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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 Lemförde (DE). **BOLZE, Patrick**; Elastogranstraße 60, 49448 Lemförde (DE). **CHEN, Po Han**; No. 18, Lugong South 5th Rd, Lukang, 50544 (TW). **JIN, Hai Liang**; No. 2333 Gang Cheng Road, Shanghai 200137 (CN). **GEHRINGER, Lionel**; Carl-Bosch-Strasse 38, 67056 Ludwigshafen am Rhein (DE).

(74) Agent: **ALTMANN STÖSSEL DICK PATENTANWÄLTE PARTG MBB**; Dr. Andreas Altmann, Isartorplatz 1, 80331 München (DE).

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(54) Title: BONDING OF PARTS TO AN ARTICLE AND SEPARATING THE ARTICLE FOR RECYCLING

(57) Abstract: The present invention is directed to A process for bonding at least two parts to form an article comprising those two parts using a composition comprising a thermoplastic polymer, wherein the thermoplastic polymer composition preferably has flow beginning temperature (Tfb) 5 measured according to method example 1 in the range of from 50 °C to 160 °C. The present invention further is directed to an article derived from a process according to the invention as well as a process for separating the respective article into its parts by using heat.



Bonding of parts to an article and separating the article for recycling

The invention belongs to the bonding of parts to form an article with a hotmelt adhesive (HMA), preferably with a hotmelt adhesive (HMA) comprising thermoplastic polyurethane (TPU) and the separating of these parts by using heat.

Producing articles from different parts by gluing these parts is a well-known process in industry. Now since environmental awareness has raised during the last years the decomposition of articles is becoming more and more important.

Consumer good manufactures increasingly demand concepts to increase sustainability by increasing recycle rates of used bonded articles. For example, high performance sport shoes are often based on thermoplastic or thermoset polymers such as thermoplastic or thermoset polyurethanes which are bonded to other materials, for example non-polyurethane materials such as ethylene-vinyl acetate, polyester textiles or synthetic leather. The non-polyurethane materials have to be removed after the life cycle of the article by a debonding on demand mechanism before recycling and re-use of the thermoplastic polymers, in particular the thermoplastic polyurethane. Also separation of cross-linked polyurethanes and subsequent recycling of separated cross-linked polyurethane foams is possible via glycolysis.

Similar needs exist in other technical areas to release bonded components of different materials to be able to separately recycle the different materials, for example car seats or instrumental boards, dashboards, meat or cheese food packaging etc. WO 2019/175151 A1 for example describes a method for making thermoplastic polyurethanes from recycled polyurethane materials. This method requires debonding non-polyurethane materials from the polyurethane materials. WO 2018/156689 describes de-bondable adhesives and uses thereof for making and debonding articles of footwear. Debonding is achieved by use of carboxylic acids and salts thereof and by use of microwave irradiation.

There remains a need for improved methods particularly in the footwear industry that facilitate the recycling of shoe components. The problem on which the invention is based is that of providing a method for preparing bonded articles made of different components, such as for example shoes, to recycle the different components (e.g. upper materials and soles) under mild conditions, with comparatively low energy consumption in short cycle-times. The bonded articles should, under normal storage, use and cleaning conditions, exhibit high resistance to premature debonding. It is a challenge to provide materials with high bond strength during regular use of the articles but which when subjected to stimulation by suitable conditions are easily debonded on demand in short time for recycling purposes.

It was an object of the present invention to provide materials which are suitable as adhesives or for bonding two or more components and allow for the debonding of the respective articles obtained. This also allows to reuse the components without complete decomposition of the respective components.

The problem is solved in accordance with the invention by a process for bonding at least two parts to form an article comprising those two parts using a composition comprising a thermoplastic polymer.

- 5 It has been found that bonded articles can be prepared according to the present invention which can be debonded using mild conditions. This allows to separate the parts and reuse or recycle the separate parts.

10 According to the present invention, at least two parts are bonded. The parts may comprise different materials and may also vary in shape and size. According to the present invention, it is also possible that the at least two parts comprise the same material. At least two parts are bonded to form an article. According to the present invention, the article may also comprise further parts or components.

15 According to the present invention, a composition comprising a thermoplastic polymer is used for bonding. The composition may comprise further components such as for example further thermoplastic polymers, solvents or additives. According to the present invention, the composition typically has a softening point above about 50°C and below 160°C. The melting point of the composition comprising the thermoplastic polymer typically has to be adapted to allow bonding
20 of the parts without affecting the surface or the properties of the parts which form the article according to the present invention. The composition comprising the thermoplastic polymer is used as an adhesive according to the present invention. Bonding is preferably achieved by physical softening at elevated temperatures and re-solidification on cooling according to the present invention.

25 The composition comprising a thermoplastic polymer may also be denoted as hotmelt adhesive in the context of the present invention.

30 A hotmelt adhesive typically is solid at room temperature, solvent-free and meltable above room temperature. The hotmelt 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. Hotmelt 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, hotmelt adhesives cool and solidify
35 to form a strong bond between articles. Bonds formed with thermoplastic hotmelt adhesives are reversible. Under sufficiently high thermal stress, thermoplastic hot-melt adhesives will liquefy and lose their cohesive strength.

40 The melting point measured by differential scanning calorimetry (DSC) of a composition comprising a thermoplastic polymer, in particular a thermoplastic polyurethane, is preferably from about 50°C to about 160°C, or from about 50°C to about 130°C. The test method refers to ASTM D 3418 - 12⁸¹ by using the Hitachi High-Tech Co., DSC7000X.

It was surprisingly found that the flow beginning temperature (Tfb) of the composition comprising the thermoplastic polymer has an influence on the bonding and debonding properties of the composition. The adjustment of the flow beginning temperature in a suitable range can be used to influence the temperature behavior of the adhesive strength to obtain good bonding properties under conditions of usage of an article but also to allow for easy debonding using comparatively mild conditions.

It has been surprisingly found that an advantageous combination of good bonding and debonding using mild conditions can be achieved using a 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 method example 1 referring to JSI K7311-1995 and K7210-1999 and by using the Shimadzu Flowtester Capillary Rheometer CFT-500D. It has been found that it is possible to avoid the delamination of the article at elevated temperature which might for example occur during a transportation period in a container.

According to a further embodiment, the present invention is also directed to a process as disclosed above, wherein the thermoplastic polymer composition has flow beginning temperature (Tfb) measured according to method example 1 in the range from 50 °C to 160 °C, preferably from 60 °C to 160 °C, more preferably from 80 °C to 160 °C, more preferably from 90 °C to 150 °C, most preferably be from 100°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, which allows them to be used as adhesives, without damaging the different parts to be bonded during application.

The compositions 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).

- 5 In some aspects, the composition includes at least one thermoplastic polymer 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.
- 10 According to a further embodiment, the present invention is also directed to a process as disclosed above, wherein the thermoplastic polymer composition comprises at least one polymer selected from a thermoplastic polyurethane, a polychloroprene, a latex, a polystyrene, a polyamide, a polyolefin, a polyacrylate, or a mixture thereof.
- 15 According to the present invention, the composition comprising the thermoplastic polymer is applied in an amount and a way that allows bonding of the parts to form an article. 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 80 to 220°C to the materials to be coated, the coated surface being coated at least partly with the composition comprising the thermoplastic polymer.
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The application amount of the composition comprising the thermoplastic polymer is preferably in the range from 10 g/m² to 700 g/m², preferred from 20 to 600 g/m², more preferred from 50 to 500 g/m², particularly preferred from 100 to 400 g/m².

- 25 The application can be effected by applying the melt by doctor blading technology, spraying, gravure, dot, or pattern or by applying a coating at higher temperature. According to the present invention, it is also possible to apply the composition comprising the thermoplastic polymer as a film.

- 30 According to a further embodiment, the present invention is also directed to a process as disclosed above, wherein the thermoplastic polymer composition is a film.

- 35 According to the present invention, it is possible to apply a film which essentially consists of the composition comprising the thermoplastic polymer is also possible to apply a film which comprises a layer essentially consisting of the composition comprising the thermoplastic polymer and a further layer comprising a further adhesive layer, for example a layer comprising a thermoplastic polymer or crosslinked adhesives such as one component polyurethane adhesives or two component polyurethane adhesives (carrier layer). According to the present invention, the carrier layer can be coated with the composition comprising the thermoplastic polymer or the composition comprising the thermoplastic polymer may be applied in a suitable pattern not covering the carrier layer completely.
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Preferably, the composition comprises a thermoplastic polyurethane. According to a further embodiment, the present invention is also directed to a process as disclosed above, wherein the thermoplastic polymer is a thermoplastic polyurethane.

- 5 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 above, wherein the thermoplastic polyurethane of the film is the reaction product of the building components a polyol, an isocyanate and eventually a chain extender.
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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.

- 15 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.
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- 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.
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- According to a further embodiment, the present invention is also directed to a process as disclosed above, wherein the isocyanate is an aromatic isocyanate, an aliphatic isocyanate, an aliphatic isocyanate, and combinations thereof.
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- 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'-methylenbis(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-1,5-diisocyanate (NDI), 4,4'-diisocyanato-
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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 above, 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 above, 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 above, wherein the aliphatic isocyanate more preferably selected from the group consisting of 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,12-dodecane diisocyanate, and combinations thereof.

According to a further embodiment, the present invention is also directed to a process as disclosed above, 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 above, 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 above, wherein the alicyclic isocyanate most preferably is 4,4'-dicyclohexylmethane 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 (M_n) of preferably from about 300 to about 10,000, 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 above, wherein the polyol is a polyol with a number average molecular weight between 0.4×10^3 g/mol and 6×10^3 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 42 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.

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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), 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)phenyl]propane (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.

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According to a further embodiment, the present invention is also directed to a process as disclosed above, 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.

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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 titanate esters, iron compounds, e.g. ferric acetylacetonate, tin compounds, e.g. stannous diacetate, stannous octoate, stannous dilaurate, bismuth compounds, e.g. bismuth

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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. These additional 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 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.

The application of TPU hot-melt adhesive preferably occurs by hot melt coatings, include but not limited to T-die extrusion, coating, spray, gravure printing, dot coating, pattern printing and injection molding etc to form include but not limited to a film, web, mesh, dot, pattern and article etc for further heat press lamination or direct hot melt coatings on laminate substrates by include but not limited to T-die extrusion, coating, spray, gravure printing, dot coating and pattern printing etc, followed by a pressing with or without heating, and cooling steps. The adhesive can be applied for example using an automated or machine assisted process, e.g. using an automatic sprayer. Adhesives are coated on one or preferable both substrates. The amount of TPU hot-melt adhesive used is preferably from 10 g/m² to 700 g/m² (solid), more preferred from 50 to 500 g/m², particularly preferred from 100 to 400 g/m². Hotmelt polyurethane adhesives are preferably applied in the molten state or as prefabricated films between the substrates, i.e. the parts to be bonded.

The bonded article comprises at least two parts or components which are bonded to one another. Parts of the bonded articles are for example an extruded part, an injection molded part, a pressed part, a foamed part, a cable sheath, a hose, a profiled element, a drive belt, a fiber material, a nonwoven, a film, a molded part, a sole, a sporting good, an part of footwear, a plug, a housing, or a damping element for the electrical industry, for the automobile industry, for machine construction, for 3D printing, for medicine, or for consumer goods. Preferred bonded articles are articles of footwear, parts of articles of footwear, car seats, dashboards, meat or cheese food packaging etc. More preferred are articles of footwear or parts of articles of footwear.

The article of footwear is preferably selected from the group consisting of a shoe, a boot, and a sandal. Suitable shoes are for example an athletic shoe, a tennis shoe, a cross-trainer shoe, a soccer shoe, a children's shoe, a dress shoe, and a casual shoe.

The bond strength preferably is above 5 N/50 mm, more preferably above 10 N/50 mm, most preferably above 20 N/50 mm. The bond strength is preferably from about 5 N/50 mm to material break, more preferably from about 10 N/50 mm to about 1000 N/50 mm, most preferably from about 20 N/50 mm to about 300N/50 mm. The bond strength is measured by a peel test according to ISO 20344:2011, 5.2.

The first part or component of the bonded article may be made from a thermoplastic polymer. The thermoplastic polymer is preferably a thermoplastic elastomer, more preferably an expanded thermoplastic elastomer. A thermoplastic polymer is a plastic polymer material that becomes pliable or moldable at a certain elevated temperature and solidifies upon cooling. Example of thermoplastic polymers are thermoplastic polyethylene, thermoplastic polypropylene, thermoplastic polyvinyl chloride, thermoplastic polystyrene, thermoplastic polyamides, thermoplastic polyesters, and thermoplastic polyurethanes. Thermoplastic elastomers preferably consist of phase-separated block copolymers and combine the performance benefits of rubber like flexibility and elasticity with the easy processability of thermoplastic polymers.

Suitable materials for the first component are thermoplastic elastomers, for example selected from the group consisting of thermoplastic polyurethane (TPU), thermoplastic copolyamide (for example thermoplastic copolyetherpolyamide), thermoplastic copolyester elastomer (for example copolyetherester or copolyesterester), styrenic block copolymers (for example styrene-butadiene block copolymer) thermoplastic ethylene vinylacetate and mixtures or blends thereof.

When a thermoplastic polyurethane is used, the thermoplastic polyurethane may be any desired thermoplastic polyurethane known to a person skilled in the art. Thermoplastic polyurethanes and their methods of making have already been extensively described, for example in Gerhard W. Becker and Dietrich Braun, *Kunststoffhandbuch*, Volume 7, Polyurethane, Carl Hanser Verlag, Munich, Vienna, 1993. The thermoplastic polyurethane is preferably prepared by reacting a mixture of isocyanates with isocyanate-reactive compounds, preferably having a molecular weight of 0.5 kg/mol to 10 kg/mol and optionally chain-extending agents, preferably having a molecular weight of 0.05 kg/mol to 0.5 kg/mol. The thermoplastic polyurethane is preferably prepared by further adding to the mixture at least one chain transfer agent, a catalyst and optionally at least one filler, auxiliary or additive.

Expanded polymers, also known as foamed materials, or foams, and particularly expanded polymer particles, also called particle foams, are known and have been extensively described in the literature, for example in Ullmann's "Enzyklopadie der technischen Chemie", 4th edition, volume 20, p. 416 ff. Most preferred materials for the first component are expanded thermoplastic polyurethanes (E-TPU). Suitable E-TPU and methods of their production are described for example in WO 2007/082838, in W02013/153190 or in WO2015/052265.

The polyurethane of the expanded thermoplastic polyurethane can be prepared by reacting a mixture of isocyanates and isocyanate-reactive compounds. Preferred are aliphatic, cyclo ali-

phatic, and/or aromatic isocyanates as organic isocyanates. Particular preference is given to using aromatic, aliphatic and/or cycloaliphatic diisocyanates. Examples of preferred diisocyanates are trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, heptamethylene diisocyanate, octamethylene diisocyanate, 2-methyl-1,5-pentamethylene diisocyanate, 2-ethyl-1,4-butylene diisocyanate, 1,5-pentamethylene diisocyanate, 1,4-butylene diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane, 1,4-bis(isocyanatomethyl)cyclohexane, 1,3-bis(isocyanatomethyl)cyclohexane, 1,4-cyclohexane diisocyanate, 1-methyl-2,4-cyclohexane diisocyanate, 1-methyl-2,6-cyclohexane diisocyanate, 2,2'-dicyclohexylmethane diisocyanate, 2,4'-dicyclohexylmethane diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, 2,2'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, 1,5-naphthylene diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, diphenylmethane diisocyanate, 3,3'-dimethylbiphenyl diisocyanate, 1,2-diphenylethane diisocyanate and phenylene diisocyanate.

The isocyanate-reactive compounds comprise at least one compound having at least two isocyanate-reactive hydrogen-containing groups. The isocyanate-reactive hydrogen-containing group is preferably a hydroxyl group. It is particularly preferable for the compound having at least two isocyanate-reactive hydrogen-containing groups to be selected from polyetherol, polyesterol and polycarbonate diol. In this context, polyesterols, polyetherols and/or polycarbonate diols are usually also subsumed under the term "polyols". The thermoplastic polyurethane is preferably prepared from at least one polyether alcohol. It is particularly preferable to use polyether diol. Polytetrahydrofuran is a particularly preferred polyether diol. Preference is given to using polyether alcohols and polytetrahydrofuran having a molecular weight between 0.4 kg/mol and 6 kg/mol. The polyether alcohols are used individually or as a mixture of various polyether alcohols.

Suitable materials for the second part or component of the bonded article are for example those commonly found in the footwear industry and can be selected for example from the group of materials mentioned for the first component or selected from the group consisting of a crepe rubber, a natural leather, a synthetic leather, a polyurethane (for example a polyurethane foam and/or a thermoplastic polyurethane TPU), a thermoplastic rubber, a styrene butadiene rubber, a polyvinyl acetate, a polyamide (PA), a polyvinyl chloride, a polystyrene, an acrylonitrile butadiene styrene, a polyethylene terephthalate (PET), a polybutylene terephthalate, a textile, a fabric, a thermoplastic polyurethane knit fiber and a combination thereof. Preferred is a shoe upper made of PET, TPU or PA. Most preferred is a shoe upper made of PET.

According to a further embodiment, the present invention is also directed to a process as disclosed above, wherein at least one part of the article is selected from the group consisting of a crepe rubber, a natural leather, a synthetic leather, a polyurethane, such as a polyurethane foam and/or a thermoplastic polyurethane, a thermoplastic rubber, a styrene butadiene rubber, a polyvinyl acetate, a polyamide (PA), a polyvinyl chloride, a polystyrene, an acrylonitrile butadiene styrene, a polyethylene terephthalate (PET), a polybutylene terephthalate, a textile, a fabric, a thermoplastic polyurethane knit fiber and a combination thereof.

In particular, one part of the article may be a polyurethane, preferably a thermoplastic polyurethane.

A preferred bonded article is an article wherein a first component is an expanded thermoplastic polyurethane and a second component is a material selected from the group consisting of a crepe rubber, a natural leather, a synthetic leather, a polyurethane, a thermoplastic polyurethane, a thermoplastic rubber, a styrene butadiene rubber, a vinyl acetate, a polyamide, a polyvinyl chloride, a polystyrene, an acrylonitrile butadiene styrene, a polyethylene terephthalate, a textile, a fabric, and a combination thereof.

According to a further embodiment, the present invention is also directed to a process as disclosed above, wherein one part comprises a material selected from the group consisting of a rubber, a natural leather, a synthetic leather, a polyurethane, a thermoplastic polyurethane, a styrene butadiene rubber, a vinyl acetate, a polyamide, a polyvinyl chloride, a polystyrene, an acrylonitrile butadiene styrene, a polyethylene terephthalate, a polybutylene terephthalate, a textile, a fabric, a thermoplastic polyurethane knit fiber, or a combination thereof.

An aspect of the invention is a recyclable article of footwear or portion thereof comprising a first component, a second component, and a polyurethane adhesive adhesively bonding the first component to the second component wherein at least one of the components is made from thermoplastic polyurethane, preferably from an expanded thermoplastic polyurethane.

The first part or component, the second part or component, or both can be any components commonly found in an article of footwear, and preferably comprise a component selected from the group consisting of an upper, an insole, an outsole, a midsole, a strobil, a vamp, a tip, a foxing, a tongue, an eyestay, and a combination thereof. For example, the polyurethane adhesives can adhesively bond an upper and an outsole, an upper and an insole, a midsole and an outsole, or any other combination of components commonly found in the footwear industry.

Preferably, the first component is a shoe sole made of a rubber, a natural leather, a synthetic leather, a polyurethane, a thermoplastic polyurethane, a styrene butadiene rubber, a vinyl acetate, a polyamide, a polyvinyl chloride, a polystyrene, an acrylonitrile butadiene styrene, a polyethylene terephthalate, a polybutylene terephthalate, a textile, a fabric, a thermoplastic polyurethane knit fiber, or a combination thereof, in particular thermoplastic polyurethane; and the second component is a shoe upper, preferably made of polyethylene terephthalate. The first component shoe sole preferably contains a midsole made of expanded thermoplastic polyurethane. The adhesive preferably bonds the shoe upper and the shoe sole and/or the midsole.

According to a further embodiment, the present invention is also directed to a process as disclosed above, wherein one part is a midsole, more preferred a midsole comprising a polyurethane, a polyurethane foam, a thermoplastic polyurethane, an expanded polyurethane, an expanded thermoplastic polyurethane, expanded thermoplastic polyurethane beads, or a mixture thereof.

In some aspects, the adhesives bond two sole components such as an outsole and a midsole. In some aspects, the adhesives bond a sole or sole component to an upper (or to a component of the upper). In some aspects, the upper component is a vamp or a quarter. For example, a thermoplastic polyurethane adhesive described herein can be used to bond an upper surface of an outsole to a lower surface of a midsole. This will allow for easier debonding of the outsole and midsole. An adhesive described herein can be used to bond an upper surface of a midsole to a lower surface of an upper. This will allow for easier debonding of the sole from the upper.

For example a shoe can be formed from a shoe sole and an upper, and the shoe sole includes a shoe outsole and a shoe midsole. Each of these components can be bonded using a de-bondable adhesive described herein. The use of de-bondable adhesives described herein allows for easy debonding, for example for separate recycling of the materials of the upper, the shoe outsole, and/or the shoe midsole.

According to a further embodiment, the present invention is also directed to a process as disclosed above, wherein the article is a shoe.

According to a specific example, the present invention therefore is also directed to a process which comprises suitable steps for preparing a shoe. The process may for example comprise one or more of the following steps:

- (a) surface treatment of the bottom of shoe upper
- (b) applying the composition comprising the thermoplastic polymer, preferably in form of a film;
- (c) preparing and adhering the shoe mid-sole to the shoe upper;
- (d) adhering the shoe midsole could to the shoe upper and shoe outsole.

Surface treatment according to step (a) may include a surface treatment such as a physical treatment, a chemical treatment, a solvent treatment, or any combination thereof. Physical treatments can include treating a surface with an abrasive to increase a surface roughness. Chemical treatments can include etching a surface with acid. Solvent treatments can include contacting a surface with a solvent to remove contaminants from the surface. Preferably, the treating step does not include a primer treatment (i.e. coating with a primer solution before application of the adhesive).

According to step (b), the composition could be applied with the combination of heat treatment and pressure treatment. The heat treatment could be conducted under temperature between for example 100-170°C to softening the surface of film. The pressure treatment is applied for a period of time. The pressure can be for example from about 2000 kPa to about 5500 kPa and the

period of time can be from about 1 minutes to about 30 minutes. The film could be applied to the top surface of shoe outsole as well, with the same process.

The shoe mid-sole could be prepared separately and adhered to the shoe upper by the composition comprising the thermoplastic polymer with the same heat treatment and pressure treatment procedure according to step (c). In detail, treating the bottom surface of HMA adhered shoe upper under temperature between for example 100-170°C to softening the surface of film. Then place the shoe mid-sole to the bottom of HMA adhered shoe upper and apply pressure treatment for a period of time to adhere the shoe mid-sole to shoe upper with HMA in the between. The same process could be applied to adhere the shoe outsole to shoe midsole as well.

According to step (d), the shoe midsole could be adhered to the shoe upper and shoe outsole directly, for example through direct injection process. The bottom of the shoe upper should be adhered to a TPU hotmelt film. The shoe outsole could be adhered with or without TPU HMA film on the top surface.

In case a molding process is used, this process might comprising the steps of:

(d*1) cleaning the bottom die and shoe last, and correspondingly placing the bottom die, a top die and the last so that the last, the top die and the bottom die are sequentially arranged from top to bottom;

(d*2) placing the TPU HMA film adhered shoe upper onto the last to enable the inner side of the shoe upper to be closely attached to the shoe last;

(d*3) placing the TPU HMA adhered shoe outsole on the bottom die in a fitting manner;

(d*4) descending the shoe last to press the part between the bottom of the shoe upper and the top of the bottom die correspondingly, and the shoe last, the shoe upper and the bottom die are closely attached;

(d*5) descending simultaneously the top die and the shoe last are to closely attached to the bottom die.

(d*6) injecting PU mid-sole foaming stock between the TPU HMA adhered shoe upper and the TPU HMA adhered shoe outsole through a feeding hole on the left side of the bottom die, foaming and shaping, melting the surface of TPU HMA at both bottom of shoe upper and top of shoe outsole, further bonding the shoe upper and shoe outsole with PU shoe mid-sole through heat and pressure generated during foaming.

(d*7) cooling, demolding, remove the extra TPU HMA film from the final shoe product.

According to a further embodiment, the present invention is also directed to the use of a composition comprising a thermoplastic polymer with a flow beginning temperature (Tfb) measured according to method example 1 in the range of from 50 °C to 160 °C, preferably from 60 °C to 160 °C, more preferably from 80 °C to 160 °C, more preferably from 90 °C to 150 °C most preferably from 100°C to 150 °C, as an adhesive for the preparation of consumer goods, industrial goods, construction goods, sports equipment, car interior or flooring.

Therefore, according to a further aspect, the present invention is also directed to a process for preparing an article comprising at least a first part (C1) and a second part (C2), the process comprising the steps

(x) providing a first part (C1) and a second part (C2),

(y) providing a composition comprising a thermoplastic polymer with a flow beginning temperature (Tfb) measured according to method example 1 in the range of from 50 °C to 160 °C, preferably from 60 °C to 160 °C, more preferably from 80 °C to 160 °C, more preferably from 90 °C to 150 °C most preferably from 100°C to 150 °C,

(z) bonding the first component and the second component by means of the composition comprising the thermoplastic polyurethane provided in step (y).

According to step (x) a first and a second part are provided. In the context of the present invention, the parts may also be denoted as components. It is also possible to combine three or more parts or components according to the present invention. The components may consist of the same material or of different material and may have the same or different dimensions.

According to a further embodiment, the present invention is also directed to the process as disclosed above, wherein the first component (C1) comprises a thermoplastic polymer.

According to a further embodiment, the present invention is also directed to the process as disclosed above, wherein the first component (C1) comprises a foamed thermoplastic polymer.

According to a further embodiment, the present invention is also directed to the process as disclosed above, wherein the second component (C2) comprises a thermoplastic polymer.

According to the present invention it is for example possible to combine a woven component and one or more further components, for example foamed beads in one step using the composition comprising the thermoplastic polymer as an adhesive.

According to the present invention it is for example possible to combine one component essentially consisting of a polymer foam with a second component which is essentially a woven structure.

The method of bonding the first component to the second component can include various surface treatments of the first component, the second component or both, commonly applied with adhesives. The methods of bonding may include treating one or both of the surface of the first component and the surface of the second component prior to applying the polyurethane adhesive.

The methods of bonding the first component to the second component can include applying pressure to ensure a proper level of bonding between the components. For example, the bonding methods can include applying pressure to the first component and the second component for a period of time to adhesively bond the first component and the second component. The pressure can be for example from about 2000 kPa to about 5500 kPa and the period of time can be from about 5 seconds to 30 minutes, preferably from 1 minute to 25 minutes, in particular from 10 minutes to about 20 minutes but are not limited to it. The methods of bonding can further include applying of heat to adhesively bond the first component and the second component. Suitable ranges are for example from 50 to 170°C.

The composition comprising the thermoplastic polymer could for example be applied in form of a film on the first part, for example the bottom of shoe upper, with the combination of heat treatment and pressure treatment. The heat treatment could be conducted under temperature between for example 50-170°C to softening the surface of the film. The pressure treatment is applied for a period of time. The pressure can be for example from about 2000 kPa to about 5500 kPa and the period of time can be from about 5 second to about 30 minutes. The composition, for example the film could be applied to the second part, for example the top surface of shoe outsole as well, with the same process.

According to the present invention, it is also possible that one or more of the parts is prepared by injection molding as described above. The composition comprising the thermoplastic polymer may for example be placed in a suitable mold, preferably in form of a film and the part can be prepared in situ according to this embodiment.

According to a further aspect, the present invention is also directed to an article derived from a process for bonding as disclosed above. According to a further aspect, the present invention is also directed to an article obtained or obtainable by a process as disclosed above.

The article according to the present invention can be used for a variety of applications, such as shoes, in furniture, seating, automotive interior, automotive exterior, medical equipment, industrial applications, consumer goods such as consumer electronics, wearable devices, headphones, speakers, packaging, protection equipment, as cushioning, toys, animal toys, saddles, balls and sports equipment, for example sports mats, sport gloves, or as floor covering and wall paneling.

The article may also be footwear or part of footwear, preferably selected from the group consisting of a shoe, a boot, and a sandal. Suitable shoes are for example an athletic shoe, a tennis shoe, a cross-trainer shoe, a soccer shoe, a children's shoe, a dress shoe, and a casual shoe.

5 It has been found that the articles according to the present invention can be disassembled using suitable mild conditions which makes them easier to recycle. According to the present invention, it is possible to disassemble the article and obtain the individual components allowing to separate these components and recycle them. This way, mixing of different components can be reduced or avoided. Furthermore, the individual components obtained may also be reused.

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According to a further embodiment, the present invention therefore is also directed to the article as disclosed above, wherein the article can be disassembled into components C1 and/or C2.

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According to a further embodiment, the present invention is also directed to the article as disclosed above, wherein the article is recyclable. In case the components can be recovered in the recycling process, it is possible that the components can be reused as such. Furthermore, it is also possible to recycle the components in a process which includes a further extrusion step of the thermoplastic elastomer.

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According to the present invention it is for example possible to prepare an article by bonding individual components, at least components C1 and C2, to obtain an article. The article can then be disassembled and components C1 and/or C2 can be recovered. Subsequently after suitable separation steps, the components C1 and/o C2 may be reused to prepare an article as set out above.

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According to a further embodiment, the present invention is also directed to the article as disclosed above, wherein the recycling of the article results in components (C1) and/or (C2).

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The article according to the present invention may be suitable for different applications such as for example consumer goods. According to a further embodiment, the present invention is also directed to the article as disclosed above, wherein the article is a consumer good or part of a consumer good.

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It has been found that the articles can be debonded using mild conditions. The debonding can be conducted by treating the article at elevated temperature, for example in an oven or with a solution and depending on the flow beginning temperature of a given material at a temperature in the range of from 75°C below the flow beginning temperature of the composition comprising the thermoplastic polymer to 50°C above the flow beginning temperature of the composition comprising the thermoplastic polymer, preferably in a range from 65°C below the flow beginning temperature of the composition comprising the thermoplastic polymer to 40°C above the flow beginning temperature of the composition comprising the thermoplastic polymer, preferably in a

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range from 50°C below the flow beginning temperature of the composition comprising the thermoplastic polymer to 30°C above the flow beginning temperature of the composition comprising the thermoplastic polymer, preferably in a range from 40°C below the flow beginning temperature of the composition comprising the thermoplastic polymer to 20°C above the flow beginning temperature of the composition comprising the thermoplastic polymer. The debonding can be conducted by treating the article at elevated temperature for a time period of 1 second to 15 minutes, preferentially 15 seconds to 10 minutes, or also at a temperature in the range of from 20°C below the flow beginning temperature of the composition comprising the thermoplastic polymer to 35°C above the flow beginning temperature of the composition comprising the thermoplastic polymer for a time period of 1 second to 15 minutes, preferentially 15 seconds to 10 minutes.

Typically, debonding could be carried out at a temperature in the range from 50°C to 160°C, preferably in a range of from 60°C to 140°C, more preferable in a range of from 70°C to 120°C. Typically debonding is carried out in air, in water environment, steam environment, or dry environment. According to the present invention, debonding may be carried out at a temperature in the range from 50°C to 160°C, in air, in water environment, steam environment, or dry environment.

According to a further embodiment, the present invention is also directed to a process as disclosed above, wherein the article is separated into its parts by using heat. The heat can be supplied via heating in an oven, treatment with heated air, treatment with heated water, heated aqueous solutions including further additives such as for example surfactants, or steam or can be generated using radiation such as for example microwave radiation according to the present invention. According to the present invention, also combinations of these methods can be used.

The at least two components of the bonded article may be debonded by treatment at elevated temperature. If necessary, the bonded article is cut into smaller pieces before debonding.

Debonding occurs preferably after treatment of the bonded article (or of pieces thereof) at temperatures above 75°C below the flow beginning temperature of the composition comprising the thermoplastic polymer, preferably 60°C below the flow beginning temperature of the composition comprising the thermoplastic polymer, in particular 50°C below the flow beginning temperature of the composition comprising the thermoplastic polymer, more preferably in the range of from 50°C below the flow beginning temperature of the composition comprising the thermoplastic polymer to 50°C above the flow beginning temperature of the composition comprising the thermoplastic polymer, in particular more preferably in the range of from 40°C below the flow beginning temperature of the composition comprising the thermoplastic polymer to 50°C above the flow beginning temperature of the composition comprising the thermoplastic polymer for preferably from 5 seconds to 120 minutes, more preferable from 30 seconds to 90 minutes, in particular from 2 to 60 minutes.

According to a further embodiment, the present invention is also directed to a process as disclosed above, wherein the heat for separating the article is at least the temperature of flow begin (Tfb) of the thermoplastic polymer composition.

- 5 According to a further aspect, the present invention is also directed to a process for disassembling an article obtained or obtainable by a process according to the present invention comprising the steps (A) and (B):

10 (A) treating the article at a temperature in the range of from 50°C below the flow beginning temperature of the composition comprising the thermoplastic polymer to 50°C above the flow beginning temperature of the composition comprising the thermoplastic polymer;

(B) recovering component (C1) and/or (C2).

15 Preferably, no residual adhesive remains on the surfaces of the debonded components. This has the advantage that residual adhesive does not interfere in the recycling of the debonded components. According to the present invention it is also possible that a layer of the residual adhesive remains on the debonded components which may be used in a further process without a
20 recycling step.

According to a further embodiment, the present invention is also directed to a process as disclosed above, wherein the heat for separating the article is not higher than 50 °C above the flow
25 beginning temperature (Tfb) of the thermoplastic polymer composition, preferably not higher than 30 °C above, more preferably not higher than 20 °C above, more preferably not higher than 10 °C above, most preferably not higher than 5 °C above.

30 A further object of the invention is a method for debonding and recycling bonded article, wherein a bonded article is debonded according to the method as described above and recycling is accomplished by physically comminuting the debonded thermoplastic polyurethane and chemically treating the comminuted material to produce new thermoplastic polyurethane, for example as described in WO 2019/175151. The comminuted thermoplastic polyurethane is for example used in shredded form, in the form of granules, as an agglomerate, or as a powder.

35 Further embodiments of the present invention can be found in the claims and the examples. It will be appreciated that the features of the subject matter/processes/uses according to the invention that are mentioned above and elucidated below are usable not only in the combination specified in each case but also in other combinations without departing from the scope of the
40 invention. For example, the combination of a preferred feature with a particularly preferred feature or of a feature not characterized further with a particularly preferred feature etc. is thus also encompassed implicitly even if this combination is not mentioned explicitly.

Illustrative embodiments of the present invention are listed below, but these do not restrict the present invention. In particular, the present invention also encompasses those embodiments which result from the dependency references and hence combinations specified hereinafter.

- 5 1. A process for bonding at least two parts to form an article comprising those two parts using a composition comprising a thermoplastic polymer.
- 10 2. A process according to embodiment 1, wherein the thermoplastic polymer composition comprises at least one polymer selected from a thermoplastic polyurethane, a polychloroprene, a latex, a polystyrene, a polyamide, a polyolefin, a polyacrylate, or a mixture thereof.
- 15 3. A process according to any one of embodiments 1 or 3, wherein the thermoplastic polymer composition is a film.
4. A process according to any one of embodiments 1 to 3, wherein the thermoplastic polymer is a thermoplastic polyurethane.
- 20 5. A process according to any one of embodiments 1 to 4, wherein at least one part of the article is selected from the group consisting of a crepe rubber, a natural leather, a synthetic leather, a polyurethane, such as a polyurethane foam and/or a thermoplastic polyurethane, a thermoplastic rubber, a styrene butadiene rubber, a polyvinyl acetate, a polyamide (PA), a polyvinyl chloride, a polystyrene, an acrylonitrile butadiene styrene, a polyethylene terephthalate (PET), a polybutylene terephthalate, a textile, a fabric, a thermoplastic polyurethane knit fiber and a combination thereof.
- 25 6. A process according to any one of embodiments 1 to 5, wherein the thermoplastic polymer composition has flow beginning temperature (Tfb) measured according to method example 1 in the range of from 50 °C to 160 °C, preferably from 60 °C to 160 °C, more preferably from 80 °C to 160 °C, more preferably from 90 °C to 150 °C, most preferably from 100 °C to 150 °C.
- 30 7. A process according to any one of embodiments 1 to 6, wherein the thermoplastic polyurethane of the film is the reaction product of the building components a polyol, an isocyanate and eventually a chain extender.
- 35 8. A process according to embodiment 7, wherein the polyol is a polyol with a number average molecular weight in the range of from 0.4×10^3 g/mol to 6×10^3 g/mol.
- 40 9. A process according to any one of embodiments 7 or 8, wherein the isocyanate is an aromatic isocyanate, an aliphatic isocyanate, an alicyclic isocyanate, and combinations thereof.

10. A process according to any one of embodiments 7 to 9, 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.
11. A process according to any one of embodiments 7 to 10, wherein the aromatic isocyanate most preferably is 4,4'-diphenylmethane diisocyanate (4,4'-MDI).
12. A process according to any one of embodiments 7 to 11, wherein the aliphatic isocyanate more preferably selected from the group consisting of 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,12-dodecane diisocyanate, and combinations thereof.
13. A process according to any one of embodiments 7 to 12, wherein the aliphatic isocyanate most preferably is 1,6-hexamethylene diisocyanate (HDI).
14. A process according to any one of embodiments 7 to 13, wherein the alicyclic isocyanate is 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.
15. A process according to any one of embodiments 7 to 14, wherein the alicyclic isocyanate is 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI).
16. A process according to any one of embodiments 7 to 15, 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.
17. A process according to any one of embodiments 1 to 16, wherein the article is a shoe.
18. A process according to any one of embodiments 1 to 17, wherein one part is a midsole, more preferred a midsole comprising a polyurethane, a thermoplastic polyurethane, a polyurethane foam, an expanded polyurethane, an expanded thermoplastic polyurethane, expanded thermoplastic polyurethane beads, or a mixture thereof.
19. A process according to any one of embodiments 1 to 18, wherein one part comprises a material selected from the group consisting of a rubber, a natural leather, a synthetic leather, a polyurethane, a thermoplastic polyurethane, a styrene butadiene rubber, a vinyl

acetate, a polyamide, a polyvinyl chloride, a polystyrene, an acrylonitrile butadiene styrene, a polyethylene terephthalate, a polybutylene terephthalate, a textile, a fabric, a thermoplastic polyurethane knit fiber, or a combination thereof.

- 5 20. An article derived from a process according to any one of embodiments 1 to 19.
21. A process according to any one of embodiments 1 to 19, wherein the article is separated into its parts by using heat.
- 10 22. A process according to embodiment 21, wherein the heat for separating the article is at least the temperature of flow begin (Tfb) of the thermoplastic polymer composition.
23. A process according to any one of embodiments 21 or 22, wherein the heat for separating the article is not higher than 50 °C above the flow beginning temperature (Tfb) of the thermoplastic polymer composition, preferably not higher than 30 °C above, more preferably not higher than 20 °C above, more preferably not higher than 10 °C above, most preferably not higher than 5 °C above.
- 15 24. A process for bonding at least two parts (C1) and (C2) to form an article comprising those two parts using a composition comprising a thermoplastic polymer.
- 20 25. A process according to embodiment 24, wherein the thermoplastic polymer composition comprises at least one polymer selected from a thermoplastic polyurethane, a polychloroprene, a latex, a polystyrene, a polyamide, a polyolefin, a polyacrylate, or a mixture thereof.
- 25 26. A process according to any one of embodiments 24 or 25, wherein the thermoplastic polymer composition is a film.
- 30 27. A process according to any one of embodiments 24 to 26, wherein the thermoplastic polymer is a thermoplastic polyurethane.
28. A process for bonding at least two parts (C1) and (C2) to form an article comprising those two parts using a composition comprising a thermoplastic polyurethane.
- 35 29. A process according to any one of embodiments 24 to 28, wherein at least one part (C1) or (C2) of the article is selected from the group consisting of a crepe rubber, a natural leather, a synthetic leather, a polyurethane, such as a polyurethane foam and/or a thermoplastic polyurethane, a thermoplastic rubber, a styrene butadiene rubber, a polyvinyl acetate, a polyamide (PA), a polyvinyl chloride, a polystyrene, an acrylonitrile butadiene styrene, a polyethylene terephthalate (PET), a polybutylene terephthalate, a textile, a fabric, a thermoplastic polyurethane knit fiber and a combination thereof.
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30. A process according to any one of embodiments 24 to 29, wherein the thermoplastic polymer composition has flow beginning temperature (Tfb) measured according to method example 1 in the range of from 50 °C to 160 °C, preferably from 60 °C to 160 °C, more preferably from 80 °C to 160 °C, more preferably from 90 °C to 150 °C, most preferably from 100°C to 150 °C.
31. A process for bonding at least two parts (C1) and (C2) to form an article comprising those two parts using a composition comprising a thermoplastic polymer, wherein the thermoplastic polymer composition has flow beginning temperature (Tfb) measured according to method example 1 in the range of from 50 °C to 160 °C, preferably from 60 °C to 160 °C, more preferably from 80 °C to 160 °C, more preferably from 90 °C to 150 °C, most preferably from 100°C to 150 °C.
32. A process according to any one of embodiments 24 to 31, wherein the thermoplastic polyurethane of the film is the reaction product of the building components a polyol, an isocyanate and eventually a chain extender.
33. A process according to embodiment 32, wherein the polyol is a polyol with a number average molecular weight in the range of from 0.4×10^3 g/mol to 6×10^3 g/mol.
34. A process according to any one of embodiments 32 or 33, wherein the isocyanate is an aromatic isocyanate, an aliphatic isocyanate, an alicyclic isocyanate, and combinations thereof.
35. A process according to any one of embodiments 32 to 34, 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.
36. A process according to any one of embodiments 32 to 35, wherein the aromatic isocyanate most preferably is 4,4'-diphenylmethane diisocyanate (4,4'-MDI).
37. A process according to any one of embodiments 32 to 36, wherein the aliphatic isocyanate more preferably selected from the group consisting of 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,12-dodecane diisocyanate, and combinations thereof.
38. A process according to any one of embodiments 32 to 37, wherein the aliphatic isocyanate most preferably is 1,6-hexamethylene diisocyanate (HDI).

39. A process according to any one of embodiments 32 to 38, wherein the alicyclic isocyanate is 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.
40. A process according to any one of embodiments 32 to 39, wherein the alicyclic isocyanate is 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI).
41. A process according to any one of embodiments 32 to 40, 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.
42. A process according to any one of embodiments 24 to 41, wherein the article is a shoe.
43. A process according to any one of embodiments 24 to 42, wherein one part is a midsole, more preferred a midsole comprising a polyurethane, a thermoplastic polyurethane, a polyurethane foam, an expanded polyurethane, an expanded thermoplastic polyurethane, expanded thermoplastic polyurethane beads, or a mixture thereof.
44. A process according to any one of embodiments 24 to 43, wherein one part comprises a material selected from the group consisting of a rubber, a natural leather, a synthetic leather, a polyurethane, a thermoplastic polyurethane, a styrene butadiene rubber, a vinyl acetate, a polyamide, a polyvinyl chloride, a polystyrene, an acrylonitrile butadiene styrene, a polyethylene terephthalate, a polybutylene terephthalate, a textile, a fabric, a thermoplastic polyurethane knit fiber, or a combination thereof.
45. An article obtained or obtainable according to a process according to any one of embodiments 24 to 44.
46. A process according to any one of embodiments 24 to 44, wherein the article is separated into its parts by using heat.
47. A process for debonding an article obtained or obtainable according to a process according to any one of embodiments 1 to 19 or 24 to 44, wherein the article is separated into its parts by using heat.
48. The process according to embodiment 46 or 47, wherein the heat is supplied via heating in an oven, treatment with heated air, treatment with heated water, heated aqueous solutions including further additives such as for example surfactants, or steam or is generated using radiation such as for example microwave radiation.

49. A process according to any one of embodiments 46 to 48, wherein the heat for separating the article is at least the temperature of flow begin (Tfb) of the thermoplastic polymer composition.

50. A process according to any one of embodiments 46 to 49, wherein the heat for separating the article is not higher than 50 °C above the flow beginning temperature (Tfb) of the thermoplastic polymer composition, preferably not higher than 30 °C above, more preferably not higher than 20 °C above, more preferably not higher than 10 °C above, most preferably not higher than 5 °C above.

51. Process for preparing an article comprising at least a first part (C1) and a second part (C2), the process comprising the steps

(x) providing a first part (C1) and a second part (C2),

(y) providing a composition comprising a thermoplastic polymer with a flow beginning temperature (Tfb) measured according to method example 1 in the range of from 50 °C to 160 °C, preferably from 60 °C to 160 °C, more preferably from 80 °C to 160 °C, more preferably from 90 °C to 150 °C, most preferably from 100 °C to 150 °C,

(z) bonding the first component and the second component by means of the composition comprising the thermoplastic polyurethane provided in step (y).

52. Article obtained or obtainable according to the process according to any one of embodiments 24 to 51.

53. Article according to embodiment 52, wherein the article can be disassembled into components C1 and/or C2.

54. Article according to embodiment 52 or 53, wherein the article is recyclable.

55. Article according to any one of embodiments 52 to 54, wherein the recycling of the article results in components (C1) and/or (C2).

56. Process for disassembling an article obtained or obtainable by a process according to any one of embodiments 1 to 55 comprising the steps (A) and (B):

(A) treating the article at a temperature in the range of from 70°C below the flow beginning temperature of the composition comprising the thermoplastic polymer to 50°C above the flow beginning temperature of the composition comprising the thermoplastic polymer;

(B) recovering component (C1) and/or (C2).

57. Process for disassembling an article obtained or obtainable by a process according to any one of embodiments 1 to 55 comprising the steps (A) and (B):

(A) treating the article at a temperature in the range of from 50°C below the flow beginning temperature of the composition comprising the thermoplastic polymer to 40°C above the flow beginning temperature of the composition comprising the thermoplastic polymer;

(B) recovering component (C1) and/or (C2).

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.

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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.

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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.

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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).

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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).

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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 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.

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The invention is further described by examples. The examples relate to practical and in some cases preferred embodiments of the invention that do not limit the scope of the invention.

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EXAMPLES

1. Formulation and characteristic of TPU HMA (used grades)

5 1.1 Hotmelt 1

Diisocyanate: 4,4'-MDI

Polyol: PBA1000 (monomer: adipic acid, 1,4-butanediol, OHv: 112.2 mg KOH/g, Mn: 1,000 g/mol)

10 Chain extender: 1,6-HDO (≈ 5 wt% in TPU HMA)

Hard Segment content: ≈ 15 wt%

DSC-Tm: not detected

Tfb: 105 °C

15 1.2 Hotmelt 2

Diisocyanate: 4,4'-MDI

Polyol: PBA1000 (monomer: adipic acid, 1,4-butanediol, OHv: 112.2 mg KOH/g, Mn: 1,000 g/mol)

20 Polyol: PTHF1000 (monomer: THF, OHv: 112.2 mg KOH/g, Mn: 1,000 g/mol)

Chain extender: 1,4-BDO (≈ 3 wt% in TPU HMA)

Hard Segment content: ≈ 12 wt%

DSC-Tm: 118 °C

Tfb: 125 °C

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1.3 Hotmelt 3

PBA-1000/HDO/MDI, HS ≈ 23.0 wt%

Diisocyanate: 4,4'-MDI

30 Polyol: PBA1000 (monomer: adipic acid, 1,4-butanediol, OHv: 112.2 mg KOH/g, Mn: 1,000 g/mol)

Chain extender: 1,6-HDO (≈ 7 wt% in TPU HMA)

Hard Segment content: ≈ 23 wt%

DSC-Tm: 105 °C

35 Tfb: 118 °C

1.4 Hotmelt 4

Diisocyanate: HDI

40 Polyol: PBA-4000 (monomer: adipic acid, 1,4-butanediol, OHv: 28.0 mg KOH/g, Mn: 4,000 g/mol)

Chain extender: None

Hard Segment content: 0.0 wt%

DSC-Tm: 60 °C

Tfb: 60 °C

5 1.5 Determination of the hard segment content

The hard segment content was calculated according to the following formula:

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

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HS: Hard Segment

m_{CE}: mass of chain extender

m_{iso}: mass of isocyanate

m_{polyol}: mass of polyol

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1.6 Preparation of the hotmelts

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 minute (rpm). The TPU HMA is then discharged. The TPU HMA was post-heat treated at 100°C for 1-5 hours and then pelletized.

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2. **Method 1: Measurement of flow beginning temperature (Tfb)**

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2.1 Principle:

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)).

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2.2 Device:

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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

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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 (T_{fb}), 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 (T_{fb}).

2.3 Detailed description of the measurement:

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 $30^{\circ}\text{C} \pm 2^{\circ}\text{C}$ 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 $D_i = 1\text{mm}$, $D_l = 10\text{mm}$, 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 $3^{\circ}\text{C}/\text{min}$ 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 digramm 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.

3. Experimental part

3.1 Material used

Polyol 1: Polyester based on adipic acid, monoethylene, having an OH number of 52 mg KOH/g and a functionality of 2.00

Polyol 2: Polyesterpolyol based on adipic acid, glycerin, monoethylene glycole and diethylene glycole, with functionality:2.3 and Mw: 2300g/mol

CE: 1,4-butandiol

HS: Elastostab H01® from BASF Polyurethanes GmbH

Isocyanate 1: 4,4'-diphenylmethane diisocyanate (MDI)

From the TPU hotmelts, Hotmelt 1, Hotmelt 2, Hotmelt 3 and Hotmelt 4 as defined above, coming from the BASF Elastollan hotbonds, were selected.

3.2 The thermoplastic hotmelts were used as films in different thickness and applied to the surface of a preformed shoe upper by means of a hot gun (in order to model the TPU film on the 3D upper surface). The same procedure was chosen for fixing the hotbond films to a TPU preformed outsole (Polyester based TPU (Elastollan 565, available from BASF SE).

The TPU shoe outsoles were produced according to WO 15124476 and to WO14095438. The following formulation was used:

Starting material	Weight %
Polyol 1	62.4
1,4-butandiol	4.9
Isocyanate 1	20.9
additives	11.8

The used hotmelts were characterized by a Tfb (flow beginning temperature) of 105°C, 125°C, and 118°C respectively (measured according to method 1 as described above). Table 1 reports the used hotmelts.

5 Sample 1 was used to “coat” the TPU outsole, while sample 2 for coating the shoe upper.

Sample 3 and sample 4 was used for coating both the TPU sole and the shoe upper prior shoe foam injection.

10 Table 1

		Thickness in mm	Tfb °C
Sample 1	hotmelt 1	0.12	105
Sample 2	hotmelt 1	0.25	105
Sample 3	hotmelt 2	0.11	125
Sample 4	hotmelt 3	0.22	118

Shoe foam system 1 was infused using a machine from Maingroup Technologies Srl. (Model: Pragma 1 ST) and the polyurethane foam system 1 as described below were in-
15 fused between upper and outsole to allow realization of the final part.

3.3 An additional experiment was conducted using Hotbond 4, sample 5 with a Tfb of 60C.

Hotbond granulates was molten (temperature 160 C) and applied to a PET fabric (42x20
20 cm², Standard cotton tissue with thickness of 0,45mm, Type 10A of Fa. Rocholl) by using a coating equipment (Coatmaster 510, at a temperature of 140°C, thcikness of Hotmelt in the range of 250-450µm).

25 The coated PET fabric was back-foamed using the shoe foam system 1.

For shoe foam system1, the following A and B component were used at a mixing weight ratio: 100/115 (polyol to diisocyanate)

A component:

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Starting material	W%
Mono ethylene glycol	9.36
Tap Water	0. 64
Polyol 2	80.85
tertiary amine-based catalyst	0.6
surfactant	0.4
high-molecular-weight plasticizer	2.5

B Component:

Polyester based prepolymer, based on 4,4 MDI/ 2,4 MDI (available from BASF SE as Lupranat MRS), 4,4 MDI/Carbodiimide of MDI (available from BASF SE as Lupranat MM103), polyester based on adipic acid, monoethylene glycole and 1,4 butandiol and polyester based on adipic acid, monoethylene glycole, diethylglycol and glycerin, propylene carbonate and stabilized with diglycol-bischlorformiat, NCO content: 18.2%.

The NCO content in weight-% was determined via back titration of the corresponding sample with an excess of di-n-butylamin 1M in chlorbenzene with 1 molar hydrochloric acid.

3.4 Initial adhesion of the different elements of the shoe were performed according to ISO 20344:2011,5.2 at 23°C.

The adhesion between the PET fabric and foam was measured according to ISO 20344:2011,5.2 at 23°C.

4. Bonding results

4.1 Bonding outsole/Midsole

Sample 1	1.32 N/mm
Sample 3	2.39 N/mm
Sample 4	1.19 N/mm

4.2 Bonding Upper/Midsole

Sample 2	0.68 N/mm
Sample 3	0.97 N/mm
Sample 4	0.51 N/mm

4.3 Bonding between PET fabric and shoe foam 1

Material breakage (foam surface) was observed.

Sample 5	2.62 N/mm
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5. Debonding experiments

5.1 In oven

The bonded shoe prepared according to example 3 was placed in an oven for 30 minutes. Experiments were started at an oven temperature of 60°C. After 30 minutes the temperature was raised of 10°C and kept for further 30 minutes. The experiment was repeated up to an oven temperature of 130°C. At a temperature > 80°C the different parts of the shoe could be debonded easier by hand pulling.

5.2 By treatment with hot water

100mL of water were placed in contact with a 2x3cm² shoe piece.

By means of a magnetic stirring bar, the water bath was agitated (200rpm) for 15 minutes.

For the Hotbond 1, 2 and 3, the water bath temperature was raised from room temperature to 90°C.

At a temperature of 70°C the different parts of the shoe were easier separated from each other

For the PET fabrics bonded to the shoe foam by using Hotbond 4, the water bath was kept at a temperature of 60°C: Delamination of the textile from the foam was achieved.

Claims

- 5 1. A process for bonding at least two parts to form an article comprising those two parts using a composition comprising a thermoplastic polymer.
2. A process according to claim 1, wherein the thermoplastic polymer composition comprises at least one polymer selected from a thermoplastic polyurethane, a polychloroprene, a latex, a polystyrene, a polyamide, a polyolefin, a polyacrylate, or a mixture thereof.
- 10 3. A process according to any one of claims 1 or 2, wherein the thermoplastic polymer composition is a film.
- 15 4. A process according to any one of claims 1 to 3, wherein the thermoplastic polymer is a thermoplastic polyurethane.
- 20 5. A process according to any one of claims 1 to 4, wherein at least one part of the article is selected from the group consisting of a crepe rubber, a natural leather, a synthetic leather, a polyurethane, such as a polyurethane foam and/or a thermoplastic polyurethane, a thermoplastic rubber, a styrene butadiene rubber, a polyvinyl acetate, a polyamide (PA), a polyvinyl chloride, a polystyrene, an acrylonitrile butadiene styrene, a polyethylene terephthalate (PET), a polybutylene terephthalate, a textile, a fabric, a thermoplastic polyurethane knit fiber and a combination thereof.
- 25 6. A process according to any one of claims 1 to 5, wherein the thermoplastic polymer composition has flow beginning temperature (Tfb) measured according to method example 1 in the range of from 50 °C to 160 °C, preferably from 60 °C to 160 °C, more preferably from 80 °C to 160 °C, more preferably from 90 °C to 150 °C, most preferably from 100 °C to 150 °C.
- 30 7. A process according to any one of claims 1 to 6, wherein the thermoplastic polyurethane of the film is the reaction product of the building components a polyol, an isocyanate and eventually a chain extender.
- 35 8. A process according to claim 7, wherein the polyol is a polyol with a number average molecular weight in the range of from 0.4×10^3 g/mol to 6×10^3 g/mol.
9. A process according to any one of claims 7 or 8, wherein the isocyanate is an aromatic isocyanate, an aliphatic isocyanate, an alicyclic isocyanate, and combinations thereof.
- 40 10. A process according to any one of claims 7 to 9, 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.

- 5 11. A process according to any one of claims 7 to 10, wherein the aromatic isocyanate most preferably is 4,4'-diphenylmethane diisocyanate (4,4'-MDI).
- 10 12. A process according to any one of claims 7 to 11, wherein the aliphatic isocyanate more preferably selected from the group consisting of 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,12-dodecane diisocyanate, and combinations thereof.
13. A process according to any one of claims 7 to 12, wherein the aliphatic isocyanate most preferably is 1,6-hexamethylene diisocyanate (HDI).
- 15 14. A process according to any one of claims 7 to 13, wherein the alicyclic isocyanate is 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.
- 20 15. A process according to any one of claims 7 to 14, wherein the alicyclic isocyanate is 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI).
- 25 16. A process according to any one of claims 7 to 15, 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.
- 30 17. A process according to any one of claims 1 to 16, wherein the article is a shoe.
18. A process according to any one of claims 1 to 17, wherein one part is a midsole, more preferred a midsole comprising a polyurethane, a thermoplastic polyurethane, a polyurethane foam, an expanded polyurethane, an expanded thermoplastic polyurethane, expanded thermoplastic polyurethane beads, or a mixture thereof.
- 35 19. A process according to any one of claims 1 to 18, wherein one part comprises a material selected from the group consisting of a rubber, a natural leather, a synthetic leather, a polyurethane, a thermoplastic polyurethane, a styrene butadiene rubber, a vinyl acetate, a polyamide, a polyvinyl chloride, a polystyrene, an acrylonitrile butadiene styrene, a polyethylene terephthalate, a polybutylene terephthalate, a textile, a fabric, a thermoplastic polyurethane knit fiber, or a combination thereof.
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20. An article derived from a process according to any one of claims 1 to 19.
21. A process according to any one of claims 1 to 19, wherein the article is separated into its parts by using heat.

Fig. 1

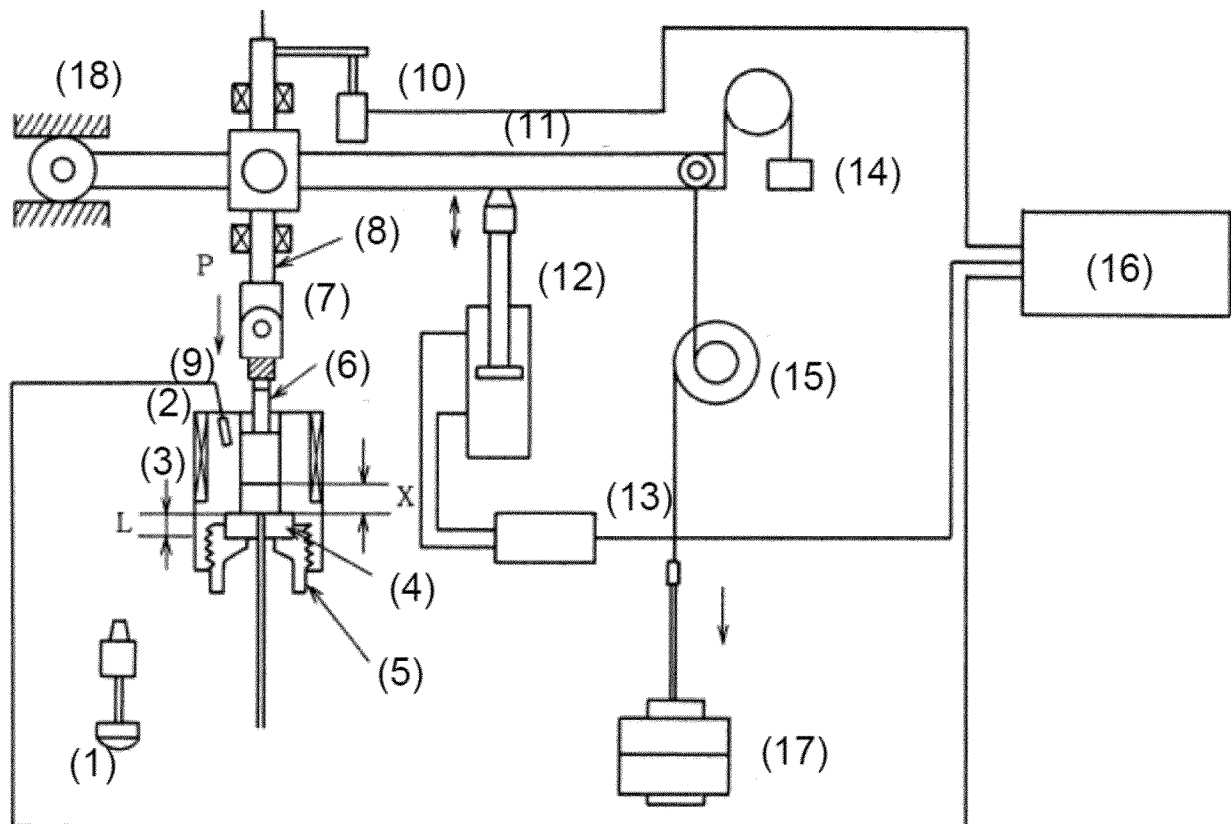


Fig. 2

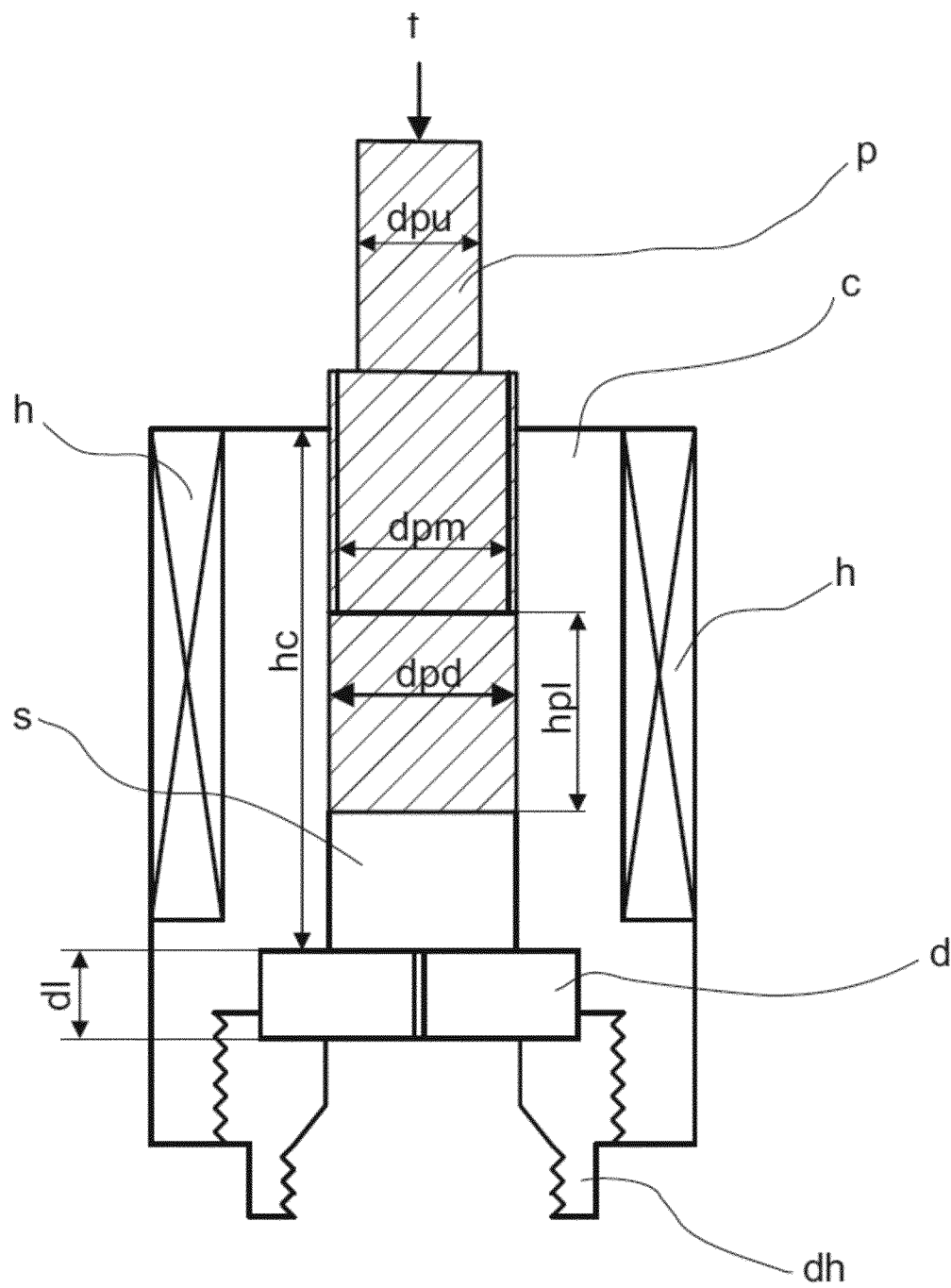


Fig. 3

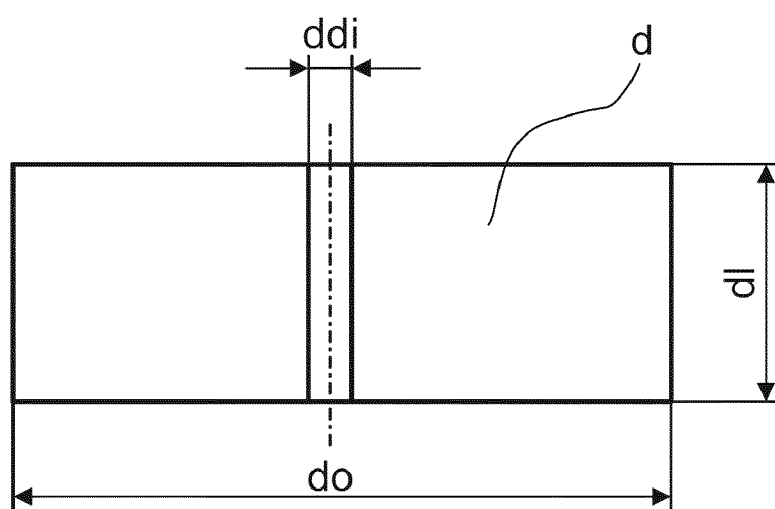
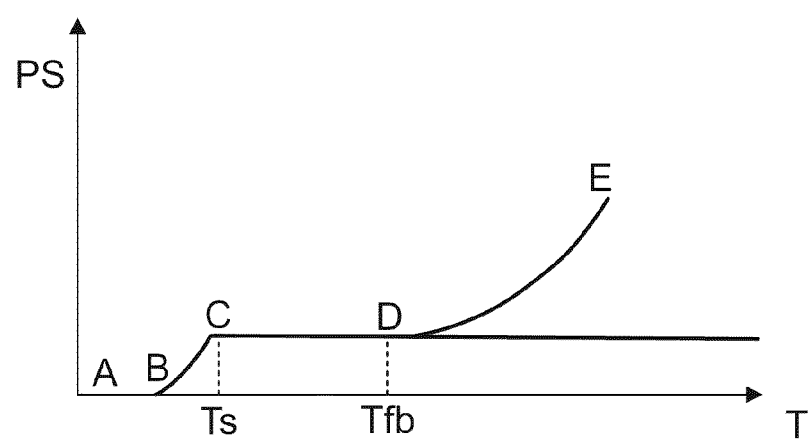


Fig. 4



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/080948

A. CLASSIFICATION OF SUBJECT MATTER		
INV. C09J5/00	A43B1/00	B29D35/00
B29D35/10	C08G18/48	C08G18/66
C09D175/04	C09D175/06	C09D175/08
A43B9/12	A43B13/04	C08G18/73
C08G18/76	C09J175/04	C09J175/06
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) C09J B29D A43B C08G		
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		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2021/249749 A1 (BASF SE [DE]) 16 December 2021 (2021-12-16) claims 1-18 page 1 – page 8 page 18 – page 24 examples 1-9, 11, 13 -----	1-21
X	WO 2016/025423 A1 (LUBRIZOL ADVANCED MAT INC [US]) 18 February 2016 (2016-02-18) paragraphs [0003] – [0010], [0020], [0028], [0039] – [0042], [0044], [0045]; claims 1-14 examples 1-8 -----	1-5, 7-20
A	paragraphs [0003] – [0010], [0020], [0028], [0039] – [0042], [0044], [0045]; claims 1-14 examples 1-8 -----	6, 21
X	KR 2020 0018755 A (LEE JUNG WOON [KR]) 20 February 2020 (2020-02-20) paragraphs [0032] – [0034]; claims 1-9; example 1 -----	1-20
	----- -/-	
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 26 January 2024		Date of mailing of the international search report 15/02/2024
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 Alevizopoulou, M

INTERNATIONAL SEARCH REPORT

International application No

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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.
X	WO 2018/156689 A1 (NIKE INNOVATE CV [US]; NIKE INC [US]) 30 August 2018 (2018-08-30) paragraphs [0002] - [0012], [0064], [0070], [0076]; claims 1-20 -----	1, 2, 4, 5, 17-21

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Information on patent family members

International application No

PCT/EP2023/080948

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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