

REACTIVE HOT MELT ADHESIVE COMPOSITIONS CONTAINING MULTI-FUNCTIONAL POLYOLS AND POLYMERIC ISOCYANATE COMPOUNDS, AND METHOD OF MANUFACTURE THEREOF

TECHNICAL FIELD

Particular aspects of the present disclosure are directed to reactive hot melt (RHM) adhesive compositions containing a combination of di-functional and tri-functional polyols in conjunction with a combination of an isocyanate compound and a polymeric isocyanate compound. Particular aspects of the present disclosure are also directed to a method of manufacturing such RHM adhesive compositions involving a two-step addition of the polymeric isocyanate compound.

BACKGROUND

Most conventional reactive hot melt (RHM) adhesives or adhesive compositions are polyurethane based materials, which cure upon exposure to moisture. A given RHM adhesive composition typically contains an isocyanate compound (e.g., methylene diphenyl diisocyanate, known as MDI); crystalline, amorphous, and/or liquid polyols (e.g., polyether and/or polyester polyols); reactive and/or non-reactive thermoplastic components (e.g., acrylic, EVA, and/or polystyrene components); moisture-curing catalysts; and various non-reactive additives. Prior to exposure to water, a RHM adhesive is considered to be a solid thermoplastic substance that can be melted repetitively during processing. This type of adhesive is generally melted and used at a temperature range between 85 – 130°C.

Prior to curing, a RHM adhesive ideally exhibits a relatively high degree of adhesion to the substrate to which it is applied on. This pre-cured adhesion is commonly referred to as a RHM adhesive's set strength, green strength, or hot tack. With respect to curing, when exposed to moisture (e.g., ambient moisture), a RHM adhesive is converted into a thermoset substance over time. This moisture curing mechanism is triggered once water reaches the terminal and free isocyanate groups within the RHM adhesive. As a result, chain-extension is induced, thus forming a larger network of polyurethane polymers. Such a crosslinked adhesive composition provides high strength, toughness, creep resistance, and heat resistance to the final bond. Hot

melt curable adhesive compositions can provide higher mechanical strength and heat resistance compared to conventional non-curable counterpart adhesive compositions.

With respect to conventional guidelines relating to the formulation of a RHM adhesive composition, the use of polyols and/or isocyanate with a lower degree of branching results in a cured or final product having reduced strength, whereas the use of polyols and/or isocyanate with a higher degree of branching can improve the strength of the cured product by adding more crosslinking density. However, excessive branching can lead to poor pot stability, also referred to as heat stability or melt stability, which is a measure of the extent to which a RHM adhesive composition in a molten state maintains consistency in key parameters including melt viscosity. Moreover, beyond a certain degree of branching, cured product strength actually degrades. Consequently, diols with a functionality number of two are typically much more favored than polyols with higher or lower functionality numbers, in order to avoid either poor pot stability, or building a polymer adhesive system that exhibits reduced mechanical strength when cured.

A need exists for RHM adhesive compositions providing improved final product strength, which also exhibit good or very good pot stability.

SUMMARY

In accordance with several embodiments of the present disclosure, a reactive hot melt (RHM) adhesive composition includes: a di-functional polyol compound; a tri-functional polyol compound; an isocyanate compound having an isocyanate functionality of two or more; and a polymeric isocyanate compound having an isocyanate functionality greater than two, wherein a mass fraction of the polymeric isocyanate compound in the RHM adhesive composition is between 10 – 20%, inclusive.

The RHM adhesive composition can further include (e.g., on an optional basis) one or more of: a reactive polymer compound, a non-reactive polymer compound, a functional polymer compound, and a non-functional polymer compound. Thus, the RHM adhesive composition can include one or more reactive or non-reactive and/or functional or nonfunctional polymer

compounds, such as at least one high molecular weight polymer compound (e.g., a thermoplastic compound) having a weight average molecular weight between 20,000 – 100,000 g/mol.

The tri-functional polyol compound can have a molecular weight between 1,000 and 3,600 (e.g., a molecular weight of 3,000 or approximately 3,000) g/mol.

The mass fraction of the tri-functional polyol compound plus the mass fraction of the polymeric isocyanate compound can be greater than or equal to approximately 20%, 25%, 30%, 35%, or 40% of the mass of the RHM adhesive composition, and more particularly the mass fraction of the tri-functional polyol compound plus the mass fraction of the polymeric isocyanate compound can be up to 46%, or approximately 45 – 47%, of the mass of the RHM adhesive composition.

The tri-functional polyol compound can include or be a polyether triol.

In various embodiments, the RHM adhesive composition exhibits a melt stability as indicated by a rate of increase of in-melt RHM adhesive composition viscosity of less than 20% per hour across a time period of approximately or at least two hours (e.g., 2 hours).

A ratio of the mass fraction of the tri-functional polyol compound to the mass fraction of the polymeric isocyanate compound in the RHM adhesive composition can be between 50 - 128%.

A ratio of the mass fraction of the tri-functional polyol compound to the mass fraction of the polymeric isocyanate compound in the RHM adhesive composition can be between 50 - 80%, wherein the RHM adhesive composition exhibits a melt stability as indicated by a rate of increase of in-melt RHM adhesive composition viscosity of less than 12% per hour across a time period of approximately or at least two hours (e.g., 2 hours).

A ratio of the mass fraction of the tri-functional polyol compound to the mass fraction of the polymeric isocyanate compound in the RHM adhesive composition can be between or approximately between 110 – 122%, wherein the RHM adhesive composition exhibits a melt

stability as indicated by the rate of increase of in-melt RHM adhesive composition viscosity of less than 17% per hour across a time period of approximately or at least two hours (e.g., 2 hours).

The di-functional polyol compound can include or be a polyether diol or a polyester diol.

In various embodiments, the RHM adhesive composition exhibits a post-melt free % NCO content of less than 3.5.

In accordance with particular embodiments of the present disclosure, a process for producing a reactive hot melt (RHM) adhesive composition in accordance with an embodiment of the present disclosure as set forth above includes: (1) a first process portion including: adding the isocyanate compound and optionally adding the polymer isocyanate compound to a melt containing the di-functional polyol compound and the tri-functional polyol compound to form an intermediate RHM adhesive composition in the melt; and allowing the free % NCO of the melt to reach and not exceed a first free % NCO target value; and (2) a second process portion initiated subsequent to the free % NCO of the melt reaching or falling below the first free % NCO target value, the second process portion including: adding or further adding the polymer isocyanate compound to the melt; and allowing the free % NCO of the melt to reach and not exceed a second free % NCO target value distinct from the first free % NCO target value, wherein the second free % NCO target value is less than or equal to 3.5 (e.g., in multiple embodiments, the second free % NCO target value is 3.5 or approximately 3.5, but not greater than 3.5), such that produced RHM adhesive composition exhibits a post-melt free % NCO of less than 3.5. The first free % NCO target value can be less than the second free % NCO target value; for instance, in several embodiments the first free % NCO target value is less than or equal to 2.5 (e.g., the first free % NCO target value is 2.5 or approximately 2.5).

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A is a graph or plot illustrating melt stability results for sample RHM adhesives A and B of Example 1, and FIG. 1B is a graph or plot illustrating melt stability results for sample RHM adhesives C, D, and E of Example 1.

FIG. 2A is a graph or plot illustrating melt stability results for sample RHM adhesives F, G, H, and I of Example 1, and FIG. 2B is a graph or plot illustrating melt stability results for sample RHM adhesives J, K, L, and M of Example 1.

FIG. 3 is a graph or plot illustrating melt stability results for sample RHM adhesives H, H1, and H2 of Example 2.

FIG. 4A is a graph or plot illustrating melt stability results for sample RHM adhesives N, O and P of Example 3, and FIG. 4B is a graph or plot illustrating melt stability results for sample RHM adhesives Q, R, and S of Example 3.

DETAILED DESCRIPTION

Particular representative embodiments in accordance with the present disclosure are described in detail below in relation to Tables 1 – 5 and FIGs. 1 – 4B. Individuals having ordinary skill in the relevant art will understand that the representative embodiments described herein are provided for purpose of clarity and to aid understanding, and the scope of the present disclosure and the claims appended thereto is not limited to these representative embodiments.

The unit of measure of molecular weight values recited in this patent application are defined or to be taken as grams per mol (g/mol), in a manner readily understood by individuals having ordinary skill in the art.

In the description herein, the terms “approximate,” “approximately,” and/or “about,” when used in association or conjunction with a specified value or value range, can mean to within +/- 20%, +/- 15%, +/- 12.5%, +/- 10%, +/- 7.5%, +/- 5%, +/- 4%, +/- 3%, +/- 2.5%, +/- 1%, or +/- 0% of the specified value or value range, depending upon embodiment details in view of the satisfaction of process and/or product objectives or requirements, such as pot stability and product mechanical strength (e.g., green strength, and/or cured product strength).

Aspects of Representative RHM Adhesive Compositions and Production Processes

Embodiments in accordance with the present disclosure are directed to reactive hot melt (RHM) adhesive compositions or RHM adhesives that include multi-functional polyol compounds or multi-functional polyol containing compounds; an isocyanate compound or isocyanate containing compound; and a polymeric isocyanate compound or polymeric isocyanate containing compound. More particularly, various embodiments in accordance with the present disclosure are directed to RHM adhesive compositions that include, contain, or are produced using a combination of (i) a di-functional polyol or di-functional polyol compound (e.g., at least one type of di-functional polyol compound or di-functional polyol containing compound), and (ii) a tri-functional polyol or tri-functional polyol compound (e.g., at least one type of tri-functional polyol compound or tri-functional polyol containing compound); plus a combination of (iii) an isocyanate or isocyanate compound (e.g., at least one type of isocyanate compound or isocyanate containing compound) having an isocyanate functionality of two or more, and (iv) a polymeric isocyanate or polymeric isocyanate compound (e.g., at least one type of polymeric isocyanate compound or polymeric isocyanate containing compound) having an isocyanate functionality greater than two. RHM adhesive compositions in accordance with embodiments of the present disclosure also contain one or more reactive or non-reactive and/or functional or nonfunctional polymer compounds, such as thermoplastic compounds, which in several embodiments can be categorized as high molecular weight polymer compounds that have a molecular weight or weight average molecular weight of 20,000 or more, e.g., between 20,000 – 100,000, or between 30,000 – 100,000. Moreover, RHM adhesive compositions in accordance with embodiments of the present disclosure can contain or have added thereto additional or other compounds, components, or ingredients, for instance, possibly one or more moisture-curing catalysts; and possibly a number of non-reactive additive substances or additives, in a manner readily understood by individuals having ordinary skill in the relevant art.

For purpose of simplicity and to aid understanding, in multiple representative RHM adhesive composition embodiments considered herein, the aforementioned di-functional polyol compound includes or is a polyether diol; the tri-functional polyol compound includes or is a polyether triol; the isocyanate compound includes or is methylene diphenyl diisocyanate (MDI); the polymeric isocyanate compound includes or is polymeric MDI; and the thermoplastic compound includes or is an acrylic compound or an ethylene vinyl acetate (EVA) compound. However, RHM

adhesive composition embodiments in accordance with the present disclosure are not limited to these specific types of compounds. In the Examples provided below, particular representative embodiments of RHM adhesives and properties thereof are described in detail. Also for purpose of simplicity and to aid understanding, these representative example RHM adhesive embodiments contain or are formulated or produced using particular, specified, or specific types of constituent compounds. Notwithstanding, individuals having ordinary skill in the relevant art will recognize that embodiments in accordance with the present disclosure are not limited to the particular, specified, or specific types of constituent compounds recited in the Examples below, and RHM adhesive compositions in accordance with embodiments of the present disclosure can be formulated or produced using a wide variety of commercially available constituent compounds.

For instance, depending upon embodiment details, in alternate embodiments the di-functional polyol compound, the tri-functional polyol compound, the isocyanate compound, the polymer isocyanate compound, the high molecular weight polymer compound(s), and/or the additional or other compounds, constituents, components, or ingredients can respectively include or be one or more types of di-functional polyol compounds, tri-functional polyol compounds, isocyanate compounds, polymer isocyanate compounds, high molecular weight polymer compounds, and/or additional or other compounds described in European Patent EP 1642915 and/or US Patent Publication No. 20030010442, in a manner readily understood by individuals having ordinary skill in the relevant art.

Embodiments in accordance with the present disclosure are further directed to a process or method by which the aforementioned RHM adhesive compositions are provided, produced, or manufactured. In various embodiments, such a RHM adhesive composition production process involves two distinct, distinguishable, or separate sub-processes, process portions, or process steps with respect to the addition or manner of addition of the polymeric isocyanate compound to a melt. For each of the two process portions or steps, the free isocyanate functional group content, i.e., free % NCO, is precisely controlled, limited, established, or adjusted.

More particularly, in a first process portion or step (e.g., a first polymerization process portion or step) involving the addition of an isocyanate compound and possibly a polymeric isocyanate compound to a melt in order to produce a first, precursor, or intermediate RHM adhesive composition, the free % NCO of the melt is controlled, limited, established, or adjusted such that it satisfies, reaches, or does not exceed a first free % NCO target value, threshold, or limit. In a second process portion or step (e.g., a second polymerization process portion or step) involving the addition or further addition of polymeric isocyanate compound to the first, precursor, or intermediate RHM adhesive composition, the free % NCO of the melt is controlled, limited, established, or adjusted such that it satisfies, reaches, or does not exceed a second free % NCO value, threshold, or limit, which is typically distinct from the first free % NCO target value. The result of the second process portion is the production of a second, intended, or final RHM adhesive composition in accordance with an embodiment of the present disclosure.

The first free % NCO target value can be defined as a target or maximum in-melt free % NCO of the first, precursor, or intermediate RHM adhesive composition prior to the initiation of the second process step; and the second free % NCO target value can be defined as a target or maximum in-melt free % NCO of the second RHM adhesive composition at the end of the second process step, prior to further processing and/or cooling of the second RHM adhesive composition. The actual or real post-melt free % NCO of the RHM adhesive composition produced is typically less than the second free % NCO target value. Careful adjustment of the in-melt free % NCO of the first, precursor, or intermediate RHM adhesive composition and the in-melt free % NCO of the second or final RHM adhesive composition results in good melt stability, as well as RHM adhesive product that exhibits good set strength. In various embodiments, the first free % NCO target value is typically not greater than 2.5 (e.g., the first free % NCO target value is less than or equal to 2.5); and the second free % NCO target value is not greater than 3.5 (e.g., the second free % NCO target value is less than, or less than or equal to, 3.5), and thus the post-melt free % NCO of the RHM adhesive composition produced is less than, or less than or equal to, 3.5.

A RHM adhesive production process in accordance with an embodiment of the present disclosure can exhibit acceptable to excellent overall process stability, including pot stability,

across an acceptable to wide relative percentage range of RHM adhesive constituent component or ingredients, and can result in the production of a RHM adhesive having a high molecular weight tri-functional polyol compound therein, yet which exhibits acceptable to excellent mechanical strength as well as acceptable to excellent process stability.

In certain embodiments, a RHM adhesive pre-polymer is prepared through condensation polymerization of a number of selected polyol compounds, including di- and/or tri-functional polyol compound(s), with or without a thermoplastic compound reacting with monomeric isocyanate with or without a polymeric isocyanate compound depending upon the sample under consideration. The reaction between the di- and/or tri-functional polyol compound(s) and the isocyanate compound and any polymeric isocyanate compound preferably reaches or meets a first free % NCO target value, which in various embodiments is 2.5. In a second polymerization process portion or step, a polymeric isocyanate compound can be added or further added and polymerized until the reaction reaches or meets a second free % NCO target value, which in various embodiments is 3.5, thereby providing or producing the RHM adhesive composition under consideration.

In several embodiments, RHM adhesive composition involves or includes a mixture of polyols such as di- and/or tri-functional polyethers or mostly polyethers in liquid form, polyester polyol, optionally a thermoplastic compound, and optionally one or more additives such as a deformer or fillers. These mixtures therein can be exposed to negative or vacuum pressure to remove moisture from mixture, in a manner readily understood by individuals having ordinary skill in the relevant art. These compounds react with monomeric isocyanate with or without a polymeric isocyanate compound depending upon the sample under consideration. The reaction between the tri-functional polyol compound and the isocyanate compound and any polymeric isocyanate compound prefer to reaches or meets a first free % NCO target value. Once the desired first free %NCO target value has been reached, a polymeric isocyanate compound can be added or further added and polymerize until reaches or meets a second free % NCO target value, thereby providing or producing the RHM adhesive composition under consideration.

Further Aspects of Representative RHM Adhesive Compositions and Production Processes

In association with experimentation directed to formulating RHM adhesive compositions, the inventors named on the present application verified that when a tri-functional polyol composition was used in the formulation of a RHM adhesive composition, the pot stability of the RHM adhesive composition dropped or degraded. However, the inventors additionally found that the pot stability improved when higher molecular weight tri-functional polyol was used, and further found that the pot stability significantly, greatly, or surprisingly improved to establish a significant domain of pot or melt stability when (a) the molecular weight of the tri-functional polyol was between 1,000 – 3,600, and in various embodiments was high or suitably high, e.g., 3,000 or approximately 3,000, or between approximately 2,500 – 3,600; and (b) the RHM composition formulation included a polymeric isocyanate having a functionality greater than two that was added to the melt in accordance with a two-step process such as that described above, in which free % NCO is carefully or precisely controlled, established, or adjusted at each process step (e.g., at the end or as an end procedure of each process step). This domain of pot stability was maintained across significant variations in the mass fraction or weight percentage of the high molecular weight tri-functional polyol relative to the mass fraction or weight percentage of the polymeric isocyanate in the formulated RHM adhesive compositions, as further elaborated upon below.

Examples

Sample RHM Adhesive Composition Raw Materials

With respect to Examples 1 – 3 described herein, Table 1 below shows raw materials or source compounds that were selectable for the formulation or production particular sample RHM adhesive compositions, referred to hereafter as sample RHM adhesives for purpose of clarity and simplicity, identified as A – H, H1 – H2, and I - S of Tables 2 – 5.

Trade name	Describe
Polimaxx 1010	polyether diols, MW 1000, available from IRPC
Poly-G 30-280	polyether triols, MW 600, available from Monument
Poly-G 30-168	polyether triols, MW 1000, available from Monument
Poly-G 30-56NF	polyether triols, MW 3000, available from Monument
Dynacoll 7360	polyester diol, MW 3500, available from Evonik
Elvacite 2013	acrylic resin, Tg 76° C, MW 34000, available from Lucite
MV02514	ethylene vinyl acetate, %VA 14, available from Exxon Mobil

UL40028CC	ethylene vinyl acetate, %VA 28, available from Exxon Mobil
Desmodur [®] 44C	methylene diphenyl diisocyanate, available from Bayer
Suprasec 2647	polymeric MDI, functionality 2.2, available from Huntsman
Lupranate M5S	polymeric MDI, functionality 2.4, available from O-BASF
Lupranate MTHS	polymeric MDI, functionality 2.7, available from O-BASF

Table 1: Raw materials selectable for use in formulating the RHM adhesive compositions of the Examples

Two-Step Sample RHM Adhesive Production Process

For the production or fabrication of each sample RHM adhesive in the Examples below, a mixture of polyols in liquid form as polyethers or mostly polyethers were combined with an additive such as a defoamer and heated to and then maintained at a first target temperature of approximately 120°C while continuously stirring. Next, one or more thermoplastic compounds were added followed by the addition of polyester polyols, which were mostly in solid form. The mixing vessel was then subjected to vacuum pressure in a conventional manner, with ongoing continuous stirring, to remove moisture from the mixture. The quantification of moisture content or the extent of moisture removal was determined by way of a Mettler C20 Coulometric KF Titrator (Karl Fischer Titration method), in a manner readily understood by individuals having ordinary skill in the art. For any given sample RHM adhesive, the extent of moisture removal was deemed sufficient or moisture removal was defined as essentially complete once the sample RHM adhesive contained less than or equal 0.05% moisture content.

After that, isocyanate and/or polymeric isocyanate were added to the liquid mixture during ongoing or continuous stirring. The resulting polymerization process was allowed to occur during a first polymerization process portion until a first free % NCO target value of 2.5 had been reached. After this first free % NCO target value had been reached, another measured amount or mass of isocyanate and/or polymeric isocyanate was added to the liquid mixture during ongoing or continuous stirring, and the resulting polymerization process was allowed to occur during a second polymerization process portion until a second free % NCO target value of 3.5 had been reached, thereby providing or producing the sample RHM adhesive under consideration.

The sample RHM adhesive was subsequently poured hot from the vessel into a foil under dry nitrogen atmosphere to prevent exposure to moisture, after which melt stability testing occurred.

Melt Stability Testing

Each sample RHM adhesive was held in a viscometer at 120°C until complete temperature equilibrium was established. An initial melt viscosity of each sample was tested or measured once temperature equilibrium was established, and the melt viscosity or melt viscosity change of each sample was tested and recorded every 15 minutes across a time period of at least 2 hours. Melt viscosity and melt viscosity change was tested, measured, or determined using a Brookfield Viscometer, spindle 27, in conjunction with a Thermosel heating unit and a melt temperature of 120°C, in a manner readily understood by individuals having ordinary skill in the relevant art.

It should be noted that a tested sample RHM adhesive was considered or defined as unacceptable, or as having unacceptable melt stability or melt viscosity stability, if the tested sample RHM adhesive's melt viscosity stability was such that melt viscosity increased more than 20% per hour, or the slope of melt viscosity vs. time data showed a transition from linear behavior to non-linear behavior, e.g., once the data has been graphed or plotted, during a 2 hour or approximately 2 hour time period having a start time corresponding to, established or defined by, or beginning with an initial melt viscosity test or measurement performed on a sample under consideration (e.g., immediately, essentially immediately, nearly immediately, or directly after the second free % NCO target was met). A tested sample RHM adhesive can be considered or defined to exhibit acceptable or good melt stability if during a 2 hour or approximately 2 hour time period corresponding to, established or defined by, or beginning with the initial melt viscosity test (e.g., which was performed essentially immediately, nearly immediately, or directly after the second free % NCO target was met), the tested sample RHM adhesive's melt viscosity stability did not increase more than 20 % per hour (e.g., was less than, or less than or equal to, 20% per hour), and the slope of the melt viscosity vs. time data did not exhibit a transition or a sustained transition from linear to non-linear behavior during this 2 hour or approximately 2 hour time period. Melt viscosity or melt viscosity change of each sample RHM adhesive was tested and recorded every 15 minutes across this 2 hour or approximately 2 hour time period. Individuals having ordinary skill in the art will understand that melt viscosity or melt viscosity

change could be tested and recorded more or less frequently (e.g., every 2, 5, 10, 20, or 30 minutes).

Example 1

In Example 1, sample RHM adhesives A – M were prepared in association with studying several RHM adhesive composition formulations containing (i) particular types of polyether triols of different molecular weights, in addition to (ii) particular mass fractions of polymeric MDI. Table 2 below provides formulation details, post-melt real free % NCO data, and melt stability test results corresponding to sample RHM adhesives A – E; and Table 3 below provides formulation details, post-melt real free % NCO data, and melt stability test results corresponding to sample RHM adhesives F – M.

Sample:		A	B	C	D	E
Polimaxx 1010		40.00	40.00	40.00	40.00	40.00
(%w/w)		(36.46)	(36.34)	(34.87)	(34.74)	(32.97)
Poly-G 30-280		4.00	4.00	-	-	-
(%w/w)		(3.65)	(3.63)	-	-	-
Poly-G 30-168		-	-	8.00	8.00	12.00
(%w/w)		-	-	(6.97)	(6.95)	(9.89)
Dynacoll 7360		20.00	20.00	20.00	20.00	20.00
(%w/w)		(18.23)	(18.17)	(17.43)	(17.37)	(16.49)
Elvacite 2013		20.00	20.00	20.00	20.00	20.00
(%w/w)		(18.23)	(18.17)	(17.43)	(17.37)	(16.49)
Desmodur [®] 44C		14.74	4.05	15.25	4.11	5.05
(%w/w)		(13.44)	(3.68)	(13.29)	(3.57)	(4.16)
Suprasec 2647		10.97	22.01	11.47	23.03	24.26
(%w/w)		(10.00)	(20.00)	(10.00)	(20.00)	(20.00)
Theo. %	Step 1	2.50	2.50	2.50	2.50	2.50
NCO	Step 2	3.50	3.50	3.50	3.50	3.50
Real final % NCO		3.36	3.36	3.42	3.44	3.40
Appearance		Clear	Clear	Clear	Clear	Clear
Viscosity (cPs)		6,567	13,130	6,608	12,670	32,380

at 120° C					
Melt stability (% increase per hour)	15.0	27.6	14.6	15.8	45.5

Table 2: Formulation Details and Melt Stability Results for Sample RHM Adhesives A – E

As shown in Table 2, samples A and B contained low molecular weight polyether triols (Poly-G 30-280, MW 600), whereas samples C, D, and E contained higher molecular weight polyether triols, which can be categorized as medium molecular weight polyether triols (Poly-G 30-168, MW 1000). In samples A and B, the added amount (e.g., mass in grams) of low molecular weight polyether triols was held constant while polymeric MDI mass fraction was respectively increased from 10% to 20%. Similarly, in samples C and D, the added amount of medium molecular weight polyether triol was held constant while polymeric MDI mass fraction was respectively increased from 10% to 20%. In sample E, the added amount of the medium molecular weight polyether triol was increased by 50%, while the mass fraction of polymeric MDI was maintained at 20%. With respect to each of samples A – E, the added amount of MDI (Desmodur® 44C) was established or adjusted accordingly for purpose of establishing or maintaining samples having intended polymeric MDI mass fractions.

FIG. 1A is a graph or plot illustrating melt stability results for sample RHM adhesives A and B, and FIG. 1B is a graph or plot illustrating melt stability results for sample RHM adhesives C, D, and E.

As indicated in Table 2 and FIGs. 1A – 1B, the use of higher molecular weight polyether triols enables the incorporation of a greater amount or higher mass fraction of polymeric MDI into a RHM adhesive composition, while still maintaining melt stability. More particularly, the use of medium molecular weight polyether triols rather than low molecular weight polyether triols resulted in an expansion or extension in the domain or range of melt stability, such that melt stability desirably remained less than or equal to 20% even though the mass fraction of polymeric MDI was increased from 10% to 20%. However, when the mass fraction of

polymeric MDI was kept at 20% and the amount of medium molecular weight polyether triols was increased by 50%, melt stability sharply decreased.

Sample		F	G	H	I	J	K	L	M
Polimaxx 1010		40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00
	(%w/w)	(33.92)	(32.52)	(31.23)	(27.92)	(26.98)	(26.08)	(25.25)	(24.47)
Poly-G 30-56NF		12.00	16.00	20.00	32.00	36.00	40.00	44.00	48.00
	(%w/w)	(10.17)	(13.01)	(15.62)	(22.34)	(24.28)	(26.08)	(27.78)	(29.36)
Dynacoll 7360		20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
	(%w/w)	(16.96)	(16.26)	(15.62)	(13.96)	(13.49)	(13.04)	(12.63)	(12.24)
Elvacite 2013		20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
	(%w/w)	(16.96)	(16.26)	(15.62)	(13.96)	(13.49)	(13.04)	(12.63)	(12.24)
Desmodur® 44C		2.35	2.40	2.45	2.60	2.62	2.70	2.70	2.70
	(%w/w)	(1.99)	(1.95)	(1.91)	(1.82)	(1.77)	(1.75)	(1.71)	(1.69)
Suprasec 2647		23.59	24.60	25.62	28.65	29.66	30.67	31.69	31.69
	(%w/w)	(20.00)	(20.00)	(20.00)	(20.00)	(20.00)	(20.00)	(20.00)	(20.00)
Theo. %	Step 1	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
NCO	Step 2	3.50	3.50	3.50	3.50	3.50	3.50	3.50	3.50
Real final % NCO		3.26	3.30	3.45	3.35	3.35	3.28	3.36	3.42
Appearance		Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear
Viscosity (cPs) at 120° C		5,533	4,982	6,525	8,950	9,525	9,087	13,440	8,275
Melt stability (% increase per hour)		10.8	11.1	11.7	16.8	16.5	20.3	26.3	26.0

Table 3: Formulation Details and Melt Stability Results for Sample RHM Adhesives F - M

As shown in Table 3, samples F - M contained high molecular weight polyether triols (Poly-G 30-56NF, MW 3000) in increasing amounts or mass fractions, under conditions of a constant 20% mass fraction of polymeric MDI. With respect to each of samples F – M, the added amount of MDI was established or adjusted accordingly for purpose of establishing or maintaining samples having the intended polymeric MDI mass fraction.

FIG. 2A is a graph or plot illustrating melt stability results for sample RHM adhesives F, G, H, and I of Example 1, and FIG. 2B is a graph or plot illustrating melt stability results for sample RHM adhesives J, K, L, and M of Example 1.

As indicated in Table 3 and FIGs. 2A – 2B, relative to samples F - J, under conditions of 20% mass fraction of polymeric MDI, melt stability unexpectedly remained excellent, good, or acceptable even when the added amount or mass fraction of high molecular weight polyether triols significantly, very significantly, or greatly increased (e.g., doubled or slightly more than doubled). Results for sample RHM adhesive K indicate that an approximate melt stability transition point occurs when the mass fraction of polyether triols approaches or exceeds 25 - 27% or about 26% relative to the 20% mass fraction of polymeric MDI. Within a range or expected range of experimental error for melt stability such as 2% or less (e.g., 1.5%), it is expected that acceptable melt stability can be achieved for RHM adhesive compositions in accordance with the present disclosure using a mass fraction of polyether triols of up to 26%, or approximately 26% (e.g., to within one-half of one percent), in conjunction with a 20% mass fraction of polymeric MDI.

In addition to the foregoing, as can be seen from the melt stability results for sample RHM adhesives F, G, and H, a range of good to excellent melt stability between 10.8 - 11.7%, or less than 12%, was observed for mass fractions of high molecular weight polyether triols ranging from 10.17 to 15.62%, or about 10% to 15.5 – 16.0% (e.g., to within one-half of one percent or less), with 20% mass fraction of polymeric MDI. More particularly, for sample RHM adhesives F, G, and H, where the ratio of the mass fraction of the tri-functional polyol compound to the mass fraction of the polymeric isocyanate compound in the RHM adhesive composition was between or approximately between 50 - 80%, melt stability, as indicated by the rate of increase of melt RHM adhesive composition viscosity, was less than or approximately less than 12% per hour. Furthermore, good to excellent melt stability was exhibited or achieved across a mass fraction increase in polyether triols of 53.59%, or at least 50%, relative to an initial or reference mass fraction of polyether triols of 10.17% or approximately 10%.

Additionally, for sample RHM adhesives I, J, and K, the results in Table indicate that when a ratio of the mass fraction of the tri-functional polyol compound to the mass fraction of the polymeric isocyanate compound in the RHM adhesive composition was between or approximately between 110 – 122%, melt stability, as indicated by the rate of increase of melt RHM adhesive composition viscosity, was less than or approximately less than 17% per hour.

Example 2

In Example 2, sample RHM adhesives H1 and H2 were prepared based on sample RHM adhesive H of Table 2 (i.e., using sample RHM adhesive H as a reference sample), in order to test the effects of another compositional variation, namely, substituting the acrylic resin with two types of ethylene vinyl acetate (EVA) resin. More particularly, Table 4 below provides formulation details, post-melt real free % NCO data, and melt stability test results corresponding to sample RHM adhesives H, H1, and H2, where sample RHM adhesive H1 included EVA having 14% vinyl acetate (VA), and sample RHM adhesive H2 included EVA having 28% VA. Additionally, FIG. 3 is a graph or plot illustrating melt stability results for sample RHM adhesives H, H1 and H2.

Sample	H	H1	H2
Polimaxx 1010	40.00	40.00	40.00
(%w/w)	(31.24)	(31.24)	(31.24)
Poly-G 30-56NF	20.00	20.00	20.00
(%w/w)	(15.62)	(15.62)	(15.62)
Dynacoll 7360	20.00	20.00	20.00
(%w/w)	(15.62)	(15.62)	(15.62)
Elvacite 2013	20.00		
(%w/w)	(15.62)	-	-
MV02514		20.00	
(%w/w)	-	(15.62)	-
UL40028CC			20.00
(%w/w)	-	-	(15.62)
Desmodur [®] 44C	2.45	2.45	2.45
(%w/w)	(1.91)	(1.91)	(1.91)

Suprasec 2647 (%w/w)		25.62 (20.00)	25.62 (20.00)	25.62 (20.00)
Theo. %	Step 1	2.50	2.50	2.50
NCO	Step 2	3.50	3.50	3.50
Real final % NCO		3.45	3.33	3.37
Appearance		Clear	Clear	Clear
Viscosity (cPs) at 120° C		6,525	5,583	5,733
Melt stability (% increase per hour)		11.7	17.3	18.9

Table 4: Formulation Details and Melt Stability Results
for Sample RHM Adhesives H, H1 and H2

As the results show, both EVA resins tested, which have significantly different %VA, give good melt stability results. Consequently, RHM adhesive compositions in accordance with embodiments of the present disclosure can include one or more types of resin other than acrylic resin, particularly one or more types of EVA resin as a substitute for acrylic resin, while still providing good melt stability.

Example 3

As indicated above, sample RHM adhesives A – M of Examples 1 and 2 included polymeric MDI having a functionality of 2.2. In Example 3, sample RHM adhesives N – S were prepared in order to test the effects of formulations including polymeric MDI having higher functionality, namely, 2.4 (Lupranate M5S) and 2.7 (Lupranate MTHS). More particularly, sample RHM adhesives N, O, and P were formulations employing different mass fractions of polymeric MDI having a functionality of 2.4; and sample RHM adhesives Q, R, and S were formulations employing different mass fractions of polymeric MDI having a functionality of 2.7. For each of samples N – S, the added amount (e.g., mass in grams) of high molecular weight polymer triols was kept constant.

Sample	N	O	P	Q	R	S
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Polimaxx 1010 (%w/w)		40.00 (31.29)	40.00 (31.12)	40.00 (31.10)	40.00 (31.18)	40.00 (31.16)	40.00 (31.12)
Poly-G 30-56NF (%w/w)		20.00 (15.64)	20.00 (15.56)	20.00 (15.55)	20.00 (15.59)	20.00 (15.58)	20.00 (15.56)
Dynacoll 7360 (%w/w)		20.00 (15.64)	20.00 (15.56)	20.00 (15.55)	20.00 (15.59)	20.00 (15.58)	20.00 (15.56)
Elvacite 2013 (%w/w)		20.00 (15.64)	20.00 (15.56)	20.00 (15.55)	20.00 (15.59)	20.00 (15.58)	20.00 (15.56)
Desmodur [®] 44C (%w/w)		15.06 (11.78)	2.83 (2.20)	1.60 (1.24)	15.45 (12.04)	14.26 (15.58)	13.10 (10.19)
Lupranate M5S (%w/w)		12.78 (10.00)	25.71 (20.00)	27.01 (21.00)	-	-	-
Lupranate MTHS (%w/w)		-	-	-	12.83 (10.00)	14.12 (11.00)	15.42 (12.00)
Theo. %	Step 1	2.50	2.50	2.50	2.50	2.50	2.50
NCO	Step 2	3.50	3.50	3.50	3.50	3.50	3.50
Real final % NCO		3.40	3.44	3.30	3.44	3.30	3.18
Appearance		Clear	Clear	Clear	Clear	Clear	Clear
Viscosity (cPs) at 120° C		4,795	16,980	27,420	10,020	7,567	19,730
Melt stability (% increase per hour)		11.3	17.7	34.9	14.8	16.5	37.0

Table 5: Formulation Details and Melt Stability Results for Sample RHM Adhesives N - S

FIG. 4A is a graph or plot illustrating melt stability results for sample RHM adhesives N, O and P (polymeric MDI functionality 2.4), and FIG. 4B is a graph or plot illustrating melt stability results for sample RHM adhesives Q, R, and S (polymeric MDI functionality 2.7).

As indicated in Table 5 and FIGs. 4A – 4B, sample RHM adhesives containing polymeric MDI with a functionality of 2.4 showed good melt stability for both 10% and 20% polymeric MDI mass fractions; and sample RHM adhesives containing polymeric MDI with a functionality of

2.7 showed good melt stability for 10% and 11% polymeric MDI mass fractions. For the polymeric MDI having a functionality of 2.4, the melt stability was better than that of the polymeric MDI having a functionality of 2.7 under identical polymeric MDI mass fraction conditions.

Individuals having ordinary skill in the art will recognize that various modifications can be made to the embodiments of RHM adhesive compositions disclosed herein (e.g., multiple modifications can be made in view of the formulations and melt stability results of Examples 1 – 3), where such modifications remain within the scope of the present disclosure and the claims below.

Claims

1. A reactive hot melt (RHM) adhesive composition comprising:
 - a di-functional polyol compound;
 - a tri-functional polyol compound;
 - an isocyanate compound having an isocyanate functionality of two or more; and
 - a polymeric isocyanate compound having an isocyanate functionality greater than two,wherein a mass fraction of the polymeric isocyanate compound in the RHM adhesive composition is between 10 – 20%, inclusive.
2. The RHM adhesive composition of claim 1, further comprising one or more reactive or non-reactive and/or functional or nonfunctional polymer compounds.
3. The RHM adhesive composition of claim 2, wherein the one or more polymer compounds comprise a high molecular weight polymer compound having a weight average molecular weight between 20,000 – 100,000 g/mol.
4. The RHM adhesive composition of claim 1, wherein the tri-functional polyol compound has a molecular weight between 1,000 and 3,600 g/mol.
5. The RHM adhesive composition of claim 4, wherein the mass fraction of the tri-functional polyol compound plus the mass fraction of the polymeric isocyanate compound is up to 46% of the mass of the RHM adhesive composition.
6. The RHM adhesive composition of claim 4, wherein the tri-functional polyol compound comprises a polyether triol.
7. The RHM adhesive composition of claim 4, wherein the RHM adhesive composition exhibits a melt stability as indicated by a rate of increase of in-melt RHM adhesive composition viscosity of less than 20% per hour across a time period of at least two hours.

8. The RHM adhesive composition of claim 4, wherein a ratio of the mass fraction of the tri-functional polyol compound to the mass fraction of the polymeric isocyanate compound in the RHM adhesive composition is between 50% - 128%.

9. The RHM adhesive composition of claim 8, wherein a ratio of the mass fraction of the tri-functional polyol compound to the mass fraction of the polymeric isocyanate compound in the RHM adhesive composition is between 50% - 80%, and wherein the RHM adhesive composition exhibits a melt stability as indicated by a rate of increase of in-melt RHM adhesive composition viscosity of less than 12% per hour across a time period of at least two hours.

10. The RHM adhesive composition of claim 8, wherein a ratio of the mass fraction of the tri-functional polyol compound to the mass fraction of the polymeric isocyanate compound in the RHM adhesive composition is between or approximately between 110 – 122%, and wherein the RHM adhesive composition exhibits a melt stability as indicated by the rate of increase of in-melt RHM adhesive composition viscosity of less than 17% per hour across a time period of at least two hours.

11. The RHM adhesive composition of claim 1, wherein the di-functional polyol compound comprises a polyether diol or a polyester diol.

12. The RHM adhesive composition of any one of claims 1 – 7, wherein the RHM adhesive composition exhibits a post-melt free % NCO content of less than 3.5.

13. A process for producing a reactive hot melt (RHM) adhesive composition of any one of claims 1 - 12, the process comprising:

a first process portion comprising:

adding the isocyanate compound and optionally adding the polymer isocyanate compound to a melt containing the di-functional polyol compound and the tri-functional polyol compound to form an intermediate RHM adhesive composition in the melt; and allowing the free % NCO of the melt to reach and not exceed a first free % NCO target value;

and

a second process portion initiated subsequent to the free % NCO of the melt reaching or falling below the first free % NCO target value, the second process portion comprising:

adding or further adding the polymer isocyanate compound to the melt; and

allowing the free % NCO of the melt to reach and not exceed a second free % NCO target value distinct from the first free % NCO target value,

wherein the second free % NCO target value is less than or equal to 3.5, such that produced RHM adhesive composition exhibits a post-melt free % NCO of less than 3.5.

14. The process of claim 10, wherein the first free % NCO target value is less than or equal to 2.5.