different from the co- or ter-polymer of layer A, comprising:
 - a) 50 to 99.9 wt% of an ethylene or a styrene monomer,
 - b) 0.1 to 50 wt% of an unsaturated anhydride-, epoxide- or carboxylic acid-containing monomer,
 - c) 0 to 50 wt% (meth)acrylic ester monomer.

2. The article according to claim 1 wherein said layer A comprises 75 to 100 wt% of the aliphatic polyester.

3. The article according to claim 1 or 2 wherein the polyester in layer A and/or layer B is a poly(lactic acid).

4. The article according to any one of claims 1 to 3 wherein layer B is adjacent to layer A.

5. The article according to any one of claims 1 to 4 wherein the polyolefin in said layer B is a polyethylene.

6. The article according to any one of claims 1 to 5 wherein said layer B is foamed.
7. The article according to any one of claims 1 to 6 wherein the polyolefin in layer A is a polyethylene.
8. The article according to any one of claims 1 to 7 wherein the unsaturated anhydride-,
5 epoxide-, or carboxylic acid-containing monomer in layer A and/or B is selected from maleic anhydride, or glycidyl methacrylate.
9. The article according to any one of claims 1 to 8 wherein the (meth)acrylic ester monomer of the terpolymer in layer A and/or B is present from 0.1 to 50 wt% based on each layer and is selected from methyl, ethyl, n-butyl, iso-butyl, 2-ethylhexyl, or n-octyl
10 (meth)acrylate.
10. The article according to any one of claims 1 to 9 wherein the article comprises a layer C comprising from 50 to 100 wt% of a polyolefin.
11. The article according to claim 10 wherein layer C is adjacent to layer B.
12. The article according to claim 10 or 11 wherein the polyolefin of layer C is a
15 polyethylene.
13. The article according to any one of claims 10 to 12 consisting of layers A, B and C, wherein:
 - layer A is the outer layer,
 - layer B is the intermediate layer adjacent to layer A and layer C,
 - 20 • layer C is the inner layer.
14. The article according to any one of claims 1 to 13 wherein said article comprises at least one cavity provided with a polyurethane.
15. The article according to any one of claims 1 to 14 wherein the outer surface is painted.

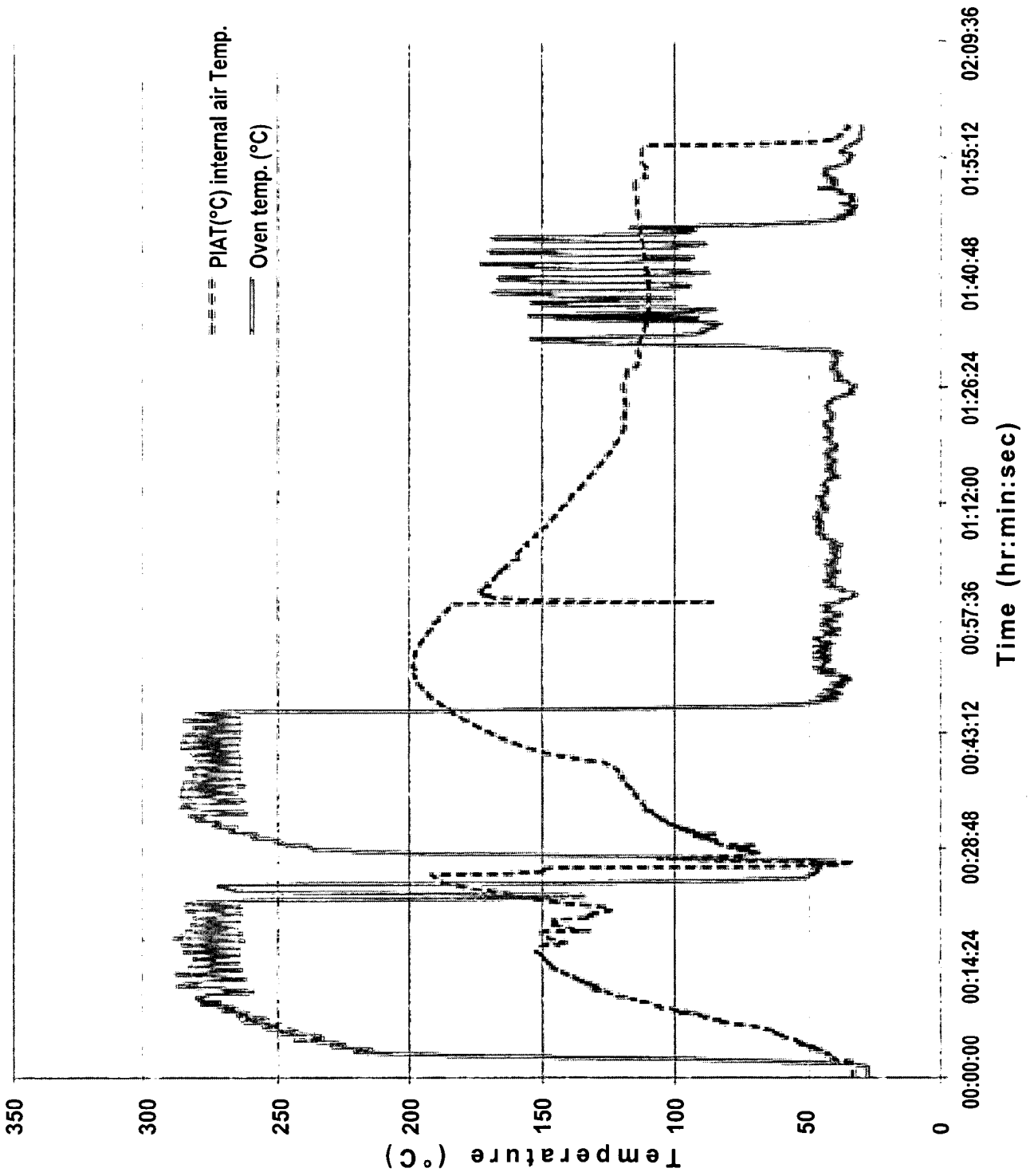


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No PCT/EP2012/067527

A. CLASSIFICATION OF SUBJECT MATTER				
INV. B29C41/06	B29C41/22	C08L23/04		
C08L25/08	B32B1/02	B32B27/08		
B32B27/32	B32B5/20	C08L67/04		
		C08L23/08		
		B32B27/36		
		B32B27/28		
According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED				
Minimum documentation searched (classification system followed by classification symbols) B29C C08L				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
Y	EP 1 721 739 A1 (TOTAL PETROCHEMICALS RES FELUY [BE]) 15 November 2006 (2006-11-15) paragraph [0016] - paragraph [0021] paragraph [0049] paragraph [0054]	1-15		
Y	EP 1 721 931 A1 (TOTAL PETROCHEMICALS RES FELUY [BE]) 15 November 2006 (2006-11-15) paragraph [0014] - paragraph [0019] paragraph [0054] paragraph [0056]	1-15		
A	US 3 976 821 A (CARROW GUY E ET AL) 24 August 1976 (1976-08-24) column 1, line 57 - column 2, line 27 column 3, line 15 - line 51	1-15		
	----- -/--			
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.				
* Special categories of cited documents : <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; border: none; vertical-align: top;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family </td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family			
Date of the actual completion of the international search	Date of mailing of the international search report			
9 October 2012	17/10/2012			
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Lichau, Holger			

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2012/067527

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X,P	WO 2012/112266 A1 (FINA TECHNOLOGY [US]; LI FENGKUI [US]; ASHBAUGH JOHN [US]; RAUSCHER DA) 23 August 2012 (2012-08-23) paragraph [0025] - paragraph [0068] -----	1-13,15
X,P	WO 2012/112267 A1 (FINA TECHNOLOGY [US]; LI FENGKUI [US]; ASHBAUGH JOHN [US]) 23 August 2012 (2012-08-23) paragraph [0025] - paragraph [0063] -----	1-13,15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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			WO 2012112266 A1 23-08-2012

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			WO 2012112267 A1 23-08-2012
