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(54) Titre : PROCEDE DE FABRICATION D'UNE MATIERE MOULABLE ET UTILISATION DANS LA FABRICATION DE REVETEMENTS DE SOLS A FAIBLES EMISSIONS

(54) Title: METHOD FOR PRODUCTION OF A MOULDABLE MASS AND USE THEREOF FOR PRODUCTION OF LOW-EMISSION FLOOR COVERINGS

(57) Abrégé/Abstract:
The invention relates to a method for the production of mouldable masses, based on polyolefins with a density of <0.918 g/cm^3, by means of at least two serial cross-linking reactions and the use of said masses for the production of low-emission floor coverings with excellent material properties.

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(54) Title: METHOD FOR PRODUCTION OF A MOULDABLE MASS AND USE THEREOF FOR PRODUCTION OF LOW-EMISSION FLOOR COVERINGS

(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG EINER FORMBAREN MASSE UND DEREN VERWENDUNG ZUR HERSTELLUNG EMISSIONSARMER BODENBELÄGE

(57) Abstract: The invention relates to a method for the production of mouldable masses, based on polyolefins with a density of <0.918 g/cm^3, by means of at least two serial cross-linking reactions and the use of said masses for the production of low-emission floor coverings with excellent material properties.

(57) Zusammenfassung: Die vorliegende Erfindung betrifft ein Verfahren zur Herstellung formbarer Massen auf Basis eines Polyolefins mit einer Dichte <0,918 g/cm^3 durch mindestens zwei zeitversetzte Vernetzungsreaktionen sowie die Verwendung derartiger Massen zur Herstellung von emissionsarmen Bodendelägen mit ausgezeichneten Materialeigenschaften.

Method for the Production of a Moldable Mass and Use thereof for the Production of Low-Emission Floor Coverings

The present invention relates to a method for the production of moldable masses on the basis of polyolefin with a density of < 0.918g/cm³ by means of at least two timely delayed cross-linking reactions, as well as the use of such masses for the production of low-emission floor coverings with excellent material properties.

Elastomer coverings on rubber basis are part of high-performance floor coverings due to their durability and multiple application possibilities. However, the curing and processing additives or agents, respectively, are inclined to emit from the floor coverings in their unchanged, or their chemically changed forms. WO 97/47802 and WO 99/58602 have therefore described floor coverings, which essentially do not cause any annoying odor or health affecting emissions. Such floor coverings are based on polyolefin with a density of < 0.918 g/cm³ for the polymer binder. In the course of further development for low-emission floor coverings, it has been shown that the processing methods in the production of such floor coverings may have a substantial influence on their material properties.

The object underlying the present is thus to provide a new method for the production of low-emission floor coverings on polyolefin basis, with which floor coverings having excellent material properties and an appealing appearance can be maintained.

This object is solved by means of the embodiments characterized in the claims. In particular, there is provided a method for production of a moldable mass, which is comprised of the following steps:

(a) Compounding of a blend that contains at least one polyolefin with a density of < 0.918 g/cm³, for example 0.86 to 0.91 g/cm³, a first organic peroxide compound, such as 2,5-dimethyl-2,5-di-(t-butylperoxy)-hexane ("DHBP"), with a decomposition temperature T1 of, for instance, approximately ≥160°C, and at a temperature of < T1, a first co-cross-linking agent, which is essentially stable at a temperature of < T1.

(b) Adding of mineral oil, preferably paraffin mineral oil with as few unsaturated proportions as possible, such as SUNPAR® 150, to the blend from step (a), preferably at a quantity of 2 to 25 weight-% based on the amount of the polyolefin, and heating of this blend to a temperature T2, such as approximately 180°C; and

(c) Adding of at least a second organic peroxide compound, such as 1,1-di-(5-butylperoxy)-3,3,5-trimethylcyclohexane, with a decomposition temperature T3 and a second co-cross-linking agent, which is essentially stable at a temperature of < T3 to the blend of step (b), and heating of the resulting blend to a temperature of ≥T3, such as to approximately ≥185°C while maintaining the moldable mass,

whereby T1 < T2 < T3.

The polyolefin used in step (a) can be a polyethylene of very low density ("PE-VLD"), or a copolymer from ethylene with at least one additional olefin, such as propene, butene, or octene, and/or a blend of at least two ethylene-copolymers, whereby as the main polymer, the ethylene-copolymer has a copolymer (i) with a density of 0.88-0.91 g/cm³, and for controlling rheology and elasticity, a copolymer (ii) with a density of 0.86-0.89 g/cm³, and an MFI of > 3 (at 190°C; 2.16kg). For example, the copolymers (i) and (ii) are copolymers of ethylene with octene. The copolymers (i) and (ii), can be present, for instance, at a weight ratio of 4:1 to 3:2. Furthermore, as an additional component in addition to polyolefin, at least one

graft polymer may be present, preferably on the basis of an HD-polyethylene. In particular, the graft polymer can be maleic acid anhydride grafted HD-polyethylene, whereby the degree of grafting is preferably 1 to 5%. The proportion of the graft polymer is, for example, 5 to 25 weight-% based on the total weight of the polymer proportions used in step (a). Accordingly, the proportion of at least one polyolefin, which in addition to the graft polymer forms the polymer proportion of the blend in step (a), can be between 75 to 95 weight percent, based on the total weight of the polymer proportions.

The first organic peroxide compound used in step (a) is not only comprised of individual compounds, but can also be comprised of a blend of at least two like peroxide compounds, provided that both the individual compounds and such a blend have a pre-determined decomposition temperature of $\geq T1$. For example, the decomposition temperature of the DHBP used in step (a) is $\geq 170°C$. Preferably, the first organic peroxide compound is present in the blend to be compounded at an amount of 0.05 to 2.0 weight-% based on the amount of polyolefin.

The first co-cross-linking agent used in step (a), which is essentially stable at a temperature of $< T1$, is preferably selected from a group consisting of di- and trimethacrylates, such as 1,4-butanedioldimethacrylate ("1,4-BDMA"), 1.3-butanediol-dimethacrylate ("1,3-BDMA"), triethyleneglycoldimethacrylate ("TEDMA"), and trimethylolpropanetrimethacrylate ("TRIM"), and blends thereof. The co-cross-linking agent is present in the blend to be compounded preferably at an amount of 0.05 to 4.0 weight-% based on the amount of polyolefin.

The blend to be compounded in step (a) may further contain common processing auxiliary agents, such as interior/exterior lubricants, such as from the group of waxes, such as metal salts; static inhibitors, such as GMS; antioxidants, such as phenol-inhibited amines, etc. These processing auxiliary agents

are used in conventional quantities, such as 1 to 5 weight-% based on the polymer proportions.

The mineral oil added in step (b) to the blend compounded in step (a) should preferably be low in aromatic compounds, i.e. have no aromatic residue or group, respectively, such as a phenyl group, whereby 2 to 25 weight-% based on the amount of the polyolefin are preferably added.

The second organic peroxide compound added in step (c) is not only comprised of individual compounds, but can also be comprised of a blend of at least two such peroxide compounds, provided that both the individual compounds and the blend have a pre-determined decomposition temperature of $\geq$T3. The second organic peroxide compound is preferably added at a quantity of 0.05 to 2.0 weight percent based on the amount of polyolefin.

The second co-cross-linking agent added in step (c), which is essentially stable at a temperature of < T3, may contain, for example, triallylcyanurate and/or triallylisocyanurate, whereby the co-cross-linking agent is added at a quantity of 0.05 to 5 weight-% based on the amount of the polyolefin.

In a preferred embodiment of the method according to the invention, the second co-cross-linking agent has an accelerating effect on the peroxidic cross-linking reaction. Especially preferred are dimethacrylates as the first co-cross-linking agent, as opposed to, for example, TRIM, because a larger amount of additive can be achieved at an equal MFI, which advantageously results in surface energy of floor coverings on the basis of the mass according to the invention by means of a higher content of polar groups.

In step (c) of the method according to the invention common fillers, such as silica flour, kaolin, talc, wood flour, dolomite, aluminumtrihydroxide, precipitated silica, barite, chalk, as well as common pigments can also be added.

The quantities of fillers and pigments used are within common ranges, and are, for example, up to 70% for fillers, and for example, up to 8% for pigments based on the total formulation.

The temperature T1 in step (a) of the method according to the invention is preferably selected so that the polyolefin used can be plasticized in addition to the compounding with the first organic peroxide compound and the co-cross-linking agent, but no decomposition of the first organic peroxide compound due to the temperature occurs. When using for example DHBP as the first organic peroxide compound, the temperature T1 is maintained at ≤160°C, preferably between approximately 120 to 160°C, i.e. below the decomposition temperature of DHBP. At this temperature, adequate plasticizing of the blend to be compounded can be achieved.

The temperature T2 in step (b) of the method according to the invention is selected so that after adding the mineral oil, the cross-linking reaction is activated between the first organic peroxide and the co-cross-linking agent. This "main reaction" of the blend plasticized and compounded according to step (a) is performed using, for example, DHBP at approximately 180°C.

The temperature T3 in step (c) of the method according to the invention is selected so that after adding the second organic peroxide compound and the second co-cross-linking agent, the "final cross-linking" is ensured, i.e. the first and second peroxide compounds used should preferably be completely converted during the residence time in the extruder. When using, for example, 1,1-di-(t-butylperoxy)-3,3,5-trimethylcyclohexane as the second organic peroxide compound, the temperature T3 is ≥185°C.

The temperature setting of steps (a) to (c) of the method according to the invention can be controlled or adjusted by means of external and/or internal reaction housing temperature units, and/or by means of friction initiating worm elements with the use of

twin screw extruders. The time for performing steps (a) to (c) of the method according to the invention usually lasts 1 to 4 minutes. For example, with the use of a twin screw extruder, the residence time depends on the type of screw equipment and is selected so that in dependency of the throughput to be achieved, the blend remains in the housing for an accordingly long time, preferably for approximately 1 to three minutes.

In a preferred embodiment of the method according to the invention, degassing of the mass achieved is performed after step (c), such as atmospheric ventilation followed by vacuum ventilation.

A further subject matter of the present invention relates to the production of floor coverings using the previously defined moldable mass. In one embodiment, the method according to the invention is comprised of providing a carrier in the shape of webs, as well as the application of the previously defined moldable mass onto one side of the carrier. Any material currently used in the floor covering sector on the basis of natural and/or synthetic woven fabric or knitted fabrics, textile material, as well as materials on the basis of non-woven materials or non-woven fabrics, may be used. For example, jute fabrics, blended fabrics made of natural fibers such as cotton and cellulose, fiber glass fabrics, fiber glass fabrics coated with bonding agents, blended fabrics made of synthetics, fabrics made of core/compound glass fiber with, for example, a core of polyester and a polyamide coating, may be used.

In another embodiment of the method according to the invention for the production of particularly homogenous floor coverings, the moldable mass created, for example, in a twin screw extruder can be processed into foil by means of a flat die and calendar stack or a roller mill. This foil can be further processed into any desired floor covering, for example, by means of sprinkling on a differently designed granulate, or continuously by means of a twin auma or twin press.

In another embodiment granulates yielded from the moldable mass, or the mill feed thereof, can be fixed to a sheeting by means of sprinkling it on a liner in a Thermofix® system. Compression and smoothing of the product web achieved in this way occurs in an auma. The direct production of a floor covering by means of stacking of mill feed or granulate is also possible in a twin auma or twin press. As far as the production of homogenous floor coverings with directional structure is concerned, multi-colored granulates or blends of several monochrome granulates can be added into the groove of a roller mill/calendar.

A further subject matter of the present invention is a floor covering, which can be quickly produced according to one of the previously defined methods. Surprisingly it was shown in the floor covering according to the invention that without a corona treatment an increase of surface energy can be achieved, which, among other reasons, is a cause of the use of the co-cross-linking agents in steps (a) and (c) of the method according to the invention. For example, by using 1,3-BDMA and/or 1,4-BDMA as the first co-cross-linking agent in step (a) of the method according to the invention, the proportion of the polar groups and thereby the surface energy can be selectively increased. Due to the higher surface energy, the floor covering according to the invention has a "direct gluability" as compared to traditional olefin floor coverings. Furthermore, a ("three-dimensional") network is constructed by means of the timely delayed decomposition of the peroxides in steps (a) and (c) of the method according to the invention and in the related cross-linking reactions, which results in excellent material properties of the floor covering.

The figures show the following:

Figure 1 is a schematic illustration of a device for the production of the floor covering according to the invention (also compare example 1). The arrangement of the housing of the extruder is comprised of ten housing zones, whereby the compound blend according to step (a) is added to the housing zone 1, the mineral oil according to step (b) is added at the end of the housing zone 3, and the blend according to step

(c) is added in the housing zone 4 by means of a twin screw feed extruder (ZSB 40) at a temperature of ≤ 28°C. The rear ventilation is located at the beginning of the housing zone 4, the atmospheric ventilation ("A") is located in the housing zone 6, and the vacuum ventilation ("A") is located in the housing zone 9. The respective housing temperature is stated in °C below each housing zone.

The present invention is explained in further detail by means of the following examples.

Example 1

A densely combing equi-directionally rotating twin screw extruder of the type ZSK 40 from Coperion Werner + Pfleiderer with L/O = 40 and D = 40 is used to perform the method according to the invention (compare figure 1). The compound blend (compare the following formulation for step (a)) is plasticized and homogenized within a 6D long feeder zone by means of suitable conveying and kneading elements. The temperature in this case is approximately 180°C. After adding the mineral oil (SUNPAR 150®, 11.5 weight-%) the temperature is increased by means of friction and shear rates of the screw elements, and initializes the peroxidic cross-linking essentially between the first organic peroxide DHBP and the co-cross-linking agent 1,4-BDMA. The temperature is now approximately 185°C. Subsequently, the blend according to step (c) is added in the following formulation by means of a lateral extruder. Since the temperature of the mass is higher than the decomposition temperature of the second organic peroxide compound, the final cross-linking is now initiated. The temperature in this case is approximately 195°C. Before exiting the extruder, a degassing by means of atmospheric ventilation followed by vacuum ventilation is performed in order to remove any volatile reaction products as well as any volatile educts so that they will be unable to pollute the air in the environment.

Formulation for example 1

Raw Materials	Quantity [g]	Proportion to total formulation
Compound blend, step (a)		
Affinity*PL 1880	375.00	5.68%
Affinity*VP 8770	2,250.00	34.10%
Dow*XU 60769.07	375.00	5.68%
Processing Auxiliary Agents		
(Additive mix)	**59.4**	**0.9%**
1,4-BDMA	5.30	0.080%
Trigonox*101-50 D-Pd	6.60	0.100%
Mineral Oil Additive, step (b)		
SUNPAR 150	330.00	5.00%
Filler blend (lateral extruder), step (c)		
Filler	2,904.00	44.02%
Trigonox*29-40 B-Pd	21.10	0.320%
Perkalink*301-50	4.25	0.064%
Pigment blend	267	4.05%

The following lists the properties of the floor covering produced according to the invention with the previously mentioned mass:

* trade-mark

1. Indentation Behavior according to EN 433

Remaining indentation after 150 min.	mm	0.01
Thickness before load	mm	2.34
Penetration depth after 150 min.	mm	0.13
Index after 150 min.	mm	5.6
Elasticity after 150 min.	%	92.3

2. Shore Hardness according to DIN 53 505

Shore A	96
Shore D	45

3. Abrasion Behavior according to DIN 53 516

Raw density, EN 436	g/cm^3	1.335
Loss of volume	mm^3	94.5

Surface energy of the floor covering produced according to the invention

Testing Method

Determination of surface energy of the samples by means of contact angle measurement. Di-iodine methane (Busscher) and water (Busscher) were used as the test liquids. The analysis is performed according to Owens, Wendt, Rabel & Kaelble.

Test Results

Sample	Surface energy [mN/m]	Disperser Proportion [mN/m]	Polar proportion [mN/m]
Elastomer Tile	36.5	34.6	1.9

CLAIMS:

1. Method for the production of a moldable mass, comprised of the following steps:

   (a) Compounding of a blend that contains at least one polyolefin with a density of < 0.918 g/cm^3, a first organic peroxide compound with a decomposition temperature T1, and a first co-cross-linking agent, which is essentially stable at a temperature of < T1,

   (b) Adding of mineral oil to the compounded blend of step (a), and heating of this blend to a temperature of T2, and

   (c) Adding of at least one second organic peroxide compound with a decomposition temperature T3, and a second co-cross-linking agent, which is essentially stable at a temperature of < T3, to the blend of step (b), and heating of the resulting blend to a temperature of ≥T3 while yielding the moldable mass,

   whereby T1 <T2 <T3.

2. Method according to claim 1, whereby the polyolefin is either polyethylene of very low density (PE-VLD), or a copolymer of ethylene with at least one additional olefin, or a blend of at least two ethylene copolymer types, and, optionally, at least one graft polymer is present as an additional component in addition to the polyolefin.

3. Method according to claims 1 or 2, whereby the polyolefin has a density of 0.86 to 0.91 g/cm^3.

4. Method according to any one of claims 1 to 3, whereby the first peroxide compound is 2,5-dimethyl-2,5-di-(t-butylperoxy)-hexane (DHBP).

5. Method according to any one of claims 1 to 4, whereby the first peroxide compound is present at a quantity of 0.05 to 2.0 weight-percent based on the amount of the polyolefin.

6. Method according to any one of claims 1 to 5, whereby the first co-cross-linking agent contains one or more di- and/or trimethacrylates.

7. Method according to claim 6, whereby the di- and trimethylacrylates are selected from the group consisting of 1,4-butane dioldimethacrylate (1,4-BDMA), 1,3-butanediol-dimethacrylate (1,3-BDMA), triethylene glycoldimethacrylate (TEDMA), and trimethylolpropane trimethacrylate (TRIM).

8. Method according to any one of claims 1 to 7, whereby the first co-cross-linking agent is present at a quantity of 0.05 to 4.0 weight-percent based on the amount of the polyolefin.

9. Method according to any one of claims 1 to 8, whereby the blend in step (a) contains one or more processing auxiliary agents.

10. Method according to any one of claims 1 to 9, whereby the mineral oil is added at a quantity of 2 to 25 weight-percent based on the amount of the polyolefin.

11. Method according to any one of claims 1 to 10, whereby the second peroxide compound is 1,1-di-(t-butylperoxy)-2,3,5-trimethylcyclohexane.

12. Method according to any one of claims 1 to 11, whereby the second peroxide compound is added at a quantity of 0.05 to 2.0 weight-percent based on the amount of the polyolefin.

13. Method according to any one of claims 1 to 12, whereby the second co-cross-linking agent contains triallylcyanurate (TAC) and/or triallylisocyanurate (TAIC).

14. Method according to any one of claims 1 to 13, whereby the second co-cross-linking agent is added at a quantity of 0.05 to 5.0 weight-percent based on the amount of the polyolefin.

15. Method according to any one of claims 1 to 14, whereby in step (c) one or more fillers, and/or one or more pigments are added.

16. Method according to any one of claims 1 to 15, in which the temperature T1 is ≤160°C, the temperature T2 is approximately 180°C, and the temperature T3 is ≥185°C.

17. Method according to any one of claims 1 to 16, in which the time for performing steps (a) to (c) is approximately 1 to 3 minutes.

18. Method according to any one of claims 1 to 17, in which degassing is performed after step (c).

19. Method according to any one of claims 1 to 18, further comprising forming the molded mass into a floor covering.

Fig. 1

ENCLOSURE ARRANGEMENT OF EXTRUDER