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(71) Applicant: BASF SE [DE/DE]; Carl-Bosch-Strasse 38, 67056 Ludwigshafen am Rhein (DE).

(72) Inventors: CRISTADORO, Anna Maria; Elastogranstrasse 60, 49448 Lemfoerde (DE). **POESELT, Elmar**; Elastogranstrasse 60, 49448 Lemfoerde (DE). **GUTMANN, Peter**; Carl-Bosch-Strasse 38, 67056 Ludwigshafen am Rhein (DE). **SEIDEMANN, Lothar**; Carl-Bosch-Strasse 38, 67056 Ludwigshafen am Rhein (DE). **GAST, Peter**; Carl-Bosch-Strasse 38, 67056 Ludwigshafen am Rhein (DE). **ALBUERNE, Julio**; Elastogranstrasse 60, 49448 Lemfoerde (DE). **CHEN, Po Han**; No. 18, Lugong South 5th Rd, Lukang, 50544 (TW). **LINNENBRINK, Martin**; Elastogranstrasse 60, 49448 Lemfoerde (DE). **KRAMER, Tobias**; Elastogranstrasse 60, 49448 Lemfoerde (DE). **HSIAO, Mon Wei**; No. 18, Lugong South 5th Rd, Lukang, 50544 (TW).

(74) Agent: BÜCHEL, Edwin; Patentanwälte Isenbruck Bösl Hörschler PartG mbB, Seckenheimer Landstraße 4, 68163 Mannheim (DE).

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(54) Title: PREPARATION OF STORAGE-STABLE PARTICLES OF A MOLDABLE THERMOPLASTIC PARTICLE FOAM AND SHAPED BODIES AND PREPARATION PRODUCTS AND USES THEREOF

(57) Abstract: The present invention relates to a process for the preparation of storage-stable particles of a moldable thermoplastic particle foam at least partly coated with a hot melt adhesive, preferably a non-reactive hot melt adhesive, comprising the steps of a_1) bringing the particles into contact with the hot melt adhesive in order to obtain the coated particles; a_2) moving the coated particles until the particles are tacky-free. The invention also relates to a storage-stable, at least partly coated particle of a moldable thermoplastic particle foam which is at least partly coated with a hot melt adhesive, preferably a non-reactive hot melt adhesive, wherein the coated particle is tacky-free as well as to a process for preparing shaped bodies and shaped bodies obtainable by said process and the use of said particles and shaped bodies.

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Preparation of storage-stable particles of a moldable thermoplastic particle foam and shaped bodies and preparation products and uses thereof

Description

The present invention relates to a process for the preparation of storage-stable particles (also herein referred to as "beads") of a moldable thermoplastic particle foam at least partly coated with a hot melt adhesive, preferably a non-reactive hot melt adhesive, comprising the steps of a_1) bringing the particles into contact with the hot melt adhesive in order to obtain the coated particles; a_2) moving the coated particles until the particles are tacky-free. The invention also relates to a storage-stable, at least partly coated particle of a moldable thermoplastic particle foam which is at least partly coated with a hot melt adhesive, preferably a non-reactive hot melt adhesive, wherein the coated particle is tacky-free, preferably obtainable by said process as well as to a process for preparing shaped bodies and shaped bodies obtainable by said process and the use of said particles and shaped bodies.

Moldable thermoplastic particle foams are used, for example, for the production of any solid foam bodies, for example for exercise mats, body protectors, lining elements in automobile construction, sound and vibration dampers, packaging or shoe soles.

Conventionally, a mold with foam particles is filled followed by melting the individual foam particles on their surface by the action of heat and in this way to connect them to one another to form a particle foam part. Thus, in addition to simple products, complex semi-finished products or molded parts with undercuts can be produced.

Moldable thermoplastic particle foams are known in the art and described, e.g., in Robin Britton (Author), Update on Moldable Particle Foam Technology, Rapra technology Ltd, 2009. Expanded thermoplastic elastomers, especially expanded thermoplastic polyurethanes (eTPU), represent specific moldable thermoplastic particle foams.

Expanded thermoplastic elastomers are known in the art. For example, WO 2018/082984 A1 describes particle foams based on expanded thermoplastic elastomers. WO 2008/087078 A1 describes hybrid systems consisting of foamed thermoplastic elastomers and polyurethanes. Hybrid eTPU systems are also described in CN 109337343 A, CN 110240795 A and CN 109080061 A.

An exemplary thermoplastic polymer is expanded thermoplastic polyurethane (eTPU), which is commercially available, e.g. marketed by BASF under the name Infinergy®. eTPU particles represent mainly closed to fully closed-cell particle foam. Thermoplastic polyurethane (e.g. Elastollan®) is expanded resulting in particle foam and can be processed on standard molding machines. Thanks to its closed particle surface and the chemical nature of the used TPU, standard eTPU grades also absorb only low amounts of water. Like the TPU, on which it is based, it can also be characterized by high breaking elongation, tensile strength and abrasion resistance, combined with good chemical resistance.

Fast prototyping of 3D objects made out of expanded thermoplastic elastomers is nowadays not easy to realize. Typically, isocyanate-containing binders are used for bonding the particles or water vapor and appropriate machines, like a steam chest molder. Both approaches are not easily accessible due to health safety reasons, energy costs or due to lack of accessibility of appropriate machinery (steam-chest molder). Moreover, the use of water vapor allows only molding particles of the same kind, whereas a coating on an eTPU particle or the usage of a water-based binder may allow bonding eTPU particles of different kind (Glass transition temperature, Melting point) and size, but also bonding of different TPUs or even different particle foams, e.g. different mixtures of eTPS, ePS, ePP, eTPA, eTPC, eTPO and the like. The application of a coating allows as well the adjustment of the mechanical performance and applicability by incorporation of additives, like for example pigments or dyes, flame retardants or antistatic agents, directly to the particle surface. Filling agents for example allow the increase of the stiffness of the final part, while the use of additives which are for example excitable by an electro-magnetic field allow the moldability of the coating and thereby reducing the required energy for molding.

As additives can be used pigments, dyes, odor, filling agents, bio-based and/or biodegradable additives, UV-, heat-stabilizer, flame retardants such as expandable graphite, additives which generate antistatic properties, electrical conductivity, additives, which reduce dirt-uptake, antimicrobial additives, wax, crosslinking agents, surface functionalized fillers, foamable additives such as Expancell®, additives which can be irradiated by an electromagnetical field, and/or radio frequency, and/or microwave.

WO 2022/223 438 A1 and European patent application with application number EP 22 202 204.8 describe different water-based binders for coating particles that can be brought into the shape of said 3D parts.

US 6 616 797 B1 describes the formation of adhesive bonds by a process that includes applying a dispersion containing a polyurethane which has structural units of formula (I) to a surface. The dispersion is first coated onto the surface to form a coating. The coating is dried to give an essentially anhydrous coating. The dried coating is then subjected to heat activation. The adhesive bond is formed by joining the heat-activated coating to itself or to another surface. However, particle coating is not described.

WO 2012/13506 A1 describes the use of an aqueous polyurethane dispersion adhesive for producing biologically disintegrable composite films with at least two substrates being bonded to one another using the polyurethane dispersion adhesive, with at least one of the substrates being a biologically disintegrable polymer film. At least 60% by weight of the polyurethane is made up of diisocyanates, polyester diols and at least one bifunctional carboxylic acid selected from dihydroxycarboxylic acids and diaminocarboxylic acids.

WO 2005/003247 A1 relates to a method for bonding substrates with different surface energies. The adhesive used for bonding consists of at least 15% by weight of a polyurethane (water or other organic solvents with a boiling point below 150°C at 1 bar not counted), the adhesive is applied to the substrate with the lower surface energy and the resulting adhesive-coated substrate is bonded to the substrate with the higher surface energy.

WO 2021/249749 A1 describes the recycling of bonded articles, including TPU – foam substrates, by using aqueous polyurethane dispersions of specified molecular weights as adhesives. It is not mentioned that the foamed particles are coated.

US 2019/367698 A1 describes methods for the preparation of foamed thermoplastic polyurethane elastomer products using hot melt adhesives like Mirathane® H306. However, the coated particles are not moved until the particles are tacky-free, but instead filled directly into a product mold for vulcanization. The vulcanization process implicates crosslinking happening among the particles, which lead to the realization of a 3 D material, which loses his thermoplastic characteristics, such as re-meltability and re-cyclability.

WO 2019/073607 A1 describes a member for shoe soles, a part or the whole of which is formed from a resin composite body that comprises a non-foamed elastic matrix which is composed of an elastomer and a plurality of resin foam particles that are dispersed in the elastic matrix. Furthermore, a shoe is disclosed which is provided with this member for shoe soles.

Even though different binders are described, which are generally useful for bonding particles, there is a need for the preparation of storage stable coated particles, where agglomeration of stored particles is prevented. This includes particles with better flowability, lower electrostatic charging by friction, and which allow a much easier realization of 3 D part by using an easy molding process (e.g. standard convective oven or heat press).

Accordingly, there is a need for a material that should combine the following advantages:

- Different eTPE beads or even other material-classes can be mixed;
- Hot melt can be used as carrier for e.g. stabilizers, pigments etc.;
- Hot melt can be recycled together with the eTPU;
- Particle foam bodies, made out of hot melt coated particles can be debonded and the eTPU parts can be recovered;
- Hot melt coated beads can be fused together by easy hotpress or by using other molding technology such as radio frequency and steam chest molding.

A tacky-free coating of the particles allows easy filling into e.g. molds or cavities during processing due to better flowability and lower electrostatic charging by friction.

Additionally, the particles can be processed differently e.g. by standard convective oven or heat press, but also by an electro-magnetic field. Thereby the beads can be filled for example into interspaces and be glued together by a trigger.

Thus, an object of the present invention is to provide a process for the preparation of storage-stable coated particles.

The object is achieved by a process for the preparation of storage-stable particles of a moldable thermoplastic particle foam at least partly coated with a hot melt adhesive, preferably a non-reactive hot melt adhesive, comprising the steps of

a_1) bringing the particles into contact with the hot melt adhesive in order to obtain the coated particles;
a_2) moving the coated particles until the particles are tacky-free.

The object is also achieved by a process for the preparation of a shaped body comprising the steps of

b_1) coating of particles according to the process for the preparation of storage-stable particles according to the present invention;
b_2) shaping the particles obtained from step b_1).

The object is also achieved by a storage-stable, at least partly coated particle of a moldable thermoplastic particle foam which is at least partly coated with a hot melt adhesive, preferably a non-reactive hot melt adhesive, wherein the coated particle is tacky-free, preferably obtainable by a process for the preparation of storage-stable particles according to the present invention.

The object is also achieved by a shaped body obtainable from a process for the preparation of a shaped body according to the present invention or obtained by molding of particle foams according to the present invention.

Surprisingly it was found that the use of hot-melt adhesives results in tacky-free coatings, which can be used for realization of 3 D parts without the need of steam, even if steam chest compatibility is still given. In view of the low melting point of the hot melt adhesive the energy used in the processes, according to the present invention, is low even when steam chest molding is used and cycle time is short. The coating allows by heat press the realization of 3D parts with excellent mechanical values, which are comparable and even superior to 3D parts made by using standard steam chest molding processes. In addition, shorter cycle times during processing are possible. Especially, the use of molten hot melt is advantageous since cost and energy intensive removal of solvent, especially aqueous solvent, can be prevented.

In order to prepare storage-stable particles of a moldable thermoplastic particle foam which are at least partly coated with a hot melt adhesive the particles are brought into contact with the hot melt adhesive in order to obtain the coated particles in a step a_1).

Different methods are available in order to achieve the coating.

In a first aspect, the hot melt adhesive is brought into contact in form of its molten state. A typical temperature used is in the range from 60 °C to 200 °C, preferably from 60 °C to 180 °C, more preferably from 80 °C to 180 °C.

Preferably, the hot melt adhesive in its molten state has a viscosity in the range from 0.1 mPas to 800000 mPas, more preferably from 1 mPas to 600000 mPas, even more preferably from 10 mPas to 500000 mPas, measured at 160°C. Preferably, the viscosity is measured by using a Brookfield viscosimeter. The Brookfield viscometer measures the torque required to rotate the selected spindle in a fluid. This torque value is directly related to the viscosity of a fluid. In more detail, a Brookfield/Ametek rotationviscosimeter (HB DV2T Extra) can be used, which measures the torque required to rotate the spindle (SC4-27) in a fluid at 0.4 rpm.

Preferably, the particles are kept under agitation (kitchen mixer, cement mixer or spray coating drum). The mixer is preferably kept at a temperature from 15 °C to 100 °C, preferably from 30 °C to 100 °C, even more preferably, from 60 °C to 100 °C.

Accordingly, in a preferred embodiment the particles are tempered before step a_1) so that the temperature of the particles at least at the beginning of step a_1), preferably during the whole step a_1), is from 15 °C to 100 °C, preferably from 30 °C to 100 °C, even more preferably, from 60 °C to 100 °C.

In a second aspect, the hot melt adhesive is brought into contact in form of its solid state by powder coating. Powder coating is a well-known method and a person skilled in the art is able to conduct said powder coating.

In a third aspect, the hot melt adhesive is brought into contact in form of a solution, wherein the hot melt adhesive is dissolved in an organic solvent, followed by the step of

a_3) removing the organic solvent and/or drying the particles after step a_2) at a temperature below the melting point of the hot melt adhesive in order to obtain the coated particles.

Suitable organic solvents are organic solvents, like acetone, acetonitrile, butanol, t-butyl alcohol, butanone (MEK), chlorobenzene, chloroform, cyclohexane, diethylene glycol, diethyl ether, dimethoxy ethane, dimethylformamide, dioxane, ethanol, ethyl acetate, ethylene glycol, glycerin, heptane, hexane, methanol, methyl t-butyl ether, N-methyl-2-pyrrolidinone, methylene chloride, pentane, propanol, pyridine, tetrahydrofuran, toluene, triethyl amine, xylene. A preferred organic solvent is MEK. The draying in step a_3) can be carried out by conventional methods.

A most preferred embodiment is the use of the hot melt adhesive in form of its molten state.

The processes of the present invention refer to the preparation of coated particles of a moldable thermoplastic particle foam. Such foams are known in the art (see e.g. Robin Britton (Author), Update on Mouldable Particle Foam Technology, Rapra technology Ltd, 2009). Preferably, the moldable thermoplastic particle foam is an expanded thermoplastic elastomer.

Particles of expanded thermoplastic elastomers are known in the art. Suitable thermoplastic elastomers are, for example, thermoplastic polyurethanes (TPU), thermoplastic polyester elastomers (e.g. polyetherester and polyesterester) (TPC), thermoplastic copolyamides (e.g. Polyether copolyamides) (TPA), thermoplastic polyolefins (TPO) or thermoplastic styrene butadiene block copolymers (TPS). Foam particles based on thermoplastic polyurethane (TPU) are particularly preferred. Thus, preferably the expanded thermoplastic elastomer is eTPU.

Examples of methods for preparing expanded thermoplastic elastomer particles are described in WO 2008/087078 A1, WO 2018/082984 A1, US 10 005 218 B2 and WO 2007/082838 A1.

Preferably, the glass transition temperature (Tg) of the moldable thermoplastic particle foam, like the expanded thermoplastic polymer particles is, according to the named patents, < 100 °C and is measured via DSC according to DIN EN ISO 11357-3:2013, preferably with a heating rate of 20 °C/min after a first pre-drying step at 100 °C for 10 min. The Tg of the soft phase can be measured in the first heating run.

Preferably, in step a_1) the bringing into contact is realized by mixing the foamed beads with the hot melt adhesive using kitchen or cement mixers or spraying, like mixing with a Vollrath mixer or spray drying. The amount of liquid/solution relative to the product weight may be in the range of from 1 ml/kg/min to 1000 ml/g/min. The size of droplets may vary from 1 mm to 1000 mm in diameter. Suitable nozzles would be hollow cone nozzles, full cone nozzles or flat jet nozzles, as well as spray discs that produce droplets through rotational movement and centrifugal force. A suitable mixer that can be used is an EMT 30 L. EMT L 30 is a discontinuous paddle mixer. It is suitable for mixing, agglomeration and coating experiments. It consists of a rigid vessel with rotatable mixing tools. Depending on the field of application there are various available installation possibilities nozzles. The mixer is heatable due to a double jacket. The rotation speed is adjustable via a mechanical variator. Melt containers and pressure vessels are used for the addition of liquids.

In general, common methods for coating, like spray coating, e.g. as described in EP 0 009 727 A1, can be used. In a preferred embodiment of coating, the particles are spray-coated keeping them in motion via blowing them with e.g. air or mixtures of different gases.

The at least partly coated particles are coated in an amount of from 0.1 wt.-% to 40 wt.-%, preferably from 5 wt.-% to 25 wt.-% based on the total weight of particle and coating. Preferably, the at least partly coated particles are coated in an amount of at least 90 %, preferably at least 95 %, more preferably at least 99 %, more preferably fully coated based on the total surface of the particle.

The step a_3) refers to the drying the coated particles in case the hot melt adhesive is brought into contact in form of a solution, wherein the hot melt adhesive is dissolved in an organic solvent. In principle, all suitable methods are possible, like convective drying, contact drying, infrared drying and also microwave technology. In case of the use of a hot melt in the molten state such it is only required to bring the coated particles to room temperature.

In the case of contact drying, the temperature difference between the product and the wall in should be limited to 1 - 100 K, in the case of convective drying the gas composition can be N_2 or air. The gas quantity is preferably 1-1000 liters/min per 1 kg product and the product temperature in the mixer should be between 1°C and 100°C, preferably 10°C to 60°C.

In step a_2) the coated particles are moved until the particles are tacky-free. The term "tacky-free" refers to the realization of a non-sticky surface at room temperature, preferably in the range from 20 °C to 25 °C. This is given when the coated particles do not agglomerate in contact with each other and do not adhere to a second surface at room temperature. This translates to a Tfb (further described in the following) of the hot melt higher than 40 °C, preferentially higher than 60 °C. Tacky-free particles are important to provide storage-stable particles.

The moving of the coated particles in step a_2) can take place simultaneously with step a_1) or afterwards or both, starting with or during step a_1) and continued after completion of step a_1).

Preferably, after step a_1) and before step a_2) the particles are separated from each other. This can be achieved, e.g. by using a vibrating belt or the like. Also, this option prevents agglomeration of the particles.

Preferably, the hot melt adhesive is a composition comprising a thermoplastic polymer, preferably a thermoplastic polyurethane.

A hot melt adhesive typically is solid at room temperature, solvent-free and meltable above room temperature. The hot melt adhesive generally is an unreactive thermoplastic. Hot-melt adhesives (HMA) are adhesive systems which are solid at room temperature, become tacky or sticky upon heating and melt to a liquid or fluid state. They typically solidify rapidly upon cooling at ambient temperatures to develop internal strength and cohesion. Hot melt adhesives are one-part, solvent free thermoplastic adhesives which are characterized by low to medium viscosity when applied at the required dispensing temperature. Once applied, hot melt adhesives cool and solidify to form a strong bond between articles. Bonds formed with thermoplastic hot melt adhesives are reversible. Under sufficiently high thermal stress, thermoplastic hot melt adhesives will liquefy and lose their cohesive strength.

The melting point, measured by differential scanning calorimetry (DSC), of the composition comprising the thermoplastic polymer, in particular the thermoplastic polyurethane, is preferably from about 50 °C to about 180 °C, or from about 50 °C to about 160 °C. The test method refers to ASTM D 3418 - 12 (Standard Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry) by using the Hitachi High-Tech Co., DSC7000X with a heating rate of 10 °C/min and a cooling rate of 10 °C/min. It was surprisingly found that the flow beginning temperature (Tfb) of the composition comprising the thermoplastic polymer has an influence on the coating properties of the composition. The adjustment of the flow beginning temperature in a suitable range can be used to influence the temperature behaviour of the adhesive strength to obtain good coating properties under conditions of usage, but also to allow for easy recycling. It has been surprisingly found that an advantageous combination of good coating using mild conditions can be achieved using the composition comprising a thermoplastic polymer which has a flow beginning temperature (Tfb) of at least 50°C, preferably at least 60°C, more preferably at least 70°C as measured according to Example 1 referring to JSI K7311-1995 and K7210-1999 and by using the Shimadzu Flowtester Capillary Rheometer CFT- 500D.

According to a further embodiment, the present invention is also directed to process according to the present invention, wherein the thermoplastic polymer composition has flow beginning temperature (Tfb) measured according to Example 1 of in the range from 50 °C to 160 °C, preferably from 60 °C to 160 °C, more preferably from 70 °C to 160 °C, more preferably from 70 °C to 150 °C.

Preferably, the composition comprising the thermoplastic polymer, used according to the present invention, has a relatively low softening temperature and also a low flow beginning temperature.

The composition comprising the thermoplastic polymer can include a variety of polymers commonly used in adhesive. For example, the composition can include at least one polymer selected from a polyurethane, a polychloroprene, a latex, a polystyrene, a polyamide, a polyolefin, a polyacrylate, a polyester, a polyether, a copolymer thereof, and any combination thereof. In some aspects, the polystyrene is or includes a polystyrene block copolymer. Suitable polystyrenes can include poly(styrene-isoprene-styrene), poly(styrene-butadiene-styrene), poly(styrene-ethylene-butene-styrene), and a poly(styrene-ethylene-propene).

In some aspects, the composition comprising the thermoplastic polymer includes at least one thermoplastic polymer selected from a thermoplastic polyurethane, a thermoplastic polyamide, a thermoplastic polyolefin, a thermoplastic polyester, a thermoplastic polyether, a thermoplastic copolymer thereof, and any combination thereof. In some aspects, the composition includes a polyolefin such as a polyethylene, a polypropylene, a copolymer thereof, or any combination thereof. The polyolefin can be an ethylene copolymer. In some aspects, the composition includes a thermoplastic polyolefin. The thermoplastic polyolefin, in some aspects, includes a thermoplastic polyethylene, a thermoplastic polypropylene, a thermoplastic copolymer thereof, or any combination thereof. The thermoplastic polyolefin can include a thermoplastic ethylene copolymer. In some aspects, the thermoplastic ethylene copolymer is ethylene vinyl acetate (EVA).

In some aspects, the composition includes at least one thermoplastic polymer which is a polymer or copolymer including a plurality of functional groups in its chemical structure, wherein the plurality of functional groups are selected from hydroxyl groups, carboxyl groups, amine groups, amide groups, urethane groups, and combinations thereof.
According to a further embodiment, the present invention is also directed to the processes as disclosed herein, wherein the thermoplastic polymer composition comprises at least one polymer selected from a thermoplastic polyurethane, a polychloroprene, a polystyrene, a polyamide, a polyolefin, a polyacrylate, or a mixture thereof.

The composition typically is applied at elevated temperature to produce adhesive coatings. The composition can for example be applied as a melt at temperatures from preferably 60 °C to 220 °C, more preferably from 80 °C to 200 °C, even more preferably, from 80 °C to 200 °C the foam to be coated, the coated surface being coated at least partly with the composition comprising the thermoplastic polymer.

The application amount of the composition comprising the thermoplastic polymer is preferably in the range from 1 wt.-% to 30 wt.-%, more preferred from 5 wt.-% to 20 wt.-% based on the total weight of the coated particle.

Preferably, the composition comprises a thermoplastic polyurethane. According to a further embodiment, the present invention is also directed to a process as disclosed herein, wherein the thermoplastic polymer is a thermoplastic polyurethane.

Suitable thermoplastic polyurethanes typically comprise the reaction product of
a) a polyisocyanate component,
b) a polyol component, and
c) optionally a chain extender component.

The reaction may or may not be carried out in the presence of a catalyst. According to a further embodiment, the present invention is also directed to a process as disclosed herein, wherein the thermoplastic polyurethane is the reaction product of the building components a polyol, an isocyanate and eventually a chain extender.

The starting materials are preferably selected to adjust the flow beginning temperature of the thermoplastic polyurethane. The flow beginning temperature may for example be adjusted by reducing the hard segment content of the thermoplastic polyurethane.

According to the present invention, also mixtures of polyols or mixtures of chain extenders may be used to adjust the flow beginning temperature. Also, the structure of the polyol might be adjusted by choosing suitable monomers or mixtures of monomers to influence the flow beginning temperature. Furthermore, the molecular weight and/or chain length of the chain extender used may be adjusted to influence the flow beginning temperature.

Adjustment of the molecular weight of the thermoplastic polyurethane by choosing a suitable molar ratio of the NCO/OH groups also influences the flow beginning temperature. According to the present invention, also two or more of these adjustments can be used to achieve an ideal combination of hardness, flow beginning temperature, and other properties.

According to a further embodiment, the present invention is also directed to a process as disclosed herein, wherein the isocyanate is an aromatic isocyanate, an aliphatic isocyanate, an alicyclic isocyanate, and combinations thereof.

The isocyanate component may comprise one or more polyisocyanates. In some useful embodiments, the polyisocyanate component includes one or more diisocyanates. Suitable polyisocyanates include aromatic diisocyanates, aliphatic diisocyanates, cyclo aliphatic diisocyanates or combinations thereof. In some embodiments, the polyisocyanate component includes one or more aromatic diisocyanates. In some embodiments, the polyisocyanate component is essentially free of, or even completely free of, aliphatic diisocyanates. In other embodiments, the polyisocyanate component includes one or more aliphatic diisocyanates and/or cyclo aliphatic diisocyanates.

In some embodiments, the polyisocyanate component is essentially free of, or even completely free of, aromatic diisocyanates. In some embodiments, mixtures of aliphatic and aromatic diisocyanates may be useful. Examples of useful polyisocyanates include aromatic diisocyanates such as 4,4'-methylenebis(phenyl isocyanate (4,4’-MDI), 2,4-diphenylmethane diisocyanate (2,4-MDI), 2,2'-diphenylmethane diisocyanate (2,2’-MDI), m-xylene diisocyanate (XDI), phenylene-1,4-diisocyanate (1,4-PDI), naphthalene-l,5-diisocyanate (NDI), 4,4'-diisocyanato-1,2-diphenylethane, 3,3'-dimethyl-4,4'-biphenylene diisocyanate (TODI) and toluene diisocyanate (TDI); as well as aliphatic diisocyanates such as ethylene diisocyanate (EDI), 1,4-butane diisocyanate (BDI), 1,6-hexamethylene diisocyanate (HDI), decane-1,10-diisocyanate, 1,12-dodecane diisocyanate (DDI), lysine diisocyanate (LDI); and cyclo aliphatic diisocyanates like isophorone diisocyanate (IPDI), 1,4-cyclohexyl diisocyanate (CHDI), and dicyclohexylmethane-4,4'-diisocyanate (H12MDI). Isomers of these diisocyanates may also be useful. Mixtures of two or more polyisocyanates may be used. In some embodiments, the polyisocyanate is MDI and/or H12MDI. In some embodiments, the polyisocyanate consists essentially of MDI. In some embodiments, the polyisocyanate consists essentially of H12MDI.

According to a further embodiment, the present invention is also directed to a process as disclosed herein, wherein the aromatic isocyanate more preferably selected from the group consisting of 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4-diphenylmethane diisocyanate, 2,2'-diphenylmethane diisocyanate, urethane-modified liquid 4,4'-diphenylmethane diisocyanate and/or 2,4-diphenylmethane diisocyanate, 4,4’-diisocyanato-1,2-diphenylethane, 1,5-naphthalene diisocyanate, and combinations thereof.

According to a further embodiment, the present invention is also directed to a process as disclosed herein, wherein the aromatic isocyanate most preferably is 4,4'-diphenylmethane diisocyanate (4,4'-MDI).

According to a further embodiment, the present invention is also directed to a process as disclosed herein, wherein the aliphatic isocyanate is more preferably selected from the group consisting of 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,12-docecane diisocyanate, and combinations thereof.

According to a further embodiment, the present invention is also directed to a process as disclosed herein, wherein the aliphatic isocyanate most preferably is 1,6-hexamethylene diisocyanate (HDI).

According to a further embodiment, the present invention is also directed to a process as disclosed herein, wherein the alicyclic isocyanate more preferably selected from the group consisting of isophorone diisocyanate, 1,4-cyclohexane diisocyanate, 1-methyl-2,4-cyclohexane diisocyanate, 1-methyl-2,6-cyclohexane diisocyanate and its corresponding isomer mixture, 4,4'-, 2,4-, and 2,2'-dicyclohexylmethane diisocyanate and their corresponding isomer mixtures, and combinations thereof.

According to a further embodiment, the present invention is also directed to a process as disclosed herein, wherein the alicyclic isocyanate most preferably is 4,4'-dicyclohexyl-methane diisocyanate (H12MDI).

The thermoplastic polyurethanes are also made using b) a polyol component. Polyols, which may also be described as hydroxyl terminated intermediates, useful in the present invention include polyester polyols, polyether polyols, polycarbonate polyols and combinations thereof. The polyester polyols preferably are linear polyesters. Hydroxyl terminated polymeric intermediates having a number average molecular weight (Mn) of preferably from about 300 to about 10,000, 10 for example, about 400 to about 8,000 Daltons, further for example about 500 to about 6,000 Daltons. The molecular weight is determined by assay of the terminal functional groups and is related to the number average molecular weight. Unless otherwise noted, the molecular weight can be determined via end group quantification or can be calculated from the OH number according to EN ISO 4629-1:2016 in the context of the present invention.

According to a further embodiment, the present invention is also directed to a process as disclosed herein, wherein the polyol is a polyol with a number average molecular weight between 0.4 x 103 g/mol and 6 x 103 g/mol, measured according to end group quantification.

Suitable polyester intermediates may 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, or (3) ring opening polymerization, ex. polycaprolactone diol (PCL-diol), Polylactide diol (PLA-diol), etc. 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. The dicarboxylic acids of the desired polyester can be aliphatic, cycloaliphatic, aromatic, or combinations thereof. Suitable dicarboxylic acids which may be used alone or in mixtures generally have a total of from 4 to 44 carbon atoms and include: succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, isophthalic, terephthalic, cyclohexane dicarboxylic, dimer fatty acid 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 44 or from 2 to 36 carbon atoms. Suitable examples include ethylene glycol, 1,2-propanediol, 1,3-propanediol, 2-methyl-1,3-propanediol,1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 3-methyl-1,5-pentanediol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol, 1,4-cyclohexanedimethanol, decamethylene glycol, dodecamethylene glycol, dimer fatty diol and mixtures thereof.

Suitable hydroxyl terminated polyether intermediates include polyether polyols derived from a diol or polyol having a total of from 2 to 15 carbon atoms. In some embodiments, the hydroxyl terminated polyether is 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(tetramethylene glycol) comprising water reacted with tetrahydrofuran which can be described as polymerized tetrahydrofuran, and which is commonly referred to as PTMEG.

Suitable polyurethanes described herein are made using optionally c) a chain extender component. Suitable chain extenders include low molecular weight diols (molecular weight less than 500 g/mol), diamines, and combination thereof. Suitable chain extenders include relatively small polyhydroxy compounds, for example lower aliphatic or short chain glycols having from 2 to 20, or 2 to 12, or 2 to 10 carbon atoms. Suitable examples include ethylene glycol (EDO), diethylene glycol (DEG), propylene glycol (PDO), dipropylene glycol (DPG), 1,4-butanediol (BDO), 2-methyl-1,3-propanediol (MPO), 1,6-hexanediol (HDO), 1,3-butanediol (1,3-BDO), 1,5-pentanediol (1,5-PDO), neopentyl glycol (NPG), 1,4-cyclohexanedimethanol (CHDM), 2,2-bis[4-(2-hydroxyethoxy)phenylpropane (HEPP), hexamethylenediol (HDO), heptanediol, nonanediol (NDO), dodecanediol (DDO), 3-methyl-1,5-pentanediol (MPD), hydroquinone bis(2-hydroxyethyl) ether (HQEE), ethylenediamine (EDA), butanediamine (BDA), hexamethylenediamine (HDA), and hydroxyethyl resorcinol (HER), and the like, as well as mixtures thereof. In some embodiments the chain extender includes BDO, HDO, 3-methyl-1,5-pentanediol, or a combination thereof. In some embodiments, the chain extender includes BDO. Other glycols, such as aromatic glycols could be used. In some embodiments, the composition is formed using less than 40% by weight, for example only less than 30% by weight, preferably less than 25%, for example, less than 15%, further for example, less than 12%, in particular less than 8% by weight of the total reactants of a chain extender. In some embodiments, the thermoplastic polyurethanes are essentially free of or even completely free of chain extender.

According to a further embodiment, the present invention is also directed to a process as disclosed herein, wherein the chain extender is selected from ethylene glycol, propanediol, butanediol, pentanediol, hexanediol, or is a mixture thereof, more preferably the chain extender is butanediol, hexanediol, cyclohexane dimethanol (CHDM), hydroquinone bis(2-hydroxyethyl)ether (HQEE), or is a mixture thereof.

The thermoplastic polyurethanes used according to the present invention typically have a hard segment content less than 50 wt%, preferred less than 40 wt%. Optionally, one or more polymerization catalysts may be present during the polymerization reaction. Generally, any conventional catalyst can be utilized to react the diisocyanate with the polyol intermediates or the chain extender. Examples of suitable catalysts which in particular accelerate the reaction between the NCO groups of the diisocyanates and the hydroxy groups of the polyols and chain extenders are the conventional tertiary amines known from the prior art, e.g. triethylamine, dimethylcyclohexylamine, N-methylmorpholine, N,N'-dimethylpiperazine, 2-(dimethylaminoethoxy)ethanol, diazabicyclo[2.2.2]octane and the like, and also in particular organometallic compounds, such as titanic esters, iron compounds, e.g. ferric acetylacetonate, tin compounds, e.g. stannous diacetate, stannous octoate, stannous dilaurate, bismuth compounds, e.g. bismuth trineodecanoate, or the dialkyltin salts of aliphatic carboxylic acids, e.g. dibutyltin diacetate, dibutyltin dilaurate, or the like. The amounts usually used of the catalysts are from 0.001 to 0.1 part by weight per 100 parts by weight of polyol component. In some embodiments, the reaction to form the thermoplastic PU used according to the present invention is substantially free of or completely free of catalyst.

Various types of optional components can be present during the polymerization reaction, and/or incorporated into the composition comprising the thermoplastic polymer described above to improve processing and other properties. These additives include but are not limited to antioxidants, such as phenolic types, rheology modifiers, such as hydrophobic or hydrophilic fumed silica, and adhesion promoters, such as malonic acid, fumaric acid, chlorinated rubber, vinyl chloride/vinyl acetate copolymers, vinyl chloride/vinyl acetate/maleic acid terpolymers. Other additives may be used to enhance the performance of the composition or blended product, such as other resins, including but not limited to coumarone-indene or terpene-phenolic which may help increase the tackiness of the hot-melt adhesive when hot and slow the recrystallization time. All of the additives described above may be used in an effective amount customary for these substances.

Further additives can be used including pigments, dyes, odor, filling agents, bio-based and/or biodegradable additives, UV-, heat-stabilizer, flame retardants such as expandable graphite, additives which generate antistatic properties, electrical conductivity, additives, which reduce dirt-uptake, antimicrobial additives, wax, crosslinking agents, surface functionalized fillers, foamable additives such as Expancell®, heat conductive additives and additives which can be irradiated by an electromagnetical field, and/or radio frequency, and/or microwave.

Exemplary additives are mentioned in DE 10 2021 205 928 A1, like heat conductive additives, e.g. a metal nitride, a metal oxide, a metal carbide, a metal sulfide, a metal silicate, a silicon carbide and silicon nitride, particularly preferably boron nitride, BN, SILATHERM® (a mixture of Al_2O_3 and SiO_2) or SILATHERM® Advance. Exemplary electrical conductive additives are a mixture of a carbon material and an inorganic material, carbon fiber, glassy carbon, carbon nanotubes, carbon nanobuds, aerographite, linear acetylenic carbon, q-carbon, graphene, a salt, a monocrystalline powder, a polycrystalline powder, an amorphous powder, a glass fiber.

The additives can be incorporated into the components of, or into the reaction mixture for the preparation of the thermoplastic polymer and then melted or they can be incorporated directly into the melt of the thermoplastic polymer.

The thermoplastic polyurethane can be manufactured by any means known to those of ordinary skill in the art, such as for example batch processes, REX line procedure or Belt line procedure. For example, the components: (a) the diisocyanate component, (b) the polyol component, and (c) the optional chain extender component are reacted together to form the thermoplastic PU useful in this invention. Any known processes to react the reactants may be used to make the thermoplastic PU. In one embodiment, the process is a so-called "one-shot" process where all the reactants are added together, mixed and reacted. The equivalent weight amount of the diisocyanate to the total equivalent weight amount of the hydroxyl containing components, that is, the polyol intermediate and, if included, the chain extender glycol, can be from about 0.5 to about 1.30, or, from about 0.6 to about 1.20, or from about 0.7 to about 1.10. Reaction temperatures utilizing a urethane catalyst can be from about 175 °C to about 245 °C preferably from 180 °C to 220 °C in the reaction zone of a Twin-Screw Reactive Extruder (REX line) procedure; or from about 80°C to about 160°C preferably from 90°C to 150°C in the reaction zone of a Belt line procedure.

As another example, the thermoplastic PU can also be prepared utilizing a pre-polymer process.

In the pre-polymer route, the polyol component is reacted with generally an equivalent excess of one or more diisocyanates to form a pre-polymer solution having free or unreacted diisocyanate therein in the presence of a suitable urethane catalyst. Subsequently, a chain extender, as noted above, is added in an equivalent amount generally equal to the isocyanate end groups as well as to any free or unreacted diisocyanate compounds. The overall equivalent ratio of the total diisocyanate to the total equivalent of the polyol intermediate and the chain extender is thus from about can be from about 0.5 to about 1.30, or, from about 0.6 to about 1.20, or from about 0.7 to about 1.10. Typically, the pre-polymer route can be carried out in any conventional device.

The described process for preparing the thermoplastic PU includes both the "pre-polymer" process and the "one-shot" process, in either a batch or continuous manner. That is, in some embodiments the thermoplastic PU may be made by reacting the components together in a "one shot" polymerization process wherein all of the components, including reactants are added together simultaneously or substantially simultaneously to a mixer and reacted to form the thermoplastic PU. While in other embodiments the thermoplastic PU may be made by first reacting the polyisocyanate component with some portion of the polyol component forming a pre-polymer, and then completing the reaction by reacting the pre- polymer with the remaining reactants, resulting in the thermoplastic PU. After exiting the extruder, the composition may be pelletized and stored and is ultimately sold in pellet form; or could be extruded directly from the reaction extruder through a die into a final product profile.

For reasons of better recycling it is preferred that the chemical nature of the particles and the coating is the same, especially a PU hot melt adhesive and eTPU particles.

Another aspect of the present invention is a process for the preparation of a shaped body comprising the steps of

b_1) coating of particles according to the process of the present invention.

b_2) shaping the particles obtained from step b_1).

Preferably, the shaping in step b_2) is carried out by steam-less thermo-pressing, steam chest molding and/or by means of an electromagnetic field, especially radio frequency, preferably steam-less thermo-pressing.

Preferably, the thermo-pressing (also called hot press or heat press) is carried out at a temperature of from 60 °C to 160 °C, more preferably from 80 °C to 160 °C, even more preferably from 90 °C to 140 °C, even more preferably from 100 °C to 140 °C.

Preferably, after shaping by thermo-pressing the resulting shaped bodies are cooled down to room temperature, which can improve mechanical properties.

Preferably, the shaped body is a composite material of the particles with other materials, like textile, leather, a thermoplastic film or parts containing metals, especially electronic parts.

Another aspect of the present invention relates to a method for disposing a shaped body comprising the steps of

c_1) preparing a shaped body according to the process of the present invention;

c_2) disassembling the particles by subjecting the shaped body to heat, preferably by contacting the particles with hot water, which may optionally contain a surfactant.

The at least partly coated particles according to the present invention can be used pure, as a mixture of different particles and/or other materials to obtain 3D parts, like the shaped bodies of the present invention, for various utilities including industrial, consumer, transportation, and construction-application used solely or as a component for sealing, insolation of e.g. houses, pipelines or gas-tanks, part of a shoe, shoe midsole, shoe insert, shoe combi sole, bicycle seats, bicycle tires, dampening element, shock protection, sound and vibration dampers, decoration, furniture, upholstery, mattress, yoga matts, underlayment, railway pads, handles, protective sheet, packaging, fall protection, automotive interior and exterior, headliner, arm rest, door lining, seats, battery housing, sport equipment, balls, tennis-racket, base-ball club, treadmill, toys, flooring, running tracks, artificial turf, play-grounds, sport halls, and sidewalks.

Accordingly, another aspect of the present invention is the use of a storage-stable, at least partly coated particle or a shaped body of the present invention for industrial, consumer, transportation, and/or construction-applications, especially for the utilities mentioned above.

Description of the figures

Figure 1 shows a structure drawing Shimadzu Flowtester CFT-500EX.
(1) die orifice stopper
(2) cylinder
(3) heater
(4) die
(5) die presser
(6) piston
(7) press joint
(8) load shaft
(9) temperature detector
(10) potentiometer(for stroke detection)
(11) load lever
(12) weight lifting air cylinder
(13) solenoid valve
(14) balance weight
(15) wheel set
(16) control unit (CPU)
(17) weight
(18) movement supporting point

It is composed of the main unit which heats and pressurizes the sample inserted into the cylinder, extrudes the melted sample through the die orifice for test, and the control unit which calculates the shear rate and viscosity based on the measured data concerning the cylinder temperature and the piston moving distance.

The sample is charged in the cylinder and heated by the heater outside the cylinder. The force generated by the weight is multiplied by the load lever, applied to the piston through the load shaft and extrudes the sample through the die orifice. The piston stroke is detected by the potentiometer.

The potentiometer value is read by the instrument control unit. The now rate is then calculated from the relationship between the extrusion time and the piston stroke to obtain shear rate and viscosity.

The loading mechanism generates load force 10 times larger than the weights by combining the wheel set with lever ratio 1:2 and the load lever with lever ratio 1:5. The wheel set and the load lever operate in unison via the connecting steel strip. As the load shaft upper and lower portions are secured with the guide bearings, the load shaft moves vertically but its horizontal movement is restricted. When the weight lifting cylinder is going up or down, the load force is not generated by the weights. However, when the cylinder is going down, the load force is generated in the load shaft, which extrudes the sample. When the load shaft goes up and down, the weight lever movement supporting point moves on the flat supporting point bearing horizontally to prevent any force other than the horizontal force from applying to the load shaft.

Figure 2 shows a schematic view of the cylinder unit. The cylinder (c) comprises the die holder (dh) and the heater (h). The sample (s) is placed between the die (d) and the piston (p).

Figure 3 shows a schematic view of the die. The die (d) has a die length (dl), a die orifice diameter (ddi) and a die width (do).

Figure 4 shows a schematic flow test curve with a constant heating-rate method. The piston stroke (PS, y-axis) is plotted versus the temperature (T, x-axis). The points A and B mark the preheating period. B and C determine the softening region. Between points 40 C and D, there is a non-flow region. Starting at D and continuing over point E, a flow region is shown. The softening temperature (Ts) and the flow beginning temperature (Tfb) are also marked.

Figure 5 shows a set up involving a more direct coating unit which made up of a jacketed hot melt container (19) up to 170 ml and 4 bar connected to a Schlick atomise nozzle (20), which is heated by a gas heater unit (21) and process air (arrows). A ploughshare (22) has been chosen in order to enable thorough mixing properties until the beads are tacky-free. The set up temperature is controlled by a thermostat (23).

Examples

Used materials:

1) Polyurethane based hot melts:

All selected PU hot melts are not sticky at room temperature, remain stable under storage condition, and will activate when temperature increase. Unlike cross-linking TPU, mechanical properties (hardness, tensile strength…) are given by hydrogen bonding (or other intermolecular force such as VDW and π- π interaction) between polymer chain which are reversible. The following are specified properties for selected hot melts:

Hot melt 1:

- Consists of Polyester made of adipic acid and butanediol with F= 2 and Mn: 3000g/mol, 1,4-butanediole (BDO), and Methylene diphenyl diisocyanate (4-4'-MDI)
- Hardness: 96A/45D
- Hard segment: ~6%
- Lamination temperature: 100 – 110 °C
- Melting point: ~50 °C
- Tfb: 80 °C

Hot melt 2:

- Consists of Polyester made of adipic acid and butanediol with F= 2 and Mn: 1000g/mol, HDO, and 4,4’-MDI
- Hardness: 80A
- Hard segment: ~15%
- Lamination temperature: 110 – 150 °C
- Tfb: 105 °C

Hot melt 3:

- Consists of Polyester made of adipic acid and butanediol with F= 2 and Mn: 1000g/mol, PTHF 1000g/mol and F=2, BDO, and a 50/50 mixture of 4,4’-MDI and 2,4’-MDI
- Hardness: 60A
- Hard segment: ~26%
- Lamination temperature: 110 – 120 °C
- Tfb: 95 °C

Hot melt 4:

- Consists of Polyethylene glycol with Mn: 3400g/mol and F=2, BDO, and 4,4’-MDI
- Hardness: 96A/45D
- Hard segment: ~9%
- Melting point: ~50 °C

Hot melt 5:

- Consists of Polyester made of adipic acid and butanediol with F= 2 and Mn: 5000g/mol and 4,4'-MDI
- Hardness: 97A/50D
- Hard segment: 0%
- Melting point: ~60 °C
- Tfb: 60 °C

Hot melt 6:

- Consists of Polyester made of adipic acid and butanediol with F= 2 and Mn: 1000g/mol, BDO and Hexamethylene diisocyanate (1,6-HDI)
- Hardness: 90A
- Hard segment: ~7%
- Melting point: ~110 °C
- Tfb: 110 °C

Hardness of the PU hot melts was measured according to ASTM D2240 - 15 Standard Test Method for Rubber Property — Durometer Hardness

The amount of hard segments (HS) in wt.-% was calculated according to the following equation, wherein m(CE) is the mass in g/mol of the chain extender, m(iso) the mass in g/mol of the isocyanate and m(polyol) the mass in g/mol of the polyol:

$$HS = \frac{m(CE) + m(iso\ reacted\ with\ CE)}{m(polyol) + m(CE) + m(iso)}$$

The melting point was measured via DSC according to ASTM D3418 – 12 Standard Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry, heating rate: 10 °C/min, cooling rate: 10 °C/min.

The molecular weight of the polyols was calculated from their hydroxyl number, which was measured according to ASTM E1899 - 16 Standard Test Method for Hydroxyl Groups Using Reaction with p-Toluenesulfonyl Isocyanate (TSI) and Potentiometric Titration with Tetrabutylammonium Hydroxide:

$$hydroxyl\ number\ (OH\#) = \frac{(V_2 - V_1) * N * 56.1}{sample, g}$$

with N = concentration of Bu_4NOH in meq/mL,
V_1 = mL Bu_4NOH to first potentiometric end point,
V_2 = mL Bu_4NOH to second potentiometric end point, and
sample, g = mass of sample in grams.

$$molecular\ weight\ \left(\frac{g}{mol}\right) = \frac{56100 * number\ of\ OH\ groups\ per\ molecule}{OH\#}$$

Preparation of the PU hot melts

A mixture of each component was heated to 80 °C with stirring by using a paddle mixer (SHIN KWANG GR-150R) for 1-3 minutes at a rotation speed of 500-1,000 revolutions per 25 minutes (rpm). The TPU HMA is then discharged. The TPU HMA was post-heat treated at 100°C for 1-5 hours and then pelletized.

2) Polyester hot melt adhesive

Hot melt adhesive Dynacoll® 7130: Solid, amorphous, saturated copolyester. Chemical structure according to WO 2009/010324 A1.
Tg: 30 °C
OH number: 35 mg KOH/g

Example 1 - Measurement of flow beginning temperature (Tfb)

The flow beginning temperature (Tfb) of a sample is measured by putting a sample (s) in a hollow cylinder with a die comprising a channel, allowing molten sample to flow through this channel, put the sample under a piston in the hollowed cylinder with a load, heating the sample until the sample melts and leaks through the channel, and determining the temperature the sample begins to flow (=flow beginning temperature (Tfb)).

The experimental setup is described in JIS K 7311 and JIS K 7210 standard. The general setup of the apparatus used is shown in Figure 1. A heatable concentric hollow cylinder with a piston in this hole as presented in Figure 2. The hole of the cylinder is closed on the bottom with a die comprising a channel as in detail described in Figure 3. This cylinder is placed in a device for determining the Tfb. The device is constructed to allow the channel of the die to be closed by screwing the die presser at the bottom of the cylinder and press the die strictly fitting to the bottom of the cylinder. Closing of the channel of the die is important for removing air from the sample before the experiment starts. Removing the air is done by compressing the sample in the hole of the cylinder with a piston being pressed towards the die with a specific load without increasing the temperature of the cylinder. After removing the air, the piston with a specific load is set on the sample and the sample is heated by heating the cylinder with a constant increase of the temperature and in parallel plotting the temperature around the sample. As soon as the sample reaches the flow beginning temperature (Tfb), the melt starts leaking through the channel of the die by the pressure of the piston loaded with the specific load. The temperature, the piston starts to move is detected by a suitable move detecting means. The temperature the piston starts to move is the flow beginning temperature (Tfb).

The device used in all experiments is Shimadzu CFT-500D, from Shimadzu Corporation, Tokyo, Japan. The sample was collected and cut to pieces not greater in maximal diameter than not larger than the diameter of the cylinder, preferable not larger than 5 mm, most preferable not larger than 2 mm. The temperature of the cylinder with the piston was conditioned to 30 ° C +/- 2 °C well before the measurement.

1.9 g of cut pieces of the sample were filled in the hole of the preheated cylinder closed with a die with a channel of 1 mm (details see Figure 1). A plunger rod was used to bring the sample to the bottom of the hole. The hole with the sample then was closed with the piston. The die being used in this measurement has a Di = 1mm, Dl = 10mm, as shown in Figure 3.

The channel of the die then was closed with the means for closing the channel and the air was removed from the sample by pressing the piston 3 times repeatedly towards the sample with a load of 100 kg. After that, the means for closing the channel was removed to open the channel again.

The sample under the piston with a load of 100 kg then was held at a temperature of 30°C for 240 seconds. After that, under continued load of 100 kg the sample was heated with a heating rate of 3 °C/min and the temperature close to the sample was continuously plotted.

The flow beginning temperature (Tfb) is the temperature when the piston started to move under the load when molten sample started to pass through the channel of the die. A typical diagram for determining the flow beginning temperature (Tfb) can be taken from Figure 4.

It is not obligatory to use Shimadzu CFT-500D, from Shimadzu Corporation, Tokyo, Japan for measuring the flow beginning temperature (Tfb). Other devices with a similar geometry of the cylinder will lead to the same results of the flow beginning temperature (Tfb) within the scope of this invention.

Example 2 - Experiments with hot melt adhesive solutions

Preparing a Polyurethane hot melt adhesive solution

Dissolve selected Polyurethane hot melt in MEK solution, adjust amount of PU hot melt to achieve 50 – 100 (cps, 25 °C) solution viscosity, using a Brookfield viscometer to measure the solution viscosity (TPU holt melt already dissolve in MEK solution), with 61 LV spindle at 30 rpm, the solid content of these solution is 5 – 15%w/w

Coating hot melt on eTPU bead via solution coating pathway

The selected PU hot melt adhesive was dissolved in MEK solution, the solution viscosity should below 100 cps (25 °C) which can be achieve by adjust solid content. Above solution were mixed with eTPU beads (made according to WO2013/153190 A1, Infinergy 230 based on Diisocyanate 4, BDO, and Polyol 1, company BASF SE) using mechanical agitator for 30 second at room temperature. The beads were dried on a Teflon coated plate at RT, keeping attention to isolate them from each other. After 5 – 20 minutes drying, the coated beads are tack-free and storage stable. The coating amount of hot melt were 7% to 12% to the beads.

Heat press molding

Put coated eTPU beads into shoe cavity plate, then heat press molding with specified conditions

- Temperature: 120, 130, 140, 150 °C
- Heating time: 10, 15 min
- Cooling time: 5 – 15 min

eTPU beads coated with hot melt 1 and 2, accordingly to the procedure described in experiment 2 were heat press (15 minutes, heating at 140 °C and 15 minutes cooling, mold temperature 140 °C). The mechanical properties are reported in the table below. As a comparison a eTPU plate made via steam chest molding is reported.

Forming process	**Coating agent**	**Tensile strength (MPa)***	**Elongation at break (%)***
Heat pressing molding	Hot melt 1 7.7 w/w% on bead	2.6	360
Heat pressing molding	Hot melt 2 11 w/w% on bead	2.3	340
Steam chest molding	-	1.2	211

***** according to ASTM D412-16 (2021): “Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers, and by using a eTPU strip of dimension: 10.5x2.5x1.5cm^3 (length, bright, depth)

Example 3 - Experiment with molten hot melt adhesive and spray coating

The setup according to Figure 4 was used and successfully tested with the commercial non-reactive hot melt adhesive Dynacoll® 7130. The setup works at maximum of 200 °C and a viscosity of 10 mPas. The thermoplastic particle foams (eTPU foamed particles) were tempered at 80 °C prior to the coating step. The following conditions were used:

Final Product:	eTPU coated with Dynacoll® 7130
Bulk density:	0.120 kg/l

Product amount:	2000 g
Coating amount	113.0 g (5.65%)
Throughput rate:	5 g/min.
Uptake rate atomised air:	70 %
Atomised air pressure:	3.3 bar
T1 Gas heater exit:	165°C
T2 nozzle gas control:	168°C
T3 nozzle gas ahead of nozzle:	166°C
Temperature hot melt container:	165°C
Pressure hot melt container:	2.5 bar
Mixer:	ploughshare mixer
Number of revolutions mixer:	50 rpm

Coated eTPU beads were obtained.
The same experiment was repeated to with a coating amount of 7%.

Experiment 4. Coating of eTPU beads via spray gun and kitchen mixer

The hot melt 5 in granular form was placed in the cartridge unit (TR 80 LCD cartridge) of a spray gun (Reka Klebetechnik). The hot melt 5 was molten at a temperature of 160 °C and then spraying by using a pressure of 6 bar.
100 g of eTPU beads (made according to WO 2013/153190 A1, Infinergy 230 based on Diisocyanate 4, BDO, and Polyol 1, company BASF SE) were placed in a kitchen machine (Cooking Chef XL KCL95) and kept at room temperature under motion with the help of a paddle mixer. The molten hot melt was sprayed on the beads, kept under motion for a period of time of two minutes. A coating amount of 10 w/w% was achieved.

The same procedure was repeated by keeping the beads temperature during the spraying process at 70 °C, which lead to a better distribution of the hot melt coating on the eTPU beads.

The same procedure, by keeping the eTPU beads at 70 °C during the spraying process, was repeated by using the hot melt 6

Experiment 5. Realization of plates by using coated eTPU beads

65 g of eTPU beads, coated with hot melt 6 according to experiment 4, were placed in a preheated mold of dimension (16.3x9.6x3.3 cm^3 (length, bright, depth)). The filled mold was covered with a mold lid, which allows a compression/compactaction of 50%. The time in the heated press and the residual time for cooling down the 3 D parts prior to demolding are summarized in the following table.

As a reference, 65 g of eTPU beads according to WO2013/153190 A1 were placed in a pre-heated mold of dimension (16.3x9.6x3.3 cm³ (length, bright, depth)). The filled mold was covered with a mold lid, which allows a compression/compactation of 50%. This results in a plate with the following dimensions: 16x9.5x1.6 cm³. The hot press molded 3 D parts obtainable be not coated eTPU beads are reported respectively.

The tensile strength and the elongation measured according to ASTM D 5035:2011, where instead of fabric strips (150 x 25,4 x 1,6) mm³ eTPU strips were used, the rebound measured according to DIN 53512:2000-4 and the density of the obtained 3 D parts measured according to DIN EN ISO 845:2009-10, are as well reported below

Experiment	Hot melt 6	Temperature [°C]	Heating Time [min]	Cooling [min]	Tensile strength [MPa]	Elongation [%]	Rebound [%]	Density [g/cm³]
5.1	10%	140	10	5	1.54	289	71	0.29
5.1-C	0%	140	10	5	0.7	100	73	0.29

<u>Experiment 6. Coating eTPU bead via powder coating pathway with PU hot melt powder</u>

The selected PU hot melt adhesive 6 was milled to fine powder (100 to 600µm). The powder was mixed with eTPU beads (made according to WO2013/153190 A1, Infinergy 230 based on Diisocyanate 4, BDO, and Polyol 1, company BASF SE), in defined weight ratio in order to achieve a coating amount of 5w/w%, 10w/w% and 15w/w% respectively. The eTPU beads were pre-heated to at least 120 °C. After homogeneously mixing, remove residue powder by filtration. The coated beads are take-free and storage stable. The coating amount of hot melt were 5% to 15% to the beads.

By using eTPU coated beads with hot melt 6 (10.8 w/w% coating to the bead) plates were realized via heat press molding according to the procedure described in experiment 2. The temperature of the mold was kept at 110 °C for 15 minutes with a cooling time of 9 minutes.

The following mechanical data were obtained:

Forming process	**Coating agent**	**Tensile strength (MPa)***	**Elongation at break (%)***
Heat pressing molding	Hot melt 6 10.8 w/w% on bead	2.2	515
Steam chest molding	-	1.2	211

***** according to ASTM D412-16 (2021): “Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers, and by using a eTPU strip of dimension: 10.5x2.5x1.5 cm^3 (length, bright, depth)

Experiment 7. Realization of hot melt coated beads with different chemical nature than eTPU

Additional coating experiments, according to the procedure described in Example 2, 3 and 4, other beads differing from eTPU were used. The same experimental set-up was used for coating: lose ePA beads (produced by the procedure described in WO 2021/052881 A1), expanded lose ePP beads (Neopor, BASF), eTPO (Argilix-O, JSP), expanded, lose ePS beads (Styropor), and lose eTPA beads (produced by the procedure described in WO 2017/220671 A1).

Plates out of the coated beads were realized according to experiment 5 by using the same bead art or by mixing beads of different chemistry coated with the same hot melt.

Experiment 8. Realization of composite (Plate/Textile) by using Hot melt coated eTPU beads

A piece (16.3x9.6cm2) of cotton canvas (0,45mm thickness, standard cotton tissue, Type 10A of Fa. Rocholl) was placed in the mold described in experiment 5. Then, the coated eTPU beads were inserted in the preheated mold at 140 °C and a plate was realized according to the procedure described in experiment 5. A plate, bonded to the cotton canvas textile was realized.

Experiment 9. Debonding of eTPU plated made with hot melt coated beads

An eTPU plate bonded with the cotton canvas textile, according to experiment 7, was placed in an oven, previously heated to a temperature of 30 Minutes. The plate was kept for 30 Minutes in the oven: After taking it out from the oven, the cotton canvas textile was easy delaminated by hand from the eTPU plate.

Alternatively, an eTPU plate, bonded with the cotton canvas textile, according to experiment 7, was placed in a water bath kept at a temperature of 80 °C under agitation (650 rpm). After 30 minutes delamination of the plate from the textile was observed.

The same procedure war repeated, by keeping the water batch temperature at 90 °C. After 30 Minutes, not only the textile was delaminated from the plate, but also the beads of the plates got separated from each other and recovered.

The identical procedure, repeated, by keeping the water batch temperature of 60 °C or lower than 60C did not results in delamination or bead disassembly. This guarantees the stability of the assembly during lifetime, such as washing cycle at temperature identical/small than 60 °C.

Claims

1. A process for the preparation of storage-stable particles of a moldable thermoplastic particle foam at least partly coated with a hot melt adhesive, comprising the steps of

   a_1) bringing the particles into contact with the hot melt adhesive in order to obtain the coated particles;
   a_2) moving the coated particles until the particles are tacky-free.

2. The process of claim 1, wherein the moldable thermoplastic particle foam has a glass transition temperature (Tg) of below 100 °C, measured via DSC according to DIN EN ISO 11357-3:2013.

3. The process of claim 1 or 2, wherein the hot melt adhesive is a non-reactive hot melt adhesive.

4. The process of any of claims 1 to 3, wherein the hot melt adhesive is brought into contact in form of its molten state.

5. The process of any of claims 1 to 4, wherein the hot melt adhesive in its molten state has a viscosity in the range from 0.1 mPas to 800000 mPas, measured at 160 °C.

6. The process of any of claims 1 to 5, wherein the hot melt adhesive in its molten state has a viscosity in the range from 1 mPas to 600000 mPas, measured at 160 °C.

7. The process of any of claims 1 to 6, wherein the hot melt adhesive in its molten state has a viscosity in the range from 10 mPas to 500000 mPas, measured at 160 °C.

8. The process of any of claims 1 to 3, 5 to 7, wherein the hot melt adhesive is brought into contact in form of its solid state by powder coating.

9. The process of any of claims 1 to 3, 5 to 7, wherein the hot melt adhesive is brought into contact in form of a solution, wherein the hot melt adhesive is dissolved in an organic solvent, followed by the step of

   a_3) removing the organic solvent and/or drying the particles after step a_2) at a temperature below the softening point of the hot melt adhesive in order to obtain the coated particles.

10. The process of any of claims 1 to 9, wherein the moldable thermoplastic particle foam is an expanded thermoplastic elastomer.

11. The process of claim 10, wherein the expanded thermoplastic elastomer is expanded thermoplastic polyurethane.

12. The process of any of claims 1 to 11, wherein in step a_1) the bringing into contact is realized by mixing or spraying.

13. The process of any of claims 1 to 12, wherein the at least partly coated particles are coated in an amount of from 0.1 wt.-% to 40 wt.-% based on the total weight of particle and coating.

14. The process of any of claims 1 to 13, wherein after step a_1) and before step a_2) the particles are separated from each other.

15. The process of any of claims 1 to 14, wherein the hot melt adhesive is a composition comprising a thermoplastic polymer.

16. The process of claim 15, wherein the the thermoplastic polymer is a thermoplastic polyurethane.

17. The process of claim 15 or 16, wherein the composition comprising the thermoplastic polymer has a flow beginning temperature (Tfb) in the range of from 50 °C to 160 °C.

18. The process of any of claims 15 to 17, wherein the composition comprising the thermoplastic polymer has a flow beginning temperature (Tfb) in the range of from 60 °C to 160 °C.

19. The process of any of claims 15 to 18, wherein the composition comprising the thermoplastic polymer has a flow beginning temperature (Tfb) in the range of from 70 °C to 160 °C.

20. The process of any of claims 15 to 19, wherein the composition comprising the thermoplastic polymer has a flow beginning temperature (Tfb) in the range of from 70 °C to 150 °C.

21. A process for the preparation of a shaped body comprising the steps of

    b_1) coating of particles according to the process of any of claims 1 to 20;

    b_2) shaping the particles obtained from step b_1).

22. The process of claim 21, wherein the shaping in step b_2) is carried out by steam-less thermo-pressing, steam chest molding and/or by means of an electromagnetic field, especially radio frequency

23. The process of claim 22, wherein the shaping in step b_2) is carried out by steam-less thermo-pressing.

24. The process of claim 22 or 23, wherein the thermo-pressing is carried out at a temperature from 60 °C to 160 °C.

25. The process of any of claims 22 or 24, wherein the thermo-pressing is carried out at a temperature from 80 °C to 160 °C.

26. The process of any of claims 22 to 25, wherein the thermo-pressing is carried out at a temperature from 90 °C to 140 °C.

27. The process of any of claims 22 to 26, wherein the thermo-pressing is carried out at a temperature from 100 °C to 140 °C.

28. The process of any of claims 21 to 27, wherein the shaped body is a composite material of the particles with other materials, like textile, leather, a thermoplastic film or parts containing metals, especially electronic parts.

29. A storage-stable, at least partly coated particle of a moldable thermoplastic particle foam which is at least partly coated with a hot melt adhesive, wherein the coated particle is tacky-free.

30. The storage-stable, at least partly coated particle of a moldable thermoplastic particle foam of claim 29, wherein the hot melt adhesive is a non-reactive hot melt adhesive.

31. A shaped body obtainable from a process of any of claims 21 to 28 or obtained by molding of particle foams according to claim 29 or 30.

32. Use of a storage-stable, at least partly coated particle of claim 29 or 30 or a shaped body according to claim 31 for industrial, consumer, transportation, and/or construction applications.

FIG.1

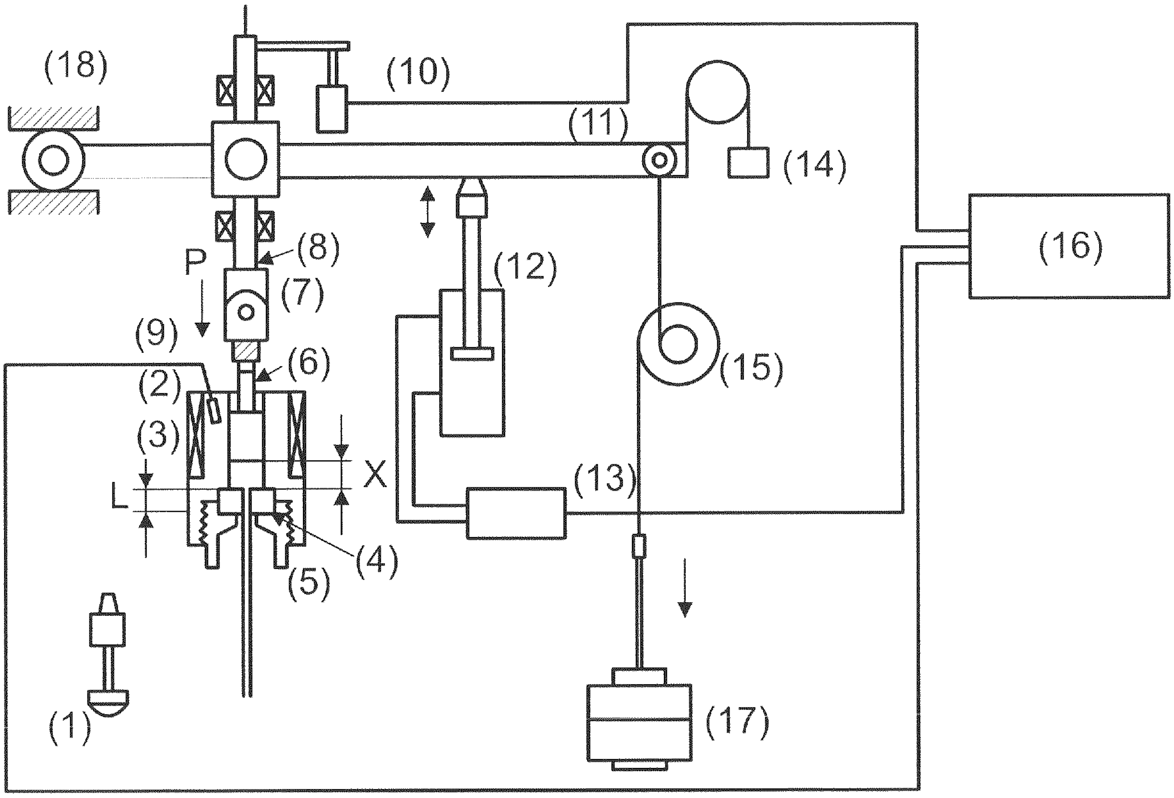


FIG.2

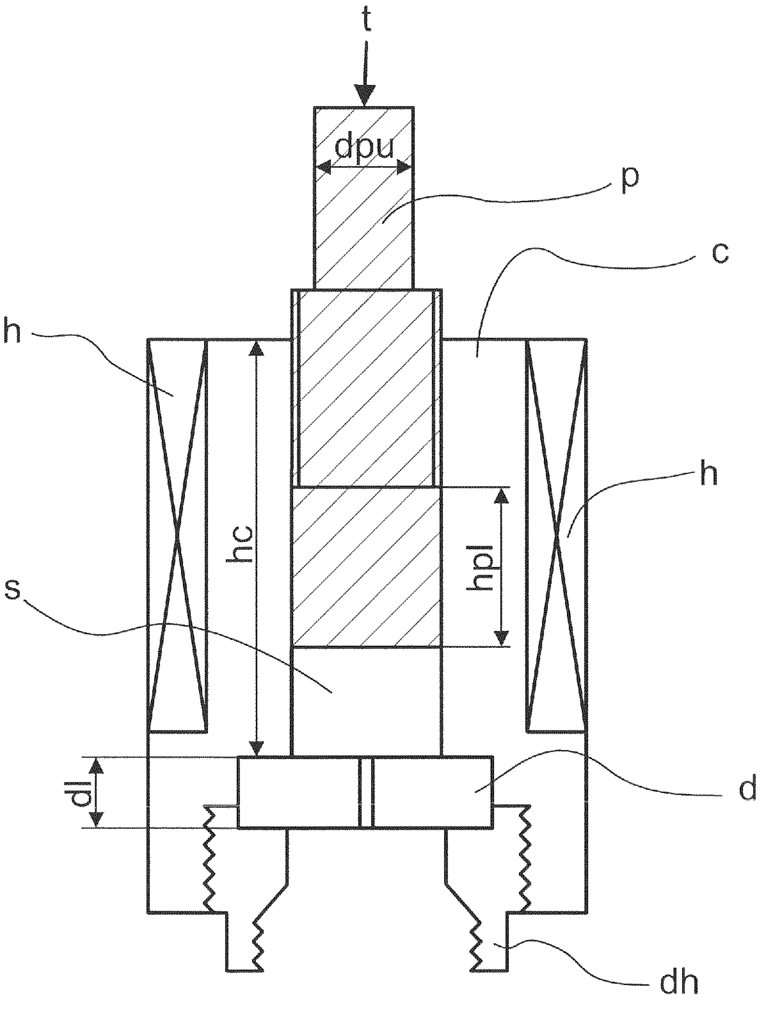


FIG.3

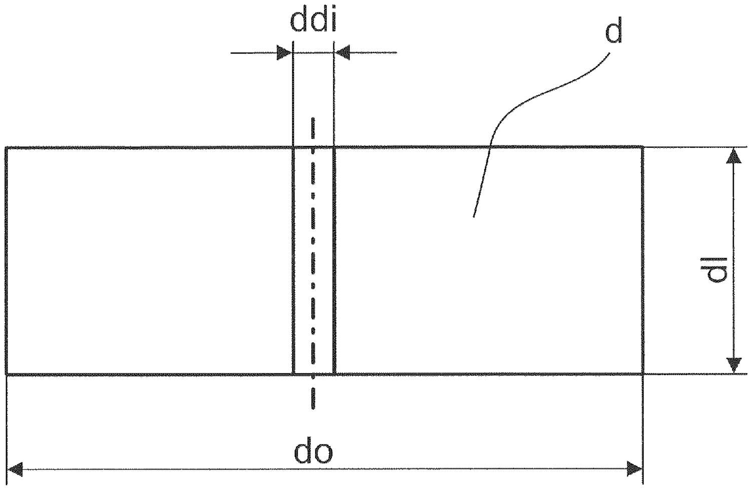


FIG.4

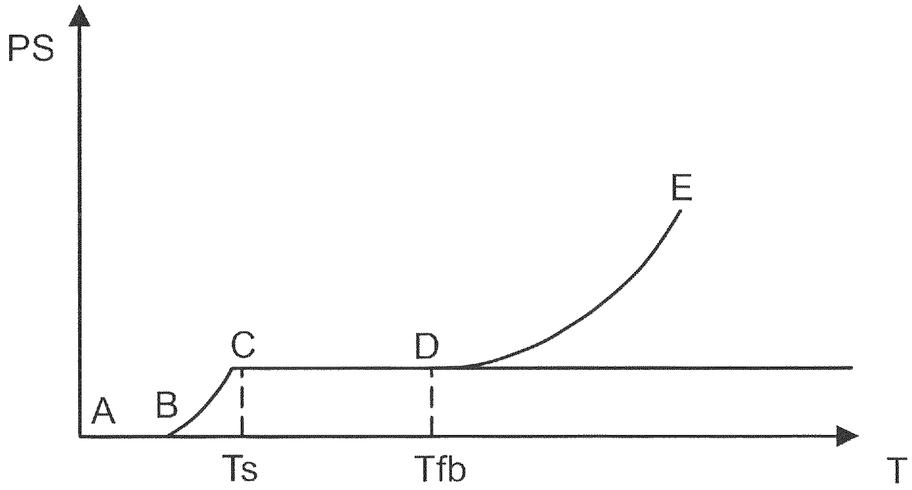
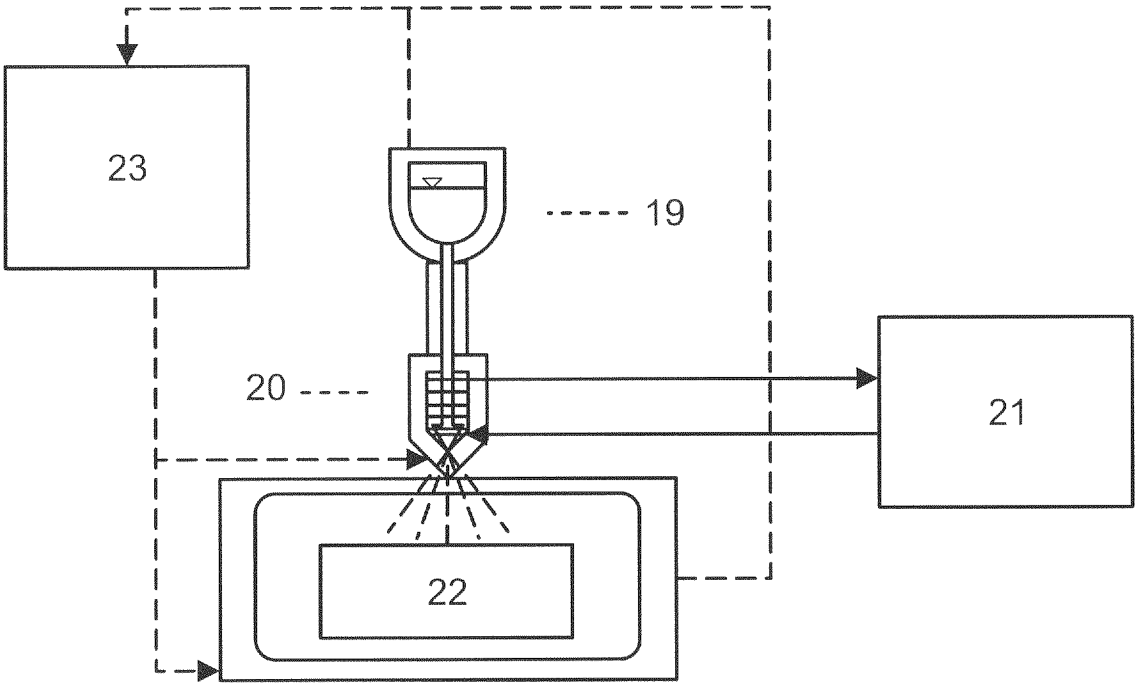


FIG.5



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/058101

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J9/224 B29C44/00 C08J7/04 C08J9/232 C08J9/236
ADD.

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)
C08J B29C

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.
X	WO 2022/117331 A1 (EVONIK OPERATIONS GMBH [DE]) 9 June 2022 (2022-06-09)	1,2,5-7, 9,12-22, 25-29, 31,32
Y	example 2 page 8, lines 6-24; claims 1-5 page 11, line 19 - page 12, line 2 page 12, line 31 - page 14, line 14 -----	3,8,10, 11,30
X	JP 2001 181437 A (SEKISUI CHEMICAL CO LTD) 3 July 2001 (2001-07-03)	1,2,4-7, 9,12-29, 31,32
Y	paragraphs [0001], [0007], [0013], [0015], [0020]; examples 3, 6 claims 1-5 ----- -/--	3,8,10, 11,30

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search 17 May 2024	Date of mailing of the international search report 03/06/2024
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 Mayer, Anne

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2019/367698 A1 (WANG GUANGFU [CN] ET AL) 5 December 2019 (2019-12-05) cited in the application claims 1-5; example 1 -----	3,8,10, 11,30

1

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Information on patent family members

International application No

PCT/EP2024/058101

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		PT 3569647 T	13-12-2022
		US 2019367698 A1	05-12-2019
		WO 2018129791 A1	19-07-2018