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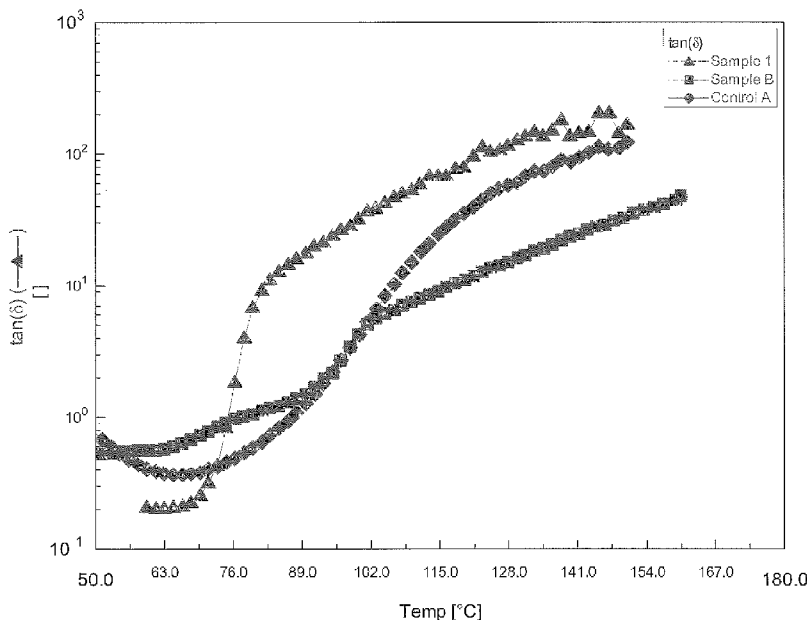


Figure 1

(57) Abstract: The present invention relates to elastic attachment adhesives that comprise non-metallocene catalyzed polymers. The elastic attachment adhesives have stable creep performance under prolonged aging parameters, making these adhesives particularly well suited for elastic applications.

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ELASTIC ATTACHMENT ADHESIVE AND USE THEREOF

FIELD OF THE INVENTION

[0001] The present invention relates to elastic attachment adhesives that comprise non-metallocene catalyzed polymers. Advantageously, the elastic attachment adhesives have similar performances to those adhesives that are formed with metallocene-catalyzed polymers. Also, the elastic attachment adhesives have stable creep performance under prolonged aging parameters, making these adhesives particularly well suited for elastic applications.

BACKGROUND OF THE INVENTION

[0002] Styrene block copolymers have been used as the primary polymers in the elastic attachment hot melt adhesives. Styrene-based adhesives have consistent sprayability with a balanced elasticity and strength, due to the elastic mid-blocks and hard end-block of the styrene block copolymer. Such adhesives typically require large additions of tackifiers and/or plasticizers due to the high viscous nature of the styrene block copolymers; however, large additions of tackifiers and plasticizers negatively affect the performance of the elastic attachment adhesive upon aging.

[0003] Other block copolymers, such as ethylene/alpha-olefin interpolymer, have also been utilized in elastic attachment adhesives, e.g., US 7,989,543 and US 20110021103. Adhesives formed with ethylene/alpha-olefin interpolymer demonstrate initial elasticity and creep resistance; however, these properties wane or disappear upon aging. Also, employing a combination of ethylene-propylene rubber (EPR) and semicrystalline propylene (e.g., EP 1214368) to achieve a balanced elasticity and strength also requires large additions of tackifiers and/or plasticizers in the adhesive, which negatively affect the adhesive performance upon aging.

[0004] Adhesives without the block-like structure in the polymer, such as polybutylenes (e.g., US 6,218,457), fail to achieve balanced elasticity and strength. Moreover, using a

blended system of a semicrystalline propylene (syndiotactic or isotactic polypropylene) and an amorphous polymer, e.g., US 6,653,385, US 6,774,069, US 7,262,251 and US 7,067,585, fails to maintain the balanced elasticity and strength upon adhesive aging.

[0005] While non-metallocene catalyzed polymers have been used for elastic adhesives to decrease cost, such adhesives spray inconsistently and unevenly. It is desirable for the adhesive to spray uniformly and consistently at the application temperature. Metallocene-catalyzed polymers in the adhesive provide better sprayability because the molecular weight distribution of the polymer is narrower than non-metallocene-catalyzed polymers; however, metallocene-catalyzed polymers tend to be more expensive and higher in viscosity. The high viscous nature of the metallocene-catalyzed polymers, therefore require large amounts of tackifiers and/or oils in the adhesive in order to be sprayable at typical application temperatures.

[0006] There is a need in the art for elastic attachment hot melt adhesives that possess good performances such as balanced elasticity and strength, balanced long-term elasticity and strength, cost and consistent sprayability at the application temperatures. The current invention fulfills this need.

BRIEF SUMMARY OF THE INVENTION

[0007] The invention provides elastic attachment hot melt adhesives formed with non-metallocene catalyzed polymers. The elastic attachment hot melt adhesives have desirable creep performance under long term aging conditions.

[0008] In one embodiment, the elastic attachment hot melt adhesive comprises a polymer having a viscosity lower than about 200,000 mPas at 200°C in accordance with ASTM D3236. The polymer comprises a non-metallocene catalyzed polymer that has been degraded with peroxide and/or heat. The non-metallocene catalyzed polymer is a polypropylene homo- or copolymer with a heat of fusion greater than 20 J/g, measured in accordance with ASTM D3418-12. The adhesive has a tan δ value greater than about 30; preferably, greater than about 40; and more preferably, greater than 50.

[0009] In another embodiment, the elastic attachment hot melt adhesive comprises a polymer that comprises (A) greater than 50wt% of a non-metallocene catalyzed polymer with a heat of fusion greater than 20 J/g and (B) less than 50% of a flexibilizer with a heat of fusion less than 15 J/g. The polymer has a viscosity lower than about 200,000 mPas at 200°C in accordance with ASTM D3236, and is formed by degradation with peroxide and/or heat. The wt% of the non-metallocene catalyzed polymer and the flexibilizer is based on the total wt% of the polymer, and the heat of fusion is measured in accordance with ASTM D3418-12.

[0010] Another embodiment is directed to a laminant comprising (a) a nonwoven substrate; (b) an elastic strand coated with an elastic attachment hot melt adhesive; and (c) a film substrate, whereby the two substrates are attached onto the elastic strand with the elastic attachment hot melt adhesive. The elastic attachment hot melt adhesive comprises a polymer that comprises greater than 50wt% of a non-metallocene catalyzed polymer with a heat of fusion greater than 20 J/g and less than 50% of a flexibilizer with a heat of fusion less than 15 J/g. The polymer has a viscosity lower than about 200,000 mPas at 200°C in accordance with ASTM D3236, and is formed by degradation process with a peroxide and/or heat. The wt% of the non-metallocene catalyzed polymer and the flexibilizer is based on the total wt% of the polymer, and the heat of fusion is measured in accordance with ASTM D3418-12.

BRIEF DESCRIPTION OF THE DRAWING

[0011] Figure 1 is a graph of $\tan \delta$ curves of elastic attachment adhesives.

DETAILED DESCRIPTION OF THE INVENTION

[0012] The elastic attachment adhesive comprises a non-metallocene catalyzed polymer that has been thermomechanically degraded with peroxide and/or heat.

[0013] The term "polymer" as used herein includes homopolymers and copolymers such as terpolymers, tetrapolymers, etc. The non-metallocene catalyzed polymer comprises at least one semi-crystalline polypropylene (co)polymer.

[0014] The term "semi-crystalline" used for the polypropylene polymer refers to those

polymeric materials that contain both crystalline and amorphous regions in the solid state. In the crystalline region, the molecular chains of the polymers are arranged in ordered, three dimensional arrays and the structures can be fully characterized by their unit cells (the smallest structural unit used to describe a crystal). The amorphous polymers, in contrast, do not have an ordered three-dimensional structure in the solid state, for their molecular chains are in a completely random fashion. Quantitatively, the semi-crystalline polymers can be distinguished from the completely amorphous polymers by observing the presence or absence of a melting point (T_m) and the associated enthalpy or heat of fusion (ΔH_m) derived from the transformation of the crystalline state to liquid state upon heating. All semi-crystalline polymers exhibit a melting point, whereas the melting point is absent for amorphous polymers. Amorphous polymers undergo a transition from a glassy solid to a rubbery elastic state in a narrow temperature range around the glass transition temperature. The glass transition temperature (T_g) is different than the melting point (T_m). Unlike the melting transition of the crystalline materials, the glass transition of amorphous polymers does not have an enthalpy change (ΔH) associated with it.

[0015] The enthalpy or heat of fusion (ΔH_m) can be determined by Differential Scanning Calorimetry (DSC). The technique is well known to those skilled in the art and is well described in the scientific literature.

[0016] The term "semi-crystalline propylene polymer or copolymers" as used in the present invention refers to propylene polymers or copolymers having a heat of fusion, as determined by DSC, of at least about 20 J/g, preferably at least about 25 J/g, and more preferably at least about 30 J/g. The term "heat of fusion" as used herein, refers to the energy absorbed in converting a material from a crystalline or semi-crystalline state to an amorphous state, and this value can be determined by various analytical methods, including ASTM D3418-12 and ISO 11357-3. Unless otherwise stated, all reported heat of fusion values are determined in accordance with ASTM D3418-12, with minor adjustments as described herein. The

semicrystalline propylene polymer or copolymer as used in the present invention is, commercially available from Lyondell Basell, Ineos, Borealis, TVK and Exxon Mobil.

[0017] The polymer may further comprise a flexibilizer that has a heat of fusion less than 15 J/g. The flexibilizers are propylene copolymers where the highly random nature of the comonomers in the copolymer gives rise to a predominantly amorphous matrix with small crystalline domains. Therefore, typical flexibilizers are less crystalline than the semi-crystalline polypropylene or copolymer, and the random structure of the copolymers in the flexibilizers decrease the crystalline domains. Useful flexibilizers include Vistamaxx grades from ExxonMobil and Versify grades from Dow. In one embodiment, the amount of the flexibilizer present is less than the amount of the non-metallocene catalyzed polymer. In another embodiment the flexibilizer is present in amounts less than 50wt% of the total of the polymer.

[0018] The elastic attachment adhesive comprises thermomechanically degraded polymer. In the context of the present invention, the term "thermomechanical degradation" is understood to mean polymer chain shortening and molecular weight reducing process of a polymer and this typically occurs in an extruder under heat and shear stress. The weight average molecular weight (M_w) of the degraded polymer is lower than the weight average molecular weight (M_w) of the original polymer. Also, the thermomechanically degraded polymer exhibits a lower melt viscosity than the original polymer. Degradation allows for the controlled scission of the polymer chain, and thus, the degraded polymer also has a narrower molecular weight distribution, in addition to the lower weight average molecular weight and the lower viscosity.

[0019] Thermomechanically degraded polymer is typically degraded under shear stress, preferably in an extruder. In order to increase the efficiency of the thermomechanical degradation, it is advantageous to carry out the degradation in the presence of at least one radical donor and/or in the presence of oxygen.

[0020] The non-metallocene catalyzed polypropylene (co)polymers, alone or combined with a flexibilizer, is degraded in the presence of at least one radical donor and/or in the presence of

oxygen. In the context of the present invention, a "radical donor" is understood to mean a substance that under external influence, such as heat and/or radiation, decomposes into radicals. The radical donors are primarily compounds that contain peroxy or diazo groups, wherein peroxides, such as for example organic peroxides, are preferred due to their commercial availability and ease of handling. Suitable radical sources can be selected for example from the following products or compounds and/or from any mixtures thereof.

TRIGONOX 101(R) (2,5-dimethyl-2,5-di-[tert-butylperoxy]hexane), TRIGONOX 301(R) (3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane), both commercially available from AKZO, di-tert-amyl peroxide, commercially available from CK Witco as DTAP(R) and from AKZO as Trigonox 201(R), dicumyl peroxide, di-tert-butyl peroxide, 2,5-dimethyl-2,5-di(tert-butyl peroxy)-3-hexyne, 1,3-bis(tert-butyl peroxy isopropyl)benzene, 1, 1-bis(tert-butyl peroxy)-3,3,5-trimethylcyclohexane, n-butyl-4,4-bis(tert-butyl peroxy)valerate, benzoyl peroxide, p-chlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide, tert-butyl peroxybenzoate, tert-butyl peroxy isopropyl carbonate, diacetyl peroxide, lauroyl peroxide, tert-butyl cumyl peroxide, tert-butyl peroxy 2-ethylhexanoate. Preferred peroxides have a half-life, determined in monochlorobenzene at 150°C, of about 0.01 to about 10 hours, preferably from about 0.1 to about 5 hours and particularly preferably from about 0.3 to about 3 hours. Preferably, the radical donor is advantageously added in an amount of from about 0.02 to about 5 wt%, more preferably from about 0.05 to about 2 w.% and especially from about 0.1 to about 1 w.%, based on the total amount of polypropylene (co)polymer.

[0021] The process for reducing the melt viscosity of the non-metallocene catalyzed polymer starting material with at least one radical donor under shear stress at a temperature above the softening point of the polymer blend starting material can be carried out in single screw extruders, twin screw extruders, Banbury mixers, kneaders and roll mills. Of these, it is particularly preferred to use single screw extruders, twin screw extruders and kneaders.

[0022] The degraded non-metallocene catalyzed polymer has a lower melt viscosity, weight

average Mw and narrower molecular weight distribution than the original polymer. In one embodiment, the degraded non-metallocene catalyzed polymer has a melt viscosity less than 200,000 mPas at 200 °C, measured in accordance with ASTM D3236. The heat of fusion of the non-metallocene catalyzed polymer is changed minimally during the thermomechanical degradation, and continues to have a value greater than about 20J/g, preferably greater than about 25J/g, and more preferably greater than about 30J/g.

[0023] The thermomechanically degraded polymer is combined with a tackifier, a plasticizer and/or a wax to form the elastic attachment adhesive.

[0024] "Tackifying resins" are understood to mean in particular polymeric additives that increase their autoadhesion (tack, inherent tack, self-adhesion). The tackifier component is present in amounts less than the polymer.

[0025] Typical tackifier has a Ring and Ball softening points, as determined by ASTM method E28, of about 70°C to about 180°C, more preferably about 95°C to about 150°C. Useful tackifying resins may include any compatible resin or mixtures thereof, such as natural and modified rosins including, for example, as gum rosin, wood rosin, tall oil rosin, distilled rosin, hydrogenated rosin, dimerized rosin, resinates, and polymerized rosin; glycerol and pentaerythritol esters of natural and modified rosins, including, for example, the glycerol ester of pale, wood rosin, the glycerol ester of hydrogenated rosin, the glycerol ester of polymerized rosin, the pentaerythritol ester of hydrogenated rosin, and the phenolic-modified pentaerythritol ester of rosin; copolymers and terpolymers of natured terpenes, including, for example, styrene/terpene and alpha methyl styrene/terpene; polyterpene resins having a softening point, as determined by ASTM method E28, from about 70 °C to about 150 °C; phenolic modified terpene resins and hydrogenated derivatives thereof including, for example, the resin product resulting from the condensation, in an acidic medium, of a bicyclic terpene and a phenol; aliphatic petroleum hydrocarbon resins having a Ball and Ring softening point from about 70°C to about 135°C; aromatic petroleum hydrocarbon resins and the hydrogenated derivatives

thereof; and alicyclic petroleum hydrocarbon resins and the hydrogenated derivatives thereof. Examples of hydrogenated tackifiers particularly suitable include Escorez 5400 from Exxon Mobil Chemicals, Arkon PI 00 from Arakawa and Regalite SI 100 from Eastman Chemical, and the like. Also included are the cyclic or acyclic C5 resins and aromatic modified acyclic or cyclic resins. Examples of commercially available rosins and rosin derivatives that could be used to practice the invention include SYLVALITE RE 1 10L, SYLVARES RE 115, and SYLVARES RE 104 available from Arizona Chemical; Dertocal 140 from DRT; Limed Rosin No.1,GB-120, and Pencil C from Arakawa Chemical. Examples of commercially available phenolic modified terpene resins are Sylvares TP 2040 HM and Sylvares TP 300, both available from Arizona Chemical.

[0026] Preferred tackifiers are synthetic hydrocarbon resins. Included are aliphatic or cycloaliphatic hydrocarbons, aromatic hydrocarbons, aromatically modified aliphatic or cycloaliphatic hydrocarbons and mixtures thereof.

[0027] Non-limiting examples include aliphatic olefin derived resins such as those available from Goodyear under the Wingtack Extra trade name and the Escorez 1300 series from Exxon. A common C5 tackifying resin in this class is a diene-olefin copolymer of piperylene and 2-methyl-2-butene having a softening point of about 95 °C. This resin is available commercially under the trade name Wingtack 95. Eastotac series from Eastman are also useful in the invention.

[0028] Also useful are aromatic hydrocarbon resins that are C9 aromatic/aliphatic olefin-derived and available from Sartomer and Cray Valley under the trade name Norsolene and from Rutgers series of TK aromatic hydrocarbon resins. Norsolene MI 090 is a low molecular weight thermoplastic hydrocarbon polymer having a Ring and Ball softening point of 95-105°C and is commercially available from Cray Valley.

[0029] Alpha methyl styrene such as Kristalex 3085 and 3100 from Eastman Chemicals, Sylvares S A 100 from Arizona chemicals are also useful as tackifiers in the invention.

Mixtures of two or more described tackifying resins may be required for some formulations.

[0030] Small quantities of alkyl phenolic tackifiers can be blended with additional tackifier agents detailed above to improve the high temperature performance of these adhesives. Alkyl phenolics added in less than 20 wt % of the total weight of the adhesive are compatible and in the proper combination increase high temperature adhesive performance. Alkyl phenolics are commercially available from Arakawa Chemical under the Tamanol trade name and in several product lines from Schenectady International.

[0031] The elastic attachment adhesives of the present invention may desirably also contain a plasticizer, including a liquid plasticizer. Suitable plasticizers include paraffinic oil, naphthenic oil, aromatic oil, long chain partial ether ester, alkyl monoesters, epoxidized oils, dialkyl diesters, aromatic diesters, alkyl ether monoester, polybutenes, phthalates, benzoates, adipic esters and the like. Particularly preferred plasticizers include mineral oil, aliphatic oils, polybutene, polyisobutylene, olefin oligomers and low molecular weight polymers, vegetable oil, animal oils and derivatives.

[0032] In one embodiment, the plasticizer is present at about 1 to about 30 wt%, more preferably about 3 to about 15 wt%, based on the total weight of the elastic attachment adhesive.

[0033] In some embodiments, however, oils may not be desired and is present at less than about 5 wt%, preferably less than about 3 wt%, more preferably less than about 1 wt%, more preferably less than about 0.5 wt% or even essentially free of oil, based upon the total weight of the adhesive.

[0034] Waxes can be optionally added to the elastic attachment adhesive. When added, waxes are added in an amount up to about 10 wt%, based on the total amount of the adhesive. The quantity is gauged so that, on the one hand, the viscosity is reduced to the required range and, on the other hand, the adhesion or the adhesive toughness is not adversely affected.

[0035] The wax can be of natural or synthetic origin and can optionally also be in chemically

modified form. Naturally occurring waxes that can be added are vegetable waxes, animal waxes, mineral waxes or petrochemical waxes. Suitable chemically modified waxes are hard waxes, such as Montan ester waxes, Sasol waxes, etc. Suitable synthetic waxes are polyalkylene waxes and polyethylene glycol waxes. Petrochemical waxes are preferably added such as petrolatum, paraffin waxes, microcrystalline waxes as well as synthetic waxes.

[0036] The adhesives of the present invention may desirably also contain at least one stabilizer and/or at least one antioxidant. These compounds are added to protect the adhesive from degradation caused by reaction with oxygen induced by, for example, heat, light, or residual catalyst from the raw materials such as the tackifying resin.

[0037] Applicable stabilizers or antioxidants included herein are high molecular weight hindered phenols and multifunctional phenols such as sulfur and phosphorous-containing phenol. Hindered phenols are well known to those skilled in the art and may be characterized as phenolic compounds which also contain sterically bulky radicals in close proximity to the phenolic hydroxyl group thereof. In particular, tertiary butyl groups generally are substituted onto the benzene ring in at least one of the ortho positions relative to the phenolic hydroxyl group. The presence of these sterically bulky substituted radicals in the vicinity of the hydroxyl group serves to retard its stretching frequency, and correspondingly, its reactivity; this hindrance thus provides the phenolic compound with its stabilizing properties. Representative hindered phenols include; 1,3,5-trimethyl-2,4,6-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-benzene; pentaerythrityl tetrakis-3(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate; n-octadecyl-3(3,5-ditert-butyl-4-hydroxyphenyl)-propionate; 4,4'-methylenebis(2,6-tert-butyl-phenol); 4,4'-thiobis(6-tert-butyl-o-cresol); 2,6-di-tertbutylphenol; 6-(4-hydroxyphenoxy)-2,4-bis(n-octyl-thio)-1,3,5 triazine; di-n-octylthioethyl 3,5-di-tert-butyl-4-hydroxy-benzoate; and sorbitol hexa[3-(3,5-di-tert-butyl-4-hydroxy-phenyl)-propionate].

[0038] Such antioxidants are commercially available from BASF and include Irganox®565, 1010, 1076 and 1726 which are hindered phenols. These are primary antioxidants that act as

radical scavengers and may be used alone or in combination with other antioxidants, such as, phosphite antioxidants like IRGAFOS®168 available from BASF. Phosphite antioxidants are considered secondary antioxidants and are not generally used alone. These are primarily used as peroxide decomposers. Other available catalysts are CYANOX®LTDP available from Cytec Industries and ETHANOX® 330 available from Albemarle Corp. Many such antioxidants are available either to be used alone or in combination with other such antioxidants. These compounds are added to the hot melts in small amounts, typically less than about 10 wt%, and have no effect on other physical properties. Other compounds that could be added that also do not affect physical properties are pigments, which add color, or fluorescing agents. Additives like these are known to those skilled in the art.

[0039] Stabilizers are preferably added in an amount of about 0.1 to about 3 wt%, preferably about 0.2 to about 1.5 wt%, each based on the total amount of the adhesive. In general stabilizers are incorporated in order to protect the adhesive as the end product of the process according to the invention against oxidative or thermal degradation reactions that can occur in storage and/or application. The usable stabilizers preferably include hindered phenols and/or multifunctional phenols, such as for example sulfur-containing and/or phosphorus-containing phenols. Hindered phenols are understood to mean compounds, in which at least one sterically hindered group, such as for example a tert-butyl group, is bonded to the phenol, wherein the sterically hindered groups are located especially in the ortho and/or para position to the phenolic OH group. Exemplary hindered phenols that are suitable stabilizers can be selected from the following compounds or from any of their mixtures: 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert.-butyl-4-hydroxybenzyl)benzene, pentaerythritol tetrakis-(3,5-di-tert.-butyl-4-hydroxyphenyl)propionate, n-octadecyl-(3,5-di-tert.-butyl-4-hydroxyphenyl) propionate, 4,4'-methylene bis(4-methyl-6-tert.-butylphenol), 4,4'-thiobis(6-tert.-butyl-o-resol), 2,6-di-tert.-butylphenol, 6-(4-hydroxyphenoxy)-2,4-bis(n-octylthio)-1,3,5-triazine, 2,4,6-tris(4-hydroxy-3,5-di-tert.-butylphenoxy)-1,3,5-triazine, di-n-octadecyl-3,5-di-tert.-butylbenzyl phosphonate, 2-(n-octylthio)ethyl-3,5-di-tert.-butyl-4-

hydroxybenzoate and sorbitol hexa-(3,3,5-di-tert.-butyl-4- hydroxyphenyl)propionate.

[0040] Further additives can be added, such as for example crosslinking agents, fillers, nucleating agents, adhesion promoters, elastomers, colorant, rheology modifiers which are known to the person skilled in the art and can be selected from a great number of commercially available products as a function of the desired properties. Additional polymers of higher or lower molecular weight (M_w) than the degraded polypropylene (co)polymer can be added to modify the adhesive properties. These polymers can be any of the conventional hot melt polymers as described in: Paul CW (2002) Hot Melt Adhesives in: Chaudhury M and Pocius AV (ed) Surfaces, Chemistry and Applications: Adhesion Science and Engineering, Elsevier Science B. V., The Netherlands pp 711 - 757.

[0041] The elastic attachment adhesive is processed by heating and blending the thermomechanically degraded polymer, the tackifier, the plasticizers, and optional components, until homogeneous. The tackifier, the plasticizer, and the optional components can be heated or heated/blended using an extruder or hot-melt processing equipment. In one embodiment, the tackifier, the plasticizer, and the optional components are added at the end of the thermomechanical degradation process of the polymer at the extruder to form the elastic attachment adhesive. The resultant elastic attachment adhesive can be used directly to bond and laminate substrates or it can be cooled and processed to make a solid form (e.g., pellets, pillows, or cast into molds or drums, etc.) which can be stored and/or shipped. The solid adhesive can be re-liquefied prior to bonding substrates.

[0042] An elastic attachment article is formed by applying the molten elastic attachment adhesive onto a substrate, at an application temperature of about 340°F (171°C) or less, preferably less than about 320°F (160°C), more preferably less than about 300°F (149°C), and placing another substrate onto the molten adhesive, whereby the adhesive is sandwiched in between the two substrates. In another embodiment, a multilayer elastic attachment laminant is formed by applying the molten elastic attachment adhesive onto both sides of a substrate, at an

application temperature of about 340°F (171°C) or less, preferably less than about 320°F (160°C), more preferably less than about 300°F (149°C), and placing the substrate in between two additional substrates, whereby the adhesive adheres three substrates together.

[0043] The elastic attachment adhesive is typically applied onto a portion of an elastic strand. Non-limiting examples of elastic strand comprise polyester, polyurethane, polyether, polyamide, polyacrylate, polyester-b-polyurethane block copolymer, polyether-b-polyurethane block copolymer or polyether-b-polyamide block copolymer. Suitable elastic multifilament strands include Lycra (Invista, Inc.) Confi-Fit™ (Fulflex).

[0044] The adhesive according to the invention may be used to bond or laminate the same or different substrates materials to one another. In one embodiment, the elastic strand is attached onto a nonwoven substrate with a basis weight in the range of about 10 to about 25 gsm (g/m²) based on fibers of polyethylene, polypropylene, polyester or cellulose. In another embodiment, the elastic strand is attached to a flexible, elastomeric, sheet-like film. Suitable flexible, elastomer sheet-like film are formed from polyethylene, polypropylene, polyester, polyurethane, polyamide, or combinations thereof, including random or graft copolymers such as styrene block copolymers, polyether-b-polyurethane block copolymer. Yet in another embodiment, the elastic strand is positioned in between one nonwoven substrate and one elastomeric film with the elastomeric attachment adhesive. The add-on level of the elastic attachment adhesive varies, depending on the type of applicators used, but typically ranges from about 2 to about 50 gsm, preferably from about 5 to about 15 gsm for spiral application. The add-on for strand-specific applications, such as Omega™ and Surewrap™, varies from 20 to 50 milligrams of adhesive/ meter/strand. Non-limiting applications include spiral, OMEGA® (ITW), SUREWRAP® (Nordson), and such techniques are known to those skilled in the art.

[0045] Delivery of consistent and uniform adhesive applied onto the elastic strand is an important factor to ensure acceptable performance of the laminant. Adhesives that spray unevenly and inconsistently, e.g., contain polymers with wide molecular weights or that sprays

with angel hair fly-aways, typically have poor creep resistance performance as the laminant is stretched and aged. Another important factor is adhesion: the adhesive should remain adhered onto the substrates without failure under strain of deformation. The elastic attachment adhesive of the instant invention sprays evenly and consistently and remains adhered onto the substrates under strain.

[0046] The elastic attachment adhesive is well suited for elastic attachment articles. Such articles require low deformation of the adhesive during exposure to heat and strain over a number of hours. It is preferred that the deformation is as small as possible under the heat and strain. One typical method of quantifying the resistance to deformation is by measuring the creep resistance. Creep resistance is a value calculated by measuring the initial creep resistance of the article, and then applying a strain for a specified temperature and time, and then re-measuring the resistance. The elastic attachment adhesive of the instant invention has an initial creep resistance that is less than about 20% after extending the laminated adhesive to 300% at 38°C for four hours. Moreover, the elastic attachment adhesive has a creep resistance that is less than about 20% after four weeks storage at 50°C followed by extending the adhesive to 300% strain at 38°C for four hours.

[0047] For strand-specific elastic application, the ability to apply consistent and even amounts of the adhesive directly on the elastic strand is a key factor to ensure acceptable performance, such as creep resistance. The $\tan \delta$ value is a measurable value of the adhesive that can be used to correlate the ease of applying consistent and even amounts of adhesive onto a substrate. The $\tan \delta$ of the elastic attachment adhesive is the ratio of the loss modulus (G'') to the storage modulus (G'): (G''/G'). This is a dimensionless quantity that is proportional to the ratio of the energy lost to energy stored. It has been discovered that the adhesives with a $\tan \delta$ value greater than 30, preferably greater than 40 and more preferably greater than 50 at the application temperature, spray consistently and evenly with conventional applicators. The

elastic attachment adhesive has a $\tan \delta$ value of greater than about 30, preferably greater than 40, and more preferably greater than 50. The non-metallocene catalyzed polymer based elastic attachment adhesive of the instant invention has a $\tan \delta$ value greater than 50 at the application temperature and it sprays consistently and evenly onto substrates.

[0048] The elastic attachment articles are suitable as absorbent articles such as diapers, diaper pants, baby wipes, training pants, absorbent underpants, child care pants, swimwear, and other disposable garments; feminine care products including sanitary napkins, wipes, menstrual pads, panty liners, panty shields, tampons, and tampon applicators; adult-care products including wipes, pads, containers, incontinence products, and urinary shields; clothing components; athletic and recreation products; products for applying hot or cold therapy, medical gowns (i.e., protective and/or surgical gowns), surgical drapes, caps, gloves, face masks, bandages, wound dressings, wipes, covers, containers, filters, disposable garments and bed pads, medical absorbent garments, underpads; construction and packaging supplies, industrial pads including meat pads; products for cleaning and disinfecting, wipes, covers, filters, towels, bath tissue, facial tissue, nonwoven roll goods, home-comfort products including pillows, pads, cushions, masks and body care products such as products used to cleanse or treat the skin, laboratory coats, cover-alls, and the like.

[0049] Many modifications and variations of this invention can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. The specific embodiments described herein are offered by way of example only, and the invention is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled.

Examples

[0050] The heat of fusion (ΔH_m) of the polymer and flexibilizer was determined by DSC, in accordance with ASTM D3418-12.

[0051] Adhesive preparation: Sample adhesive, unless otherwise stated, was prepared by combining the components together at a temperature where the polymer was molten, and the mixture became homogeneous.

[0052] The viscosity of the adhesive was measured with a standard Brookfield viscometer, spindle 27 in accordance with ASTM D3236.

[0053] The softening point of the adhesive was measured with a Ring and Ball softening point set up in accordance with ASTM E28.

[0054] The melting point of the adhesive was measured with a differential scanning calorimetry apparatus (DSC) in accordance with ASTM 3418-12.

[0055] Storage modulus and loss modulus were measured and the $\tan \delta$ value was calculated by ARES M Rheometer from Rheometric Scientific using the Temperature Ramp Method (ARES LS). A sample was placed between parallel plates (25 mm geometry diameter) with a 2 mm gap. Dynamic temperature sweep from 160°C to 0°C was tested with a frequency of 10 rad/sec and cooling rate of 5°C/minute. The storage modulus (G') and the loss modulus (G'') were measured from torque and strain. Their ratio (G''/G'), also known as the $\tan(\delta)$, was calculated, and shown in Figure 1.

[0056] Elastic sample preparation: Elastic sample laminations were prepared by continuous elastic coating application methods known in the art. The elastic adhesive was applied with add-on levels of 25 or 35 mg/m/strand onto a Lycra Invista 800 elastic strand with ITW Omega strand applicator at a 143°C to 155°C using a high speed laminator at 1000 fpm with 0.1 sec open time. The elastic strand is then laminated between Clopay DH 276 PP polyfilm substrate and NW PGI nonwoven (15 gsm) substrate with a nip roller and cooled to room temperature.

[0057] Elastic Creep Resistance Evaluation: Elastic creep resistance values were measured for initial and aged elastic samples. For the aged samples, the elastic samples were aged at 40°C for 2 weeks or 4 weeks. The creep resistance values are listed as an average of

five samples.

[0058] Creep measurement : The length of a elastic strand adhered in the stretched condition between a nonwoven sheet and a polymeric film was measured and marked ("starting length"). A sample length is stretched outside of the marked area. The elastic strands are then cut at the marked area. The amount that the filament retracts is measured following a 4 hour period at 38°C. The percent creep is then calculated in the following manner:

$$\% \text{ creep} = \frac{(\text{starting length} - \text{final length})}{\text{starting length}} \times 100\%$$

[0059] Acceptable creep resistance of the adhesive is about 35% or less.

[0060] Control A and comparative samples B, C and D were prepared with the components listed in Table 1. Control A is Henkel DISPOMELT® 897B, a rubber-based (styrene-butadiene-styrene and/or styrene-isoprene-styrene) adhesive. Polymer in Comparative Sample B is a metallocene catalyzed ethylene-octene block olefin polymer. Comparative samples C (semicrystalline polypropylene copolymer) and D (amorphous polypropylene copolymer) were formed with metallocene catalyzed polymer and non-metallocene catalyzed polymers, respectively, that have a ΔH_m value less than 20J/g. The properties of the elastic attachment adhesives and elastic samples are listed in Table 1.

Table 1. Comparative Samples

	Control A	Comparative Sample B	Comparative Sample C	Comparative Sample D
DM-897B	100			
Infuse 9817, $\Delta H_m = 38$ J/g (Dow)		15.0		
Vistamaxx 2330, $\Delta H_m = 16$ J/g (ExxonMobil)			30.0	
Rextac RT 2814, $\Delta H_m < 5$ J/g (Rextac)				70.0
Tackifier (Escorez 5400, ExxonMobil)		60.0	54.5	29.7
Wax (Epolene C10, Westlake Chemical)		14.5		
Liquid plasticizer (Calsol 5550, Calumet)		10.0	15.0	0
Antioxidant (Irganox 1010, BASF)		0.5	0.5	0.3
Adhesive Properties				
Viscosity 150°C (mPas)	4,200	8750	201,000	3500
Softening point (°C)	76	111	148	80
Melting point (°C)	N/A	99	147	N/A
Elastic Attachment Sample Properties				
Initial elastic creep resistance at 25 mg/m/strand (%)	5 ± 1	8 ± 2	*	68
2 week aged elastic creep resistance at 25 mg/m/strand (%)	13 ± 2	55 ± 8	*	**
4 week aged elastic creep resistance at 25 mg/m/strand (%)	14 ± 3	51 ± 6	*	**
Initial elastic creep resistance at 35 mg/m/strand (%)	3 ± 1	4 ± 1	*	68
2 week aged elastic creep resistance at 35 mg/m/strand (%)	8 ± 3	46 ± 6	*	**
4 week aged elastic creep resistance at 35 mg/m/strand (%)	9 ± 4	**	*	**

* Due to the high viscosity of the adhesive at 150°C and 160°C, elastic attachment samples could not be prepared using standard coater setting point temperatures. Also application temperatures above 160°C lead to film burn-through.

** Due to the high creep resistance values of earlier tests, aged elastic creep resistance were not measured.

[0061] Elastic attachment samples made with rubber based adhesives (Control A) have low initial elastic creep resistances and maintain this resistance under the aging conditions. Elastic attachment samples made with metallocene catalyzed ethylene-octene block copolymers (Comparative Sample B) had acceptable initial creep resistance; however, upon aging, the creep resistance increased to above 55%. Elastic attachment adhesives formed with semicrystalline polypropylene copolymer (Comparative Sample C) resulted in viscosity that is over 200,000 mPas at 150°C, and thus, could not be sprayed at 143°C - 155°C. Adhesive formed with amorphous polypropylene copolymer (Comparative Sample D) did not indicate any creep resistivity.

[0062] Non-metallocene catalyzed polymers for the sample adhesives were formed by degrading them with heat and peroxide. For Polymer Blends X, Y and Z, the flexibilizer was combined with the polymer (original viscosity greater than 1,000,000 mPas), and degraded together in the manner described in US 2012/0016086 until the blend reached the noted final viscosity. The polymer was a propylene copolymer with a ΔH_m value of 32J/g and the flexibilizer was a flexible propylene copolymer with a ΔH_m value of 2.8J/g.

Table 2. Polymer Blends

Polymer Blend	X	Y	Z
Ratio of Polymer:Flexibilizer	70:30	70:30	60:40
Final viscosity (mPas)	4,300	9,900	5,200

[0063] The sample adhesives were formed by combining the polymer blends of Table 2 with additional components listed in Table 3. Sample adhesive properties and elastic attachment sample properties made with the sample adhesives are also listed in Table 3.

Table 3. Adhesive Samples

	Sample 1	Sample 2	Sample 3
Polymer Blend X	50.0		
Polymer Blend Y		45.0	
Polymer Blend Z			55.0
Tackifier (Escorez 5400, ExxonMobil)	39.5	44.5	39.5
Liquid plasticizer (Calsol 5550, Calumet)	10.0	10.0	5.0
Antioxidant (Irganox 1010, BASF)	0.5	0.5	0.5
Adhesive Properties			
Viscosity 150°C (mPas)	3,600	6,000	5,500
Softening point (°C)	131	131	133
Melting point (°C)	126	126	127
Elastic Attachment Sample Properties			
Initial elastic creep resistance at 25 mg/m/strand (%)	5 ± 3	3 ± 1	7 ± 4
2 week aged elastic creep resistance at 25 mg/m/strand (%)	26 ± 6	16 ± 5	27 ± 8
4 week aged elastic creep resistance at 25 mg/m/strand (%)	37 ± 13	17 ± 3	28 ± 8
Initial elastic creep resistance at 35 mg/m/strand (%)	2 ± 1	N/A	2 ± 2
2 week aged elastic creep resistance at 35 mg/m/strand (%)	27 ± 3	N/A	13 ± 11
4 week aged elastic creep resistance at 35 mg/m/strand (%)	31 ± 6	N/A	18 ± 9

[0064] The sample adhesives have acceptable initial and long-term creep resistance.

[0065] Sprayability: Sample 1 and Comparative Sample B and C were prepared by as described above. Sample 1 sprayed consistently and evenly throughout the entire elastic strand. This consistent and even coating observed for sample 1 is comparable to the metallocene-based adhesives of samples B and C.

[0066] Figure 1 shows $\tan \delta$ curves of Sample 1, Comparative Sample B and Control A, which is a rubber-based elastic adhesive. As shown in Figure 1, the $\tan \delta$ value of Sample 1 is 145 at the application temperature of 143°C. Sample 1, formed with a non-metallocene propylene copolymer, has similar $\tan \delta$ curve as adhesives formed with metallocene catalyzed olefins (Comparative Samples B) and rubber-based elastic adhesive (Control A).

[0067] Many modifications and variations of this invention can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. The specific

embodiments described herein are offered by way of example only, and the invention is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled.

CLAIMS

I/We claim:

1. An elastic attachment hot melt adhesive comprising a tackifier and a polymer having a viscosity lower than about 200,000 mPas at 200°C measured in accordance with ASTM D3236;
wherein the polymer comprises a non-metallocene catalyzed polymer degraded with peroxide and/or heat; and
wherein the non-metallocene catalyzed polymer is a polypropylene homo or copolymer with a heat of fusion greater than 20 J/g measured in accordance with ASTM D3418-12;
wherein the adhesive has a $\tan \delta$ value of greater than about 30 at the adhesive application temperature; and
wherein the amount of tackifier is less than the amount of the polymer in the adhesive.
2. The elastic attachment hot melt adhesive of claim 1 wherein the polymer further comprises a flexibilizer having a heat of fusion less than 15 J/g, and wherein the flexibilizer is present in amounts less than the non-metallocene catalyzed polymer.
3. The elastic attachment hot melt adhesive of claim 2, wherein the flexibilizer is a comonomer selected from the group consisting of C2, C4, C5, C6, C7, C8, C9, C10, C11 and C12.
4. The elastic attachment hot melt adhesive of claim 1, further comprising a tackifier, a plasticizer or a wax.

5. The elastic attachment hot melt adhesive of claim 4, wherein the tackifier is selected from C5 resins, petroleum distillates, hydrogenated hydrocarbons, C5 resins, C9 resins, polyterpenes, rosins, hydrogenated rosins, rosin esters and mixtures there.
6. The elastic attachment hot melt adhesive of claim 4, wherein the plasticizer is selected from the group consisting of paraffinic oil, naphthenic oil, aromatic oil, long chain partial ether ester, alkyl monoesters, epoxidized oils, dialkyl diesters, aromatic diesters, alkyl ether monoester, polybutenes, phthalates, benzoates, adipic esters and the like.
7. The elastic attachment hot melt adhesive of claim 4, wherein the wax is a crystalline wax selected from the group consisting of petroleum based waxes, conventional wax, natural-based wax, functionalized wax, polyolefin copolymer and mixtures thereof.
8. The elastic attachment hot melt adhesive of claim 4, further comprising one or more of an antioxidant, stabilizer, crosslinking agent, filler, nucleating agent, adhesion promoter, elastomer, colorant, rheology modifier and mixtures thereof.
9. An elastic attachment hot melt adhesive comprising a polymer that comprises greater than 50wt% of a non-metallocene catalyzed polymer with a heat of fusion greater than 20 J/g and less than 50% of a flexibilizer with a heat of fusion less than 15 J/g;
wherein the polymer is has a viscosity lower than about 200,000 mPas at 200°C measured in accordance with ASTM D3236 formed by degradation with a peroxide and/or heat;
wherein the wt% is based on the total wt% of the polymer; and
wherein the heat of fusion is measured in accordance with ASTM D3418-12.

10. The elastic attachment hot melt adhesive of claim 9, wherein the non-metallocene catalyzed polymer is a polypropylene homo or copolymer.
11. The elastic attachment hot melt adhesive of claim 9, wherein the flexibilizer is a comonomer selected from the group consisting of C2, C4, C5, C6, C7, C8, C9, C10, C11 and C12 monomers.
12. The elastic attachment hot melt adhesive of claim 9, further comprising a tackifier, a plasticizer or a wax.
13. The elastic attachment hot melt adhesive of claim 12, wherein the tackifier is selected from C5 resins, petroleum distillates, hydrogenated hydrocarbons, C5 resins, C9 resins, polyterpenes, rosins, hydrogenated rosins, rosin esters and mixtures there.
14. The elastic attachment hot melt adhesive of claim 12, wherein the plasticizer is selected from the group consisting of paraffinic oil, naphthenic oil, aromatic oil, long chain partial ether ester, alkyl monoesters, epoxidized oils, dialkyl diesters, aromatic diesters, alkyl ether monoester, polybutenes, phthalates, benzoates, adipic esters and the like.
15. The elastic attachment hot melt adhesive of claim 12, wherein the wax is a crystalline wax selected from the group consisting of petroleum based waxes, conventional wax, natural-based wax, functionalized wax, polyolefin copolymer and mixtures thereof.

16. The elastic attachment hot melt adhesive of claim 12, further comprising one or more of an antioxidant, stabilizer, crosslinking agent, filler, nucleating agent, adhesion promoter, elastomer, colorant, rheology modifier and mixtures thereof.

17. A laminant comprising:

(a) a nonwoven substrate,

(b) an elastic strand

(c) an elastic attachment hot melt adhesive comprising a polymer that comprises greater than 50wt% of a non-metallocene catalyzed polypropylene polymer with a heat of fusion greater than 20 J/g and less than 50% of a flexibilizer with a heat of fusion less than 15 J/g;

wherein the polymer is has a viscosity lower than about 200,000 mPas at 200°C measured in accordance with ASTM D3236 formed by degradation with a peroxide and/or heat;

wherein the wt% is based on the total wt% of the polymer; and

wherein the heat of fusion is measured in accordance with ASTM D3418-12.

18. The laminant of claim 17 wherein the flexibilizer is a comonomer selected from the group consisting of C2, C4, C5, C6, C7, C8, C9, C10, C11 and C12 comonomers.

19. The laminant of claim 17 wherein the elastic attachment hot melt adhesive further comprising a tackifier, a plasticizer or a wax.

20. The laminant of claim 17 wherein

(i) the laminant has an initial creep performance of less than about 20% after exposure to 300% strain at 38°C for about 4 hours; and

- (ii) the laminant has an aged creep performance of less than about 40% after exposure to 300% strain at 38°C for about 4 hours after aging at 40°C for 4 weeks.

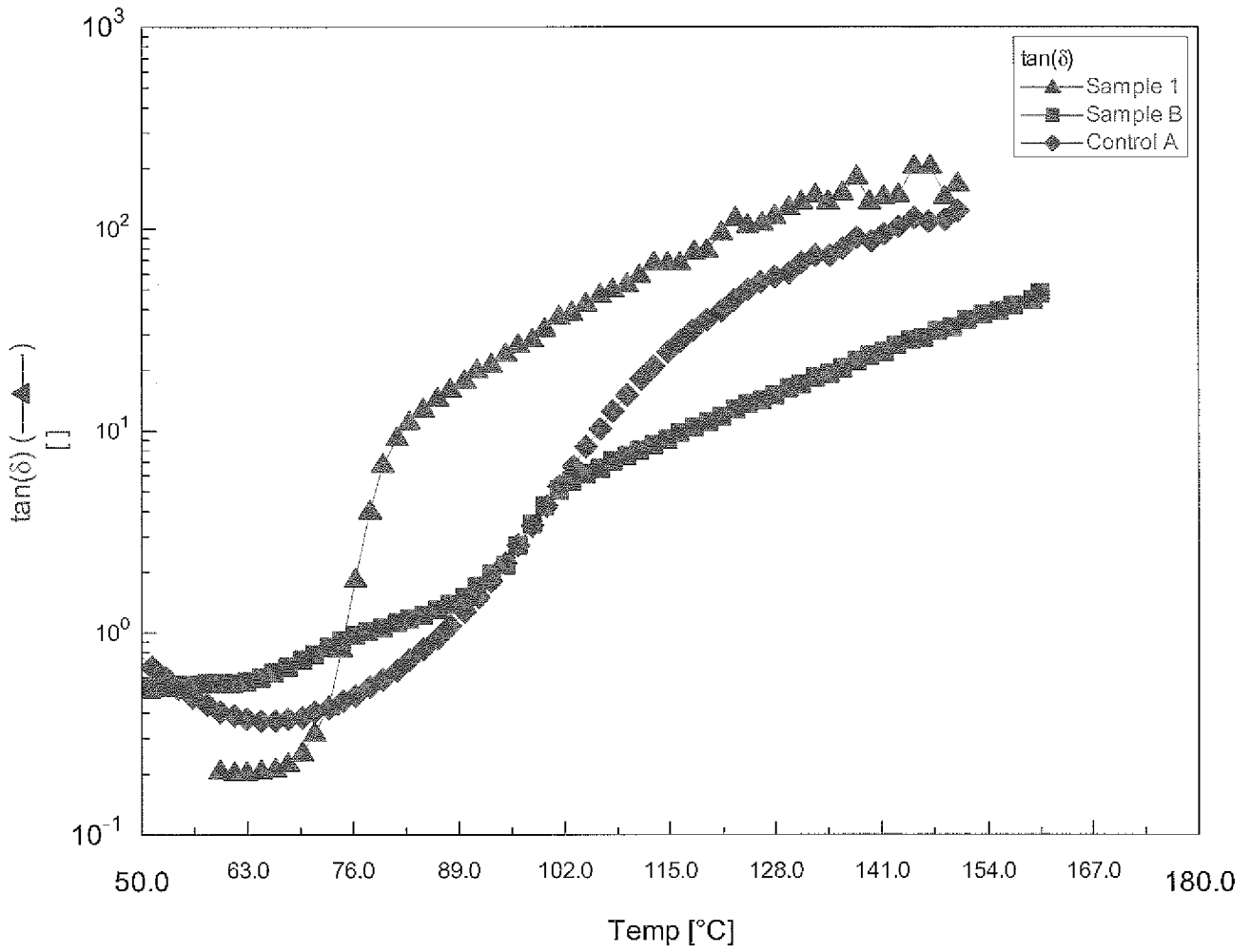


Figure 1

A. CLASSIFICATION OF SUBJECT MATTER**C09J 123/12(2006.01)i, C09J 11/00(2006.01)i, C09J 7/02(2006.01)i**

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 123/12; B01F 17/00; C08F 214/18; C08K 5/01; C09J 123/14; C08L 23/00; C08L 23/04; B32B 27/00; C09J 11/00; C09J 7/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: elastic attachment hot melt adhesives, non-metallocene catalyzed polymer, tackifier, polypropylene, heat of fusion, viscosity

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 7262251 B2 (KANDERSKI, MONINA DADAP et al.) 28 August 2007 See abstract; column 1, lines 14-22; column 22, lines 6-14; claims 1-35; and table 2.	1-20
A	US 2008-0264562 A1 (MERRILL, NATALIE A. et al.) 30 October 2008 See abstract; and claims 1-30.	1-20
A	US 6329468 B1 (WANG, BAoyu) 11 December 2001 See abstract; column 5; and claims 1-21.	1-20
A	WO 2012-149391 A1 (ADHERENT LABORATORIES, INC.) 01 November 2012 See abstract; and claims 1-24.	1-20
A	EP 1924648 B1 (BOSTIK, INC.) 20 June 2012 See abstract; and claims 1-18.	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

12 May 2014 (12.05.2014)

Date of mailing of the international search report

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Name and mailing address of the ISA/KR

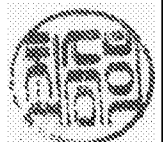
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2014/011855

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