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DESCRIPTION

FIELD

[0001] The disclosed embodiments herein relate generally to novel reactive hot melt compositions having utility as sealants, adhesives, and/or elastomers, especially in the aerospace industry.

BACKGROUND AND SUMMARY

[0002] For aerospace applications, compositions serving as sealants and/or adhesives must possess excellent fluid resistance to a variety of fluids, including jet fuel, de-icing fluid, water, hydraulic oil, lubricating oil, and the like. Compositions must also provide excellent post-cure mechanical properties, such as high flexibility.

[0003] In addition, many compositions employed as sealants and/or adhesives must be able to be applied rapidly, with minimal man-hour and material costs, and cure without dimensional changes into a multifunctional material. Rapid application is assisted by low melting temperature and relatively low melt viscosity in a pre-cured state. In addition to fluid resistance and flexibility, post-cure performance requirements include excellent adhesion to aluminum, titanium, carbon fiber-epoxy composite, and primed and/or promoted surfaces; adhesion, mechanical strength, and dimensional stability over a wide temperature range and appropriate surface tension properties for topcoating.

[0004] Existing adhesive or sealant materials that offer similar post-cure performance include variants such as two-component (2K) flexibilized epoxies; 2K or three component (3K) polysiloxanes; 2K polysulfides or polythioethers or thermoplastic polyurethanes that are melted into place. However, epoxies, polysiloxanes, and polysulfides/thioethers all suffer from the drawbacks of 2K systems, namely extra time to mix components, mixing inconsistencies (inconsistent ratios, material degradation, and entrapped air), short pot life, and long cure time. The thermoplastic polyurethanes and similar melt-in-place thermoplastics suffer from lengthy application time and high application temperatures during the melting process, poor adhesion, and low post-application maximum operating temperatures.

It would therefore be highly desirable to achieve a sealant or adhesive material with easy application and handling while in a pre-cured state which possesses excellent fluid resistance, dimensional stability, and adhesion to a variety of surfaces in a post-cured state. It is towards providing such a need that the embodiments as disclosed herein are directed.

[0005] According to embodiments disclosed herein a reactive hot melt (RHM) composition is provided, which composition comprises a mixture of a urethane prepolymer; a filler material and a leachable plasticizer. The urethane prepolymer is a reaction product of at least one

crystallizable polyol, a perfluoropolyether polyol, and at least one isocyanate, wherein the at least one isocyanate comprises a mixture of hexamethylene diisocyanate (HDI) trimer and methylenediphenyl diisocyanate (MDI) in a 1:1 weight ratio. The leachable plasticizer consists of an aliphatic ester of a carboxylic acid and is at least one selected from the group consisting of triethyl citrate, tributyl acetylcitrate and diethyl malonate and is present in an amount between 1.0 wt.% to 40 wt.%. Prior to cure, the urethane prepolymer exhibits a low melting point and a viscosity suitable for application. During the cure process, the isocyanate groups exhibit excellent bond strength to a variety of surfaces. After cure, the RHM adhesive material retains adhesion, shape, and density, after exposure to polar and non-polar solvents including water, deicing fluid, hydraulic oil, JP-8, and lubricating fluids.

[0006] As an additional step, the RHM adhesive material may be mixed with a hydroxyl and/or amine functional hardener to create an elastomer. Except for adhesion to a surface, which will be modified depending on the crosslinker and the application process, all post-cure properties (fluid resistance, elasticity, etc.) are retained or enhanced by crosslinking the isocyanate groups with hydroxyl and/or amine groups. Cure proceeds immediately upon mixing with the hardener.

[0007] The at least one crystallizable polyol may be selected from the group consisting of polyester polyols, polyethylene copolymer polyols, polysiloxane polyols and acrylic polyols.

[0008] The filler material may be at least one fibrous or particulate filler selected from the group consisting of silica, carbon or metallic filler materials. As exemplary, the filler material may be at least one selected from the group consisting of nickel, iron, aluminum, tungsten, silver, gold, platinum, palladium and carbon materials. The filler material may be employed in an amount between 0.1 wt.% to 80 wt.%, based on total composition weight.

[0009] An additive other than the filler material may be employed in other embodiments in an amount 0.1 wt.% to 80 wt.%. Such other optional additive may be one selected from the group consisting of density modifiers, dispersion additives, blocking agents, air reducing additives, antioxidants, flow improvers, conductivity modifiers and cure rate accelerators.

[0010] The RHM composition may be made by (a) forming a urethane prepolymer by reacting at least one crystallizable polyol, a perfluoropolyether polyol and at least one isocyanate, and thereafter (b) mixing the urethane prepolymer with (i) a filler material and (ii) a leachable plasticizer consisting of an aliphatic ester of a carboxylic acid, wherein the leachable plasticizer is at least one selected from the group consisting of triethyl citrate, tributyl acetylcitrate and diethyl malonate and is present in an amount between 1.0 wt.% to 40 wt.%, and wherein the at least one isocyanate comprises a mixture of hexamethylene diisocyanate (HDI) trimer and methylenediphenyl diisocyanate (MDI) in a 1:1 weight ratio.

[0011] These and other aspects of the present invention will become more clear after careful consideration is given to the following detailed description of a presently preferred exemplary embodiment thereof.

DETAILED DESCRIPTION

[0012] As noted briefly above, the RHM adhesive compositions according to the embodiments disclosed herein will necessarily include a urethane prepolymer, a filler package and a leachable plasticizer. Additives conventionally employed in hot melt adhesive compositions may also be included in suitable amounts.

[0013] The RHM adhesive compositions according to the embodiments disclosed herein offer several benefits over the existing 2K and thermoplastics options, including (1) as a 1K material, it is completely pre-mixed and no mixing by the operator is needed; (2) a low melting temperature of the RHM composition in the uncured state leads to rapid application due to low melting temperature; (3) lower-temperature tooling is needed to apply the RHM; within 5-20 seconds after application, the material cools and viscosity increases, and thereby leads to very rapid green strength, shape-retention, and adhesion with minimal slump; (4) in the green state, the material cures over time with exposure to moisture, which allows for rework over a limited period of time; (5) in the green state, the reactive groups adhere very well to any oxygen- or nitrogen-containing groups on the surface, leading to excellent adhesion to metals, nearly all polymers, and any primers or undercoats; and (6) once fully cured, the material is highly thermally stable, leading to a high maximum operating temperature.

[0014] There are three major drawbacks to RHM compositions, including (1) prior to application, any moisture exposure will degrade pot life significantly; (2) moisture-cure generates byproducts of some type (in this case CO₂, but may include ethanol, aldehydes, or other small molecules), and if filler loading is not high enough, cure rate is too rapid, and/or the material is applied too thick, bubbles can form within the material due to the generation of CO₂ or other byproducts; and (3) the material cures from the outside-in and cure is limited by moisture diffusion, and therefore may require several hours to achieve 90% of mechanical strength and adhesion depending on the thickness.

[0015] For the disclosed RHM compositions herein, all three of these drawbacks are accounted for by appropriate containers, high filler loading, balanced cure rate, and sufficient cure time. Specifically, pot life is extended by packaging in aluminum containers with small orifices or aluminum-backed plastic that is heat sealed. Significant CO₂ generation occurs during the cure of the RHM technology, but the formation of bubbles is minimized by (a) reducing the cure rate by using a controlled level of catalyst and the presence of a blocking agent such as diethyl malonate, (b) reducing cure rate by using an appropriate proportion of highly reactive isocyanate such as MDI and less reactive isocyanate such as HDI, (c) by increasing the filler loading such that a high modulus prevents the formation of large bubbles and instead encourages diffusion through the film, and (d) by casting thin films which favors diffusion through the film rather than internal bubble formation. In terms of moisture cure, there is no simple way to avoid moisture cure from the outside layer in, but the casting of thin films does reduce overall cure time.

[0016] There are many other RHM technologies that have been disclosed previously in the literature. A comparison of disclosed RHM technology to existing commercial RHM adhesives, the disclosed technology offers lower viscosity for the same filler loading level, higher resistance to bubbling during cure, significantly better fluid resistance for both polar and non-polar fluids, excellent green-strength adhesion due to the high polyester content, and significantly better retention of electrical properties after fluid immersion due to the inherent solvent resistance and the leachable plasticizer. Additionally, the disclosed compositions offer significantly reduced hazards by minimizing volatile isocyanates in the pre-cure state, using very low hazard additives and plasticizer, and only generating CO₂ (rather than e.g., ethanol or aldehydes) during the cure process.

A. Urethane Prepolymer

[0017] The urethane prepolymer component according to certain embodiments herein may be comprised of a hexamethylene diisocyanate (HDI) trimer and a methylene diisocyanate (MDI) in about equal parts by weight, a crystallizable copolyester polyol, a chain extender such as 1,4-butanediol, and a perfluoropolyether polyol may satisfactorily be employed in the composition.

[0018] The isocyanates in the urethane prepolymer may additionally include other isocyanates, such as toluene diisocyanate (TDI), isophorone diisocyanate (IPDI), or hydrogenated MDI (rMDI), provided that the reactivity and intermolecular bonding is controlled appropriately. Aliphatic isocyanates will offer improved resistance to light-induced degradation.

[0019] Crystallizable polyols, such as polyethylene copolymer polyols, polysiloxane polyols, or acrylic polyols, may be included in addition or as an alternative to the copolyester polyol provided that the viscosity and crystallization speed are not adversely affected.

[0020] Multi-functional alcohol- or amine-terminated chain extenders in addition or as an alternative to 1, 4-butanediol may be employed.

[0021] Soft segment polyols such as polypropylene glycol, polysulfide polyols and silicone polyols may be used as in addition or as an alternative to perfluoropolyether polyol so as to achieve higher elongation-at-break. Inclusion of such other soft segment polyols will, however, have a tendency to exhibit a negative impact on the fluid resistance of the composition.

[0022] Other reactive groups may be introduced into the prepolymer so as to modify the prepolymer end-group and/or crosslinking reaction, such as aminosilanes, phenol blocking agents and diamine generating molecules.

[0023] According to some embodiments, the prepolymer may be used as a one-component,

moisture-induced-cure adhesive. However, if multi-functional alcohols or amines are added as a secondary component, the prepolymer may be used in a two-component adhesive that cures upon mixing.

[0024] The urethane prepolymer is preferably present in the composition in amounts between 15 wt.% to 95 wt.% based on total composition weight. Advantageously, the urethane prepolymer may be present in an amount between 25 wt.% to 70 wt.%, based on total composition weight.

B. Filler

[0025] Virtually any filler material may be incorporated to provide multi-functional properties. Filler material is used to modify mechanical, rheological, thermal, electrical, cost-basis, or other properties. For example, carbon black provides increased mechanical modulus and strength, higher viscosity and lower slump, and low levels of conductivity. Other fillers may include silica, fumed silica, chopped carbon fiber, nickel flake, etc. Chopped carbon fiber and nickel flake will provide moderate electrical and thermal conductivity to the mixture. For thermal and electrical conductivity, other suitable conductive fillers may be composed of nickel, iron, aluminum, tungsten, silver, gold, platinum, palladium, carbon (graphite, graphene, carbon fiber, carbon nanofiber, carbon black, carbon nanotubes), and coated or alloyed fillers that include any of these elements.

[0026] The filler material will be employed in amounts sufficient to provide the desired mechanical, rheological, thermal, electrical, cost-basis, or other properties to the compositions. According to some embodiments, the filler material is preferably present in the composition in amounts between 0.1 wt.% to 80 wt.%, based on total composition weight. Advantageously, the filler material may be present in an amount between 20 wt.% to 75 wt.%, based on total composition weight.

C. Leachable Plasticizer

[0027] A leachable plasticizer is also present in the reactive hot melt compositions. The plasticizers used in the present invention include triethyl citrate, tributyl acetylcitrate and diethyl malonate. The selection of any particular plasticizer may have an effect on the mass gain and volume swell after fluid exposure, mechanical properties, and volatility.

[0028] A non-ionic miscibilizer may also be present so as to improve "leachability" of the plasticizer, such as ethylenediamine tetrakis(propoxylate-block-ethoxylate) tetrol (EDTP-b-ET) or poly(ethylene glycol) sorbitol hexaoleate (PEGSH). Other miscibilizing agents may additionally be used to reduce mass gain and volume swell after immersion in various fluids and improve mechanical or electrical properties, provided that they are not reactive with the

isocyanate or similar prepolymer reactive groups.

D. Other Additives

[0029] Virtually any conventional additives, catalysts, and/or blocking agents that are known in the art to modify density, dispersion, conductivity, and cure rate of adhesive compositions may be employed in the RHM compositions disclosed herein. If employed, such additives may be present in the compositions in an amount up to 20 wt.%, for example between 2 wt.% to 5 wt.%, based on total composition weight.

[0030] The following Table provides exemplary approximate weight percentage ranges (based on total composition weight) of the compositional components that may be employed according to certain embodiments described herein:

RANGES OF COMPOSITION:

[0031]

Component	Low (wt%)	Preferable (wt%)	High (wt%)
Hexamethylene diisocyanate (HDI) trimer or similar lower-reactivity isocyanate(s)	1.0	4.0-5.0	30.0
Methylenediphenyl diisocyanate (MDI) trimer or similar higher-reactivity isocyanate(s)	1.0	4.0-5.0	30.0
Crystallizable copolyester polyol or similar crystallizable polyol(s)	7.5	10-12	600
Perfluoropolyether polyol or similar soft-segment polyol(s)	0.5	1-2	30.0
Butanediol or similar chain extender(s)	.01	0.5-0.8	8.0
Catalyst(s)	0.001	0.005-0.05	1.0
Filler(s)	0.1	20-75	80
Air reducing additive(s)	0	0.1-0.5	2
Blocking agent additive(s)	0	0.5-1.5	5
Dispersing additive(s)	0	0.5-1	2
Leachable Plasticizer(s)	1.0	3.0-6.0	40.0
Antioxidant(s)	0	0-0.5	2
Miscibilizer(s)	0	0.1-0.5	2

EXAMPLES

Example 1

[0032] The following components were employed in this synthesis example:

DESMODUR® N3300 (hexadiisocyanate (HDI) trimer), source = Bayer Materials Science, 19.5 wt%

RUBINATE® 9433 (liquefied diphenylmethane diisocyanate (MDI)), source = Huntsman Polyurethanes, 19.4 wt%

DYNACOLL® 7360 (4000 g/mol co-polyester linear polyol), source = Evonik Industries, 51.9 wt%

FLUOROLINK® E10-H (-1500 g/mol fluorinated linear polyether), source = Solvay Solexis, 6.1 wt%

1,4-butanediol, 3.1 wt%

Dibutyl tin dilaurate (DBTDL), 0.10 wt%

[0033] 182.8 g of DYNACOLL® 7360 copolyester polyol (Evonik Industries) and 21.5 g of FLUOROLINK® E10-H dialcohol terminated, ethoxylated perfluoropolyether (Solvay Solexis Sp.A) were added to a 1 L glass reactor that had been dried overnight. The DYNACOLL® 7360 copolyester and FLUOROLINK® E10-H perfluoropolyether were heated under 25 psig vacuum at 120-130 °C for 2 hours and constant mixing with an overhead paddle mixer. The reactor was then cooled to 70 °C, vacuum was removed, and positive pressure nitrogen purge was introduced. 71.2 g of DESMODUR® N3300 aliphatic polyisocyanate (HDI timer, Bayer Material Science) and 71.6 g of RUBINATE® 9433 isocyanate (Huntsman Polyurethanes) were charged into the reactor, decreasing the temperature to ~65 °C. 0.352 g of dibutyltin dilaurate (Sigma Aldrich) was added to the reactor, and the resulting endotherm heated the mixture to ~75 °C and also increased the viscosity. The reaction mixture was allowed to react for 1 hour while mixing at 60-70 °C. 10.8 g of 1,4-butanediol (Sigma Aldrich) was added dripwise to the reactor, while mixing continued, through an addition funnel, at a rate of 1 drop every 3-5 s. This was allowed to react for 30 min, following which 14.8 g of diethyl malonate (Sigma Aldrich) was added to the reactor, allowed to mix in for 3 minutes while under nitrogen purge. The resin reaction product in the reactor was thereafter poured into dried moisture-tight containers.

[0034] This resin reaction product was then formulated with several other components, using a planetary mixer (Flakteck Speedmixer) to achieve mixing. 8.0 g of the obtained resin reaction product was added to a small Flakteck cup, followed by 0.356 g of chopped carbon fiber (Electronic Fiber Technologies), 0.110 g of BYK®-A 535 defoamer (Byk Additives), 0.286 g of

BYK® 410 liquid rheology additive (Byk Additives), 1.437 g of TEC acrylic additive, and 0.180 g of poly(ethylene glycol) sorbitol hexaoleate (PEGSH, Sigma Aldrich). Prior to mixing, the cup was dried in an oven and the additives or fillers were dried over molecular sieves or with silica gel moisture-absorbing packets. This mixture was mixed for 4 minutes at 2250 rpm. The resulting mixture was then pressed into films having a thickness of 0.005 to 0.040 inches between release films, removed from the release films after the adhesive had hardened, and then allowed to cure for 3-7 days at 40-99% RH.

[0035] After curing, films were then weighed in air and water, immersed in deionized water for 7 days at 60 °C, surface dried by rinsing in isopropanol alcohol and wiped dry, and weighed in air and water again. Immersion in water led to a mass gain of <2% and a volume swell of <5%.

Example 2

[0036] Similar formulations to those made by Example 1 above were processed into cured 0.02-0.040"-thick films, and then immersed in jet fuel, hydraulic oil, deicing fluid, and lubricating oil for 7 days at 60 °C. After exposure to these fluids, cured films exhibited <5% mass gain and <8% volume swell. These films were also analyzed by tensile testing, differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), and dynamic mechanical analysis (DMA). Tensile testing showed >1000 psi tensile strength and >100% elongation at break. DSC showed an endotherm at 50 °C that corresponded to melting of the polyester segments, but no other transitions from -40 to 175 °C. TGA showed <1 % weight loss up to 175 °C. DMA showed a significant decrease in modulus between 0 and 50 °C due to the polyester segments melting, but was otherwise mechanically robust up to 175 °C.

Example 3

[0037] When applied in an uncured state to primed aluminum test specimens and allowed to cure for 3-7 days at 40-99% RH, similar formulations to those obtained by Example 1 also demonstrated >500 psi lap shear strength at room temperature.

Example 4

[0038] The uncured adhesive formulation in Example 1 was also mixed with 5-10 wt% carbon black and 1-5 wt% fumed silica. This obtained a low-slump RHM adhesive. After pressing into films and curing for 3-7 days at at 40-99% RH, this formulation also demonstrated similar fluid resistance and lap shear strength to primed aluminum specimens as the adhesive in Example 1.

Example 5

[0039] The uncured adhesive in Example 1 was also mixed with 40-50 wt% nickel flake. This obtained an adhesive, that when cured for 3-7 days at 40-99% RH, yielded moderate electrical conductivity and radio-frequency (RF) electromagnetic shielding properties.

Example 6

[0040] 20 g of the uncured resin in Example 1 was mixed with 0.898 g of glycerol in Flakteck cup for 2 min and quickly pressed into a film. After curing for 48 h at room temperature, the resulting elastomeric film exhibited a sessile water contact angle of $95\pm 3^\circ$ and, when pulled on a tensile tester at 2 to 10 in/min, exhibited an ultimate tensile strength of 3200 ± 300 psi, elongation-at-break of $135\pm 10\%$, and Young's modulus of 7100 ± 500 psi.

[0041] While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiment, it is to be understood that the invention is not to be limited to the disclosed embodiment, but on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope thereof, limited by the following claims.

Krav

1. En reaktiv varm flydende (RHM) sammensætning omfattende en blanding af:
en urethanprepolymer som er et reaktionsprodukt af
 - 5 (i) mindst en krystalliserbar polyol,
 - (ii) en perfluoropolyetherpolyol, og
 - (iii) mindst en isocyanat;et fyldstofsmateriale; og
en udvaskelig blødgører bestående af en alifatisk ester af en carboxylsyre, hvor
 - 10 - den udvaskelige blødgører er mindst en valgt blandt gruppen bestående af triethylcitrat, tributylacetylcitrat og diethylmalonat,
 - den udvaskelige blødgører er til stede i en mængde på mellem 1.0 vægt% og 40 vægt%, og
 - den mindst ene isocyanat omfatter en blanding af hexamethylendiisocyanat (HDI) trimer og methyldiphenyldiisocyanat (MDI) i et 1:1 vægtforhold.
- 15 2. RHM sammensætningen ifølge krav 1, hvor den mindst ene krystallisebare polyol er valgt blandt gruppen bestående af polyesterpolyoler, polyethylencopolymerpolyoler, polysiloxanpolyoler og acrylpolyoler.
- 20 3. RHM sammensætningen ifølge krav 1, yderligere omfattende mindst en blød segment polyol valgt blandt gruppen bestående af polyalkylenglycoler, polysulfidpolyoler og silikonepolyoler
- 25 4. RHM sammensætningen ifølge krav 1, hvor fyldstofsmaterialet er mindst et fibrøst eller partikelformigt fyld valgt blandt gruppen bestående af silica, carbon eller metalliske fyldstofsmaterialer.

5. RHM sammensætningen ifølge krav 4, hvor fyldstofmaterialet er mindst et valgt blandt gruppen bestående af nikkel, jern, aluminium, wolfram, sølv, guld, platin, palladium og carbonmaterialer.

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6. RHM sammensætningen ifølge krav 5, hvor det mindst ene fyldstofmateriale er til stede i en mængde på mellem 0.1 vægt% og 80 vægt%, baseret på den totale sammensætnings vægt.

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7. RHM sammensætningen ifølge krav 1, yderligere omfattende et nonionisk blandemiddel valgt blandt gruppen bestående af ethylendiamintetrakis(propoxylate-block-ethoxylate)tetrol (EDTP-b-ET) og poly(ethylenglycol)sorbitolhexaoleat (PEGSH)

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8. RHM sammensætningen ifølge krav 1, yderligere omfattende mellem 0.1 vægt% og 80 vægt% af mindst et additiv udover fyldstofmaterialet, som vælges blandt gruppen bestående af densitetsmodifikatorer, dispergeringsmidler, blokeringsmidler, luftreducerende additiver, antioxidant, flowforbedringsmidler, konduktivitetsmodifikatorer og hærdningsrate acceleratorer.

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9. Et substrat som er i det mindste delvist coated med RHM sammensætningen ifølge krav 1.

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10. En fremgangsmåde til dannelse af en coating omfattende anvendelse af RHM sammensætningen ifølge krav 1 på et substrat ved en smeltetemperatur for denne RHM, og at tillade denne RHM at hærde på substratet.

11. En fremgangsmåde til fremstilling af en reaktiv varm flydende (RHM)

sammensætning omfattende:

(a) dannelse af en urethanprepolymer ved at reagere (i) mindst en krystalliserbar polyol,

(ii) en perfluoropolyetherpolyol, og (iii) mindst en isocyanat; og derefter (b) blande

5 urethanprepolymeren med (1) et fyldstofsmateriale og (2) en udvaskelig blødgører bestående af en alifatisk ester af en carboxylsyre,

hvor,

- den udvaskelige blødgører er mindst en valgt blandt gruppen bestående af triethylcitrat, tributylacetylcitrat og diethylmalonat,

10 - den udvaskelige blødgører er tilstede i en mængde på mellem 1.0 vægt% og 40 vægt%,
og

- den mindst ene isocyanat omfatter en blanding af hexamethylendiisocyanat (HDI) trimer og methylendiphenyldiisocyanat (MDI) i et 1:1 vægtforhold.

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