A solventless two component laminating adhesive comprising a Part A prepolymer and a Part B curative. The prepolymer comprises a lower molecular weight polyether polyol and a higher molecular weight polyether polyol. The laminating adhesive can be applied to flexible films with high oxygen transfer rate to form flexible packaging, particularly for fresh produce, such as pre-prepared salads and other green leaf products.
SOLVENT FREE POLYURETHANE LAMINATING ADHESIVE WITH HIGH OXYGEN TRANSFER RATE

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The invention concerns two component laminating adhesive compositions comprising at least one polyurethane prepolymer and at least one polyfunctional curative. The two component laminating adhesive composition is particularly suited for application to flexible films to make laminated packaging, particularly for application to flexible films with high oxygen transfer rate ("OTR").

The Related Art

[0002] Flexible packaging has evolved to provide laminated packaging materials with intense and colorful graphics that can be buried and protected within the laminated structure. Typically two, three or four films are laminated together to produce a structure that possess the properties of each film incorporated into the flexible laminated material. Laminating adhesives are used in a wide variety of these flexible packaging applications. The lamination process, final package requirements and cost requirements are all important factors into determining the adhesive selection.

[0003] Two-component, reactive urethane adhesives provide adhesion, clarity, processing and product resistance suited for laminated flexible packaging. Also, such adhesives are available as essentially 100% solids material which provides environmental advantages, particularly because solid materials are solvent free.
As such, these adhesives have been finding significant commercial success in many laminating packaging applications such as snack foods, meat and cheeses, coffee packaging, bottle labels and many others.

[0004] Certain two component solvent free laminating adhesives have some limitations that have prevented such adhesives from being universally used in flexible packaging processes and applications. For example, in certain applications, such as in packaging fresh produce, like prepared salad mixes, transfer of oxygen and other gasses through the packaging material is desired. Although films have been developed that provide adequate OTR for such applications, the selection of adhesive for use with those films can have an adverse effect on OTR by impairing the transfer of oxygen and other gasses through laminating packaging materials comprising these films. Thus, laminating adhesives that have no or little effect on OTR and/or have good OTR properties are highly desired for packaging applications where relatively higher OTR is desired.

[0005] All parts and percentages set forth in this specification are on a weight-by-weight basis unless otherwise specified.

**SUMMARY OF THE INVENTION**

[0006] The two component laminating adhesive composition comprises Part A prepolymer having at least one polyether polyol and Part B curative having at least one polyfunctional component, such as an isocyanate reactive material. The compositions are generally solvent free meaning that they comprise little or no solvent.
The two component laminating adhesive composition has little-to-no negative effect on oxygen transfer while maintaining a good balance of adhesive processing and application performance; for example good bonds, good clarity, easy processing with good stability, no odor and the like. The adhesive compositions are suited for use with flexible packaging materials to make laminated flexible packaging. Because the two component laminating adhesive composition has no or little affect on OTR and has good OTR properties, the two component laminating adhesive composition may be used in applications where at least one of the films in the laminated packaging material has high OTR characteristics because the adhesive will not affect the OTR of the films, such as by the adhesive having good OTR, and has other beneficial properties like clarity. For example, the two component laminating adhesive composition can be used as a laminating adhesive for making flexible laminating packaging materials for fresh produce, such as pre-prepared salads and other green leaf products.

DETAILED DESCRIPTION OF THE INVENTION

The Part A prepolymers comprises at least one polyether polyol, and preferably at least two polyether polyols. Typically, the Part A prepolymers comprises at least one lower molecular weight polyether polyol and at least one higher molecular weight polyether polyol. The higher molecular weight polyether polyol has a molecular weight of about at least about 1,000 g/mol, preferably at least about 2,000 g/mol, higher than the molecular weight of lower molecular weight polyether polyol. The lower molecular weight polyether polyol includes polyether polyol having a molecular weight of about 3,000 g/mol or less, such as
a molecular weight less than about 2,000 g/mol, for example a molecular weight between about 1,000 g/mol to 4,000 g/mol, such as about 2,500 g/mol to about 3,250 g/mol. The higher molecular weight polyether polyol includes polyether polyol having a molecular weight of at least about 2,000 g/mol, including those having a molecular weight of at least about 3,000 g/mol, such as those having a molecular weight of at least about 4,000 g/mol or at least about 5,000 g/mol. For example, the higher molecular weight polyether polyol may have a molecular weight of greater than 2,000 g/mol to about 20,000 g/mol, such as greater than about 4,000 g/mol to about 15,000 g/mol, like greater than 6,000 g/mol to about 10,000 g/mol. Persons of ordinary skill in these arts, after reading this disclosure, will appreciate that all ranges and values for the molecular weight of the lower molecular weight polyol and the higher molecular weight polyol within the explicitly stated ranges above are contemplated and within the scope of the invention.

[0009] Examples of useful polyether polyols include polypropylene oxide, polypropylene glycol and combinations thereof. Polyether polyols available from Bayer Material Science, Pittsburgh, Pennsylvania, U.S.A. ("Bayer) under the trade names ARCOL® Polyol PPG 3025 (molecular weight 3,000) and ACCLAIM® Polyol 8200 N (molecular weight 8,000) may be used in the Part A prepolymer component.

[0010] Two component laminating adhesive comprising the combination of lower molecular weight polyol, such as ARCOL Polyol PPG 3025, and higher molecular weight polyol, such as ACCLAIM Polyol 8200, in the Part A prepolymer
component, when combined with a Part B curative, provides a stable laminating adhesive product having acceptable adhesive performance and good OTR. Overall, the combination of lower molecular weight polyol and higher molecular weight polyol in the Part A prepolymer provides for improved oxygen transfer through the adhesive, together with an adhesive that has phase stability, coats well, provides good clarity and provides excellent adhesion performance for bonding flexible packaging material films together.

[0011] The Part A prepolymer component typically comprises other materials such as those usually found in the prepolymer part of two-component solvent free adhesives. The Part A prepolymer component typically comprises isocyanates, however, the content of isocyanate in the Part A prepolymer of the two component laminating adhesive described herein may be less than the amount of isocyanate typically found in the prepolymer part of conventional two part adhesives. Isocyanates useful in the Part A prepolymer of the invention include hexamethylene diisocyanate, toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI) (which is available commercially as MONDUR® MR from Bayer), aliphonate-modified diphenylmethane diisocyanate (aliphonate modified MDI which is commercially available as MONDUR MA from Bayer, like MONDUR MA 2300), m- and p-phenylene diisocyanates, bitolylene diisocyanate, cyclohexane diisocyanate (CHDI), bis-(isocyanatomethyl)cyclohexane (H₂XDI), dicyclohexylmethane diisocyanate (H-12MDI), dimer acid diisocyanate (DDI), trimethyl hexamethylene diisocyanate, lysine diisocyanate and its methyl ester, isophorone diisocyanate, methyl
cyclohexane diisocyanate, 1,5-naphthalene diisocyanate, xylylene and xylene
diisocyanate and methyl derivatives thereof, polymethylene polyphenyl
isocyanates, chlorophenylene-2,4-diisocyanate, polyphenylene diisocyanates
available commercially as, for example, MONDUR MR or MONDUR MRS (both
available from Bayer), isophorone diisocyanate (IPDI), hydrogenated methylene
diphenyl isocyanate (HMDI), tetramethyl xylene diisocyanate (TMXDI),
hexamethylene diisocyanate (HDI), or oligomer materials of these materials such
as a trimer of IPDI, HDI or a biuret of HDI, and the like and combinations thereof.

[0012] The Part A prepolymer may comprise about 10% to about 30%, such as
about 15% to about 30%, of the lower molecular polyether polyol, by total weight
of the Part A prepolymer, about 30% to about 60%, such as about 30% to about
40%, of the higher molecular polyether polyol, by total weight of the Part A
prepolymer, and about 40% to about 70%, such as about 40% to about 50%,
isocyanate, by total weight of the Part A prepolymer, Persons of ordinary skill in
these arts, after reading this disclosure, will appreciate that all ranges and values
for the amount of the components of the Part A prepolymer within the explicitly
stated ranges above are contemplated and within the scope of the invention.

The Part A prepolymer may comprise, consist essentially of or consist of the
lower molecular weight polyether polyol, higher molecular weight polyether polyol
and isocyanate.

[0013] The Part B curative component of the two component laminating adhesive
described herein may be any curative typically used in two component laminating
adhesives, and typically comprises any components usually found in such
curatives. For example, the Part B curative of the two component laminating adhesive composition may comprise an isocyanate reactive material, and may consist of or consist essentially of such material. Preferably, the Part B curative comprises polyether polyol, such as Poly G® 30-280 available from the Lonza Group Limited, Basel, Switzerland, which is a polyether triol. Isocyanate reactive material selected from the group consisting of polyhydroxyls, polythiols, polyamines, and the like, and combinations thereof may be used in the Part B curative of the two component laminating adhesive. The Part B curative may also comprise isocyanates and/or oligomers, including those mentioned above with respect to the prepolymer.

[0014] In addition to the above, other materials may be included in the two component laminating adhesive composition, in the Part A prepolymer, the Part B curative or both the Part A prepolymer and Part B curative. These materials include catalyst (to shorten cure time), polymerization control agents, inhibitors, antioxidants, wetting agents, adhesion promoters, fillers and the like.

[0015] The Part A prepolymer and Part B curative are combined to form a mixed adhesive formula. Typically the mixed adhesive formula comprises about 10% to about 25%, such as about 10% to about 15%, by weight of the mixed adhesive formula of the lower molecular weight polyether polyol; about 20% to about 40%, such as about 20% to about 30%, by weight of the mixed adhesive formula of the higher molecular weight polyether polyol; about 25% to about 50%, such as about 20% to about 30%, by weight of the mixed adhesive formula of isocyanate and about 20% to about 35%, such as about 20% to about 30%, by weight of the
mixed adhesive formula of the Part B curative, for example the isocyanate reactive material, like the curative polyether polyol.

[0016] The two-component laminating adhesive described herein is applied with any type of substrates to create a laminated structure, and laminated structures made with or comprising the two-component laminating adhesive are within the scope of the invention, such as flexible laminated packaging materials, like packaging materials for fresh produce, such as pre-prepared salads and other green leaf products. The adhesive is compatible with any substrates, including, for example paper, aluminum foil, coated films, printed films, co-extruded films, polyester films, polyolefin based films, white polyolefin based films, polyamide based films and copolymer films. Suitable films include polyethylene terephthalate, polypropylene, such as biaxially oriented polypropylene ("BOPP"), polylactic acid and polyethylene. Laminated structures having the two-component laminating adhesive described herein comprise a first substrate and a second substrate and a cured adhesive layer, that is the dried residue of the two-component laminating adhesive as described above, bonding the first substrate to the second substrate.

**EXAMPLES**

**Example 1**

[0017] Part A prepolymer having the composition set forth in Table 1 was formulated. Note that the weight percentages set forth in Table 1 are by weight of the components of the Part A prepolymer. The prepolymer was made by charging both MDI resin and polyols described in Table 1 to a reactor and
heating slowly to 60 °C. Reaction was complete within 1 to 2 hours as verified by measuring the free isocyanate content (%NCO). Theoretical was 9.4%NCO.

<table>
<thead>
<tr>
<th>Table 1. Prepolymer of the invention</th>
</tr>
</thead>
<tbody>
<tr>
<td>Item</td>
</tr>
<tr>
<td>A Arcoi PPG 3025 (Bayer); polyether polyl</td>
</tr>
<tr>
<td>B Acclaim 8200 (Bayer); polyether polyl</td>
</tr>
<tr>
<td>C Mondur MA 2300 (Bayer); MDI resin</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

Example 2

[0018] Part B curative having the composition set forth in Table 2 was formulated. Note that the weight percentage set forth in Table 2 is by weight of the components of the Part B curative.

<table>
<thead>
<tr>
<th>Table 2. Curative of the invention</th>
</tr>
</thead>
<tbody>
<tr>
<td>Item</td>
</tr>
<tr>
<td>D Poly G 30-280 (Lonza Group Limited); polyether polyl</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

Example 3

[0019] Part A prepolymer of Example 1 and Part B curative of Example 2 were applied to make standard film-to-film lamination used in fresh produce packaging. Laminations were made by mixing 2.7 parts of Part A prepolymer of Example 1 with 1.0 parts of Part B curative of Example 2. The mixed adhesive formula (Part
A and Part B combined as stated above) had the composition set forth in Table 3. Note that the weight percentages set forth in Table 3 are by weight of the components of the mixed adhesive formula. The mixed adhesive formula was applied via smooth roll onto clear film followed by nipping to secondary film. The lamination was allowed to fully cure.

[0020] After curing, the film-to-film laminations, i.e. the fresh produce laminations, were evaluated. Bond strength was evaluated by applying ASTM D1876-08 "Standard Test Method for Peel Resistance - Adhesives (T-Peel Test)" which is incorporated by reference herein in its entirety, except that the load at constant head speed set forth in Section 7.1 of that standard was run at 12 inches per minute instead of 10 inches per minute. The film-to-film laminations were also tested for OTR and haze. The results are set forth in Table 3.
<table>
<thead>
<tr>
<th>Item</th>
<th>Mixed Adhesive Formula and Results</th>
<th>Mixed Adhesive Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Prepolymer from Table 1</strong></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Arcol PPG 3025 (Bayer); polyether polyol</td>
<td>12.41</td>
</tr>
<tr>
<td>B</td>
<td>Acclaim 8200 (Bayer); polyether polyol</td>
<td>27.99</td>
</tr>
<tr>
<td>C</td>
<td>Mondur MA 2300 (Bayer); MDI resin</td>
<td>32.58</td>
</tr>
<tr>
<td></td>
<td><strong>Curative from Table 2</strong></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Poly G 30-280 (Lonza Group Limited); polyether polyol</td>
<td>27.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td><strong>Performance Results</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oxygen transfer rate (fresh produce lamination)</td>
<td>excellent</td>
</tr>
<tr>
<td></td>
<td>Haze (fresh produce lamination)</td>
<td>excellent</td>
</tr>
<tr>
<td></td>
<td>Bond strength (grams / inch for fresh produce lamination)</td>
<td>958g</td>
</tr>
</tbody>
</table>
CLAIMS

I claim:

1. A two component laminating adhesive comprising a prepolymer that comprises a lower molecular weight polyol having a molecular weight and a higher molecular weight polyol having a molecular weight at least about 1,000 g/moi higher than the molecular weight of the lower molecular weight polyol and a curative comprising an isocyanate reactive material wherein the adhesive does not comprise solvent.

2. The adhesive of Claim 1 wherein the molecular weight of the higher molecular weight polyol is at least about 2,000 g/mol higher than the molecular weight of the lower molecular weight polyol.

3. The adhesive of Claim 1 wherein the molecular weight of the lower molecular weight polyol is about 3,000 g/mol or less and the molecular weight of the higher molecular weight polyol is at least about 5,000 g/mol.

4. The adhesive of Claim 1 wherein the lower molecular weight polyol and the higher molecular weight polyol each comprise a polyether polyol.

5. The adhesive of Claim 4 wherein the polyether polyol is selected from the group consisting of polypropylene oxide, polypropylene glycol and combinations thereof.

6. The adhesive of Claim 1 wherein the prepolymer further comprises isocyanate.
7. The adhesive of Claim 6 wherein the isocyanate is selected from the group consisting of hexamethylene diisocyanate, toluene diisocyanate, diphenylmethane diisocyanate, allophonate-modified diphenylmethane diisocyanate, m- and p-phenylene diisocyanates, bitolylene diisocyanate, cyclohexane diisocyanate, bis-(isocyanatomethyl)cyclohexane, dicyclohexylmethane diisocyanate, dimer acid diisocyanate, trimethyl hexamethylene diisocyanate, lysine diisocyanate and its methyl ester, isophorone diisocyanate, methyl cyclohexane diisocyanate, 1,5-napthalene diisocyanate, xylylene diisocyanate, xylene diisocyanate, methyl derivatives of xylylene diisocyanate, methyl derivatives of xylene diisocyanate, polymethylene polyphenyl isocyanate, chlorophenylene-2,4-diisocyanate, polyphenylene diisocyanate, isophorone diisocyanate, hydrogenated methylene diphenyl isocyanate (HMDI), tetramethyl xylene diisocyanate (TMXDI), hexamethylene diisocyanate (HDI), HDMt oligomer, TMXDI oligomer, HDI oligomer, biuret of HDI and combinations thereof.

8. The adhesive of Claim 1 wherein the isocyanate reactive material is selected from the group consisting of a polyhydroxyl, a polythiol and a polyamine.

9. The adhesive of Claim 1 wherein the isocyanate reactive material comprises a polyether polyol.
10. The adhesive of Claim 9 wherein the polyether polyol is a polyether triol.

11. The adhesive of Claim 1 wherein the curative further comprises an isocyanate.

12. The adhesive of Claim 11 wherein the isocyanate is selected from the group consisting of hexamethylene diisocyanate, toluene diisocyanate, diphenylmethane diisocyanate, aliphonate-modified diphenylmethane diisocyanate, m- and p-phenylene diisocyanates, bitolylene diisocyanate, cyclohexane diisocyanate, bis-(isocyanatomethyl)cyclohexane, dicyclohexyl methane diisocyanate, dinner acid diisocyanate, trimethyl hexamethylene diisocyanate, lysine diisocyanate and its methyl ester, isophorone diisocyanate, methyl cyclohexane diisocyanate, 1,5-napthalene diisocyanate, xylene disocyanate, xylene diisocyanate, methyl derivatives of xylene disocyanate, methyl derivatives of xylene diisocyanate, polymethylene polyphenyl isocyanate, chlorophenylenes, 2,4-diisocyanate, polyphenylene diisocyanate, isophorone diisocyanate, hydrogenated methylene diphenyl isocyanate (HMDI), tetramethyl xylene diisocyanate (TMXDI), hexamethylene diisocyanate (HDI), HDI oligomer, TMXDI oligomer, HDI oligomer, biuret of HDI and combinations thereof.
13. The adhesive of Claim 1 further comprising one or more of a catalyst, a polymerization control agent, an inhibitor, an antioxidant, a wetting agents, an adhesion promoter or a filler.