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(54) Title: ONE-COMPONENT STRUCTURAL ADHESIVE CONTAINING ISOCYANATE-TERMINATED PREPOLYMER

(57) Abstract: A one-component structural adhesive comprising an isocyanate-terminated prepolymer having polymerized residues of: (a) 40 to 95 wt% of a polytetramethylene ether glycol; and (b) 5 to 60 wt% of an aliphatic diisocyanate.



ONE-COMPONENT STRUCTURAL ADHESIVE CONTAINING ISOCYANATE-TERMINATED PREPOLYMER

Background

5 This invention relates generally to a one-component high modulus structural adhesive comprising an isocyanate-terminated prepolymer.

 One-component urethane adhesives based on prepolymers of polytetramethylene ether glycol (PTMEG) are known. For example, U.S. Pat. No. 5,288,797 discloses a one-component urethane system comprising a prepolymer based on PTMEG in which the
10 isocyanate component is an aromatic isocyanate. However, this reference does not disclose the adhesive described in the current invention.

Statement of Invention

 The present invention is directed to a one-component structural adhesive comprising
15 an isocyanate-terminated prepolymer comprising polymerized residues of: (a) 40 to 95 wt% of a polytetramethylene ether glycol; and (b) 5 to 60 wt% of an aliphatic diisocyanate.

 The present invention is further directed to a method for bonding coated or painted parts made of fiber-reinforced plastics by applying a one-component structural adhesive comprising an isocyanate-terminated prepolymer comprising polymerized residues of:
20 (a) 40 to 95 wt% of a polytetramethylene ether glycol; and (b) 5 to 60 wt% of an aliphatic diisocyanate to said parts.

Detailed Description

 All percentages are weight percentages, and all temperatures are in °C, unless
25 otherwise indicated. Percentages of monomer units (e.g., isocyanates and polyols) are on a solids basis, i.e., on the weight of the polymer excluding solvents and other additives.

 Aliphatic diisocyanates useful in this invention include, e.g., hexamethylene diisocyanate (“HDI”), methylene dicyclohexyl diisocyanate or (hydrogenated MDI, “HMDI”) and isophorone diisocyanate (“IPDI”). HDI is especially preferred.

30 Polytetramethylene ether glycol (PTMEG, also known as PTHF) is commonly prepared from polymerization of tetrahydrofuran and has the structure $\text{HO}\{(\text{CH}_2)_4\text{O}\}_n\text{H}$, where n can vary from about 3 to about 45, corresponding to number-average molecular weights (Mn) from about 250 to about 3000. Preferably, Mn for the PTMEG is from 500 to

3000, preferably from 800 to 2600, preferably from 1100 to 2500, preferably from 1500 to 2200.

Preferably, the isocyanate-terminated prepolymer comprises polymerized residues of: at least 50 wt% PTMEG, preferably at least 55 wt%, preferably at least 60 wt%, preferably at least 70 wt%, preferably at least 75 wt%, preferably at least 80wt%; preferably no more than 90 wt%, preferably no more than 86 wt%, preferably no more than 82 wt%, preferably no more than 78 wt%. The prepolymer may also contain small amounts of polyols having from three to six hydroxyl groups, preferably C₃-C₁₀ triols (preferably C₃-C₈ triols) or tetra-ols, e.g., trimethylolpropane, pentaerythritol. Preferably, polymerized units of polyols having from three to six hydroxy groups are present in an amount from 0 to 5 wt%, preferably from 0.1 to 3 wt%, preferably from 0.2 to 1.5 wt%. In a preferred embodiment of the invention, the prepolymer contains polymerized units of one or more additional polyols, preferably polycaprolactone polyols, preferably in a total amount from 0 to 40 wt%, preferably at least 5 wt%, preferably at least 8 wt%, preferably at least 11 wt%; preferably no more than 35 wt%, preferably no more than 30 wt%, preferably no more than 25 wt%, preferably no more than 22 wt%, preferably no more than 19 wt%. Preferably, the weight of isocyanate groups in the isocyanate-terminated prepolymer is from 1 to 6 wt%, preferably from 1.5 to 5 wt%, preferably from 2 to 4 wt%. Preferably, Mn for the polycaprolactones is from 400 to 3000, preferably from 500 to 2000, preferably from 600 to 1500, preferably from 600 to 1000. Preferably, the isocyanate-terminated prepolymer comprises polymerized residues of: at least 8 wt% aliphatic diisocyanate, preferably at least 10 wt%, preferably at least 12 wt%, preferably at least 14 wt%, preferably at least 18 wt%; preferably no more than 40 wt%, preferably no more than 50 wt%, preferably no more than 45 wt%, preferably no more than 30 wt%, preferably no more than 25 wt%.

The isocyanate-terminated prepolymer may be prepared using a mole ratio of isocyanate groups to hydroxyl groups which may vary as desired, preferably within a molar ratio of NCO/OH groups of 2.5:1 to 1.2:1, preferably from 2.4:1 to 1.3:1, preferably from 2.3:1 to 1.4:1, preferably from 2.3:1 to 1.5:1. Preferably, suitable catalysts are used to aid in formation of the prepolymer, preferably tin or zirconium catalysts, preferably Zr(IV) catalysts, e.g., zirconium acetylacetonate. Preferably, the amount of catalyst in the prepolymer is from 0.005 to 0.15 wt%, preferably 0.01 to 0.1 wt%, preferably 0.02 to 0.08 wt%.

The one-component structural adhesive comprises the isocyanate-terminated prepolymer along with other typical adhesive ingredients, e.g., fillers (e.g., carbon black, kaolin, fumed silica) and catalysts (e.g., bismuth, tin or amine catalysts). Bismuth catalysts are especially preferred, preferably Bi(III) salts, preferably carboxylate salts. The total
5 amount of catalyst(s) preferably is from 0.01 to 4 wt%, preferably from 0.02 to 3 wt%, preferably from 0.05 to 1 wt%; weights based on total weight of the adhesive. Preferably, the urea and urethane content of the adhesive is from 3 to 40 wt%; preferably at least 3.2 wt%, preferably at least 3.4 wt%, preferably at least 3.6 wt%, preferably at least 3.8 wt%; preferably no more than 30 wt%, preferably no more than 20 wt%, preferably no
10 more than 10 wt%, preferably no more than 6 wt%. Preferably, carbon black is present in an amount from 5 to 60 wt%, preferably at least 7 wt%, preferably at least 9 wt%; preferably no more than 50 wt%, preferably no more than 40 wt%, preferably no more than 30 wt%. Preferably, kaolin is present in an amount from 5 to 60 wt%, preferably at least 7 wt%, preferably at least 9 wt%; preferably no more than 50 wt%, preferably no more than
15 40 wt%. Preferably, the isocyanate-terminated prepolymer is present in the adhesive in an amount from 20 to 100 wt%; preferably at least 30 wt%, preferably at least 35 wt%, preferably at least 40 wt%; preferably at least 45 wt%; preferably no more than 90 wt%, preferably no more than 85 wt%, preferably no more than 82 wt%.

The present invention is directed to a method for bonding coated or painted parts
20 made of fiber-reinforced plastics. These parts bonded to each other or to a dissimilar material, e.g., e-coated steel frames or e-coated metal roofs. Preferred fiber-reinforced plastics are epoxy composite materials or thermoplastics, e.g., SMC. The substrates may be similar material or dissimilar material. The preferred thickness of the adhesive layer is from 1 to 5 mm, preferably from 2 to 4 mm. The compositions of the present invention can be
25 applied to desired substrates using conventional application techniques such as application from automated dispensing equipment and drum pumps.

Examples

Table 1: RAW MATERIAL LIST

Prepolymers		
Polyols	Supplier	Chemistry
ACCLAIM 6300	Bayer	6300 PPO Triol (Low Mono-ol)
VORANOL 4000LM	DOW	4000 PPO Diol (Low Mono-ol)
VORANOL 3322	DOW	3500 PPO Triol
VORANOL 2000L	DOW	2000 PPO Diol
PolyTHF 2000	BASF	2000 PTHF Diol
Trimethylolpropane	Perstorp	Short chain triol
CAPA 2077A	Perstorp	750 PCL Diol
Isocyanates		
ISONATE M125	DOW	MDI
DESMODURE H	Bayer	HDI
ISONATE M 143	DOW	Liquefied MDI
Plasticizer		
VESTINOL 9	Evonik	Diisononylphthalate
Catalysts		
METATIN S-26	DOW	Tin-(II) octoate
Zr(IV)AcAc 40% in benzyl alcohol	Sigma Aldrich / DOW	Zr (IV) Acetylacetonate
Adhesives		
Plasticizer		
VESTINOL 9	Evonik	Diisononylphthalate
Fumed Silica		
HDK 20	Wacker Chemie	Pyrogenic silica
Carbon Black:		
PRINTEX 30	Evonik	Carbon black
Calcinated Kaolin:		
POLESTAR 200R	Imerys	Calcinated Kaoline
Uncoated Kaoline		
CARBITAL 140	Imerys	Uncoated Kaoline
Isocyanates		
DESMODURE N3300	Bayer	Trimerized HDI
Catalysts:		
Cat2010	DOW	Dimethyl-tin-dilaurate / NMP / Vestinol
BiCat 8108M	Shepherd	Bi-(III)-Neodecanoate
DMDEE	BASF	2,2'-Dimorpholinodiethylether

INVENTIVE and COMPARATIVE FORMULATIONS

Seven prepolymers have been synthesized and evaluated in a typical one part PU adhesive formulation.

- 5 ▪ Comparative formulations A, B and C are using aromatic MDI as diisocyanate compound. All of them are using a PPO polyether-polyol. Formulation A is using a PPO triol, B and C PPO diols with different molecular weights and C additionally A PPO triol.
- Formulation D is similar to A but uses an aliphatic diisocyanate, HDI, instead of an aromatic (MDI)
- 10 ▪ Formulation E uses a PPO polyether-polyol together with a crystalline polyester and an aliphatic diisocyanate (HDI)
- Inventive formulation F is similar to E but uses a PTHF (PTMEG) polyether-diol instead of PPO and no polyester
- Inventive formulation G uses PTHF, polyester and aromatic diisocyanate instead of aliphatic

15 Table 2: Prepolymer formulation

Prepolymer	A	B	C	D	E	F	G
	Comp.	Comp.	Comp.	Comp.	Comp.	Inv.	Comp.
Polyols							
ACCLAIM 6300	74.69	---	---	91.52	61.04	---	---
VORANOL 4000LM	---	79.44	---	---	---	---	---
VORANOL 3322	---	---	42.40	---	---	---	---
VORANOL 2000L	---	---	42.22	---	---	---	---
PolyTHF 2000	---	---	---	---	---	85.10	65.34
Trimethylolpropane	---	---	---	---	---	0.58	0.37
CAPA 2077A	---	---	---	---	22.79	---	9.76
Plasticizer							
VESTINOL 9	15.04	10.00	---	---	---	---	---
Isocyanates							
HDI	---	---	---	8.45	16.15	14.26	---
ISONATE M125	10.26	10.55	15.37	---	---	---	---
ISONATE M143	---	---	---	---	---	---	24.47
Catalysts							
METATIN S-26	0.01	0.01	0.01	0.03	---	---	---
Zr-(IV)-AcAc 40wt% in BzOH (*)	---	---	---	---	0.02	0.06	0.06
Total:	100.00	100.00	100.00		100.00	100.00	100.00
Calc. NCO [%]	1.882	1.880	1.885	2.304	4.227	3.000	3.000
NCO/OH	2.20:1	2.13:1	1.57:1	2.22:1	2.10:1	1.723:1	1.716

(*) **Zr-(IV)-AcAc 40% in BzOH:** 40% Zirconium-(IV)-acetylacetonate dissolved in benzyl alcohol.

General Prepolymer Preparation:

Combine Polyol (1), Polyol (2) and plasticizer in a lab reactor. Stir the mixture under vacuum and heat it up to 120°C. When the material temperature has reached 120°C, cool it down to 50°C under vacuum. Then add the isocyanate and stir the mixture for 5 min under nitrogen. Add the catalyst and let the mixture react for 30 min. and then determine the isocyanate content. If the isocyanate content is from 0.25% below to 0.1% above the calculated value (by addition of excess dibutylamine and back titration with 1N HCl), set vacuum and let the mixture mix for additional 20 min. Table 3 presents the content of urethane and urea units (hard segments) in the prepolymers. Columns H and L demonstrate that the difference between referenced and inventive prepolymer formulations is mainly in the amount of the total UREA & URETHANE hard segments

Table 3: urethane & urea contents in the comparative and inventive prepolymers

	PREPOLYMER				ADHESIVE		
	(F)	(G)	(H)	(I)	(J)	(K)	(L)
Prepoly.	total urethane in the prepoly., wt%	total urea after prepoly. curing, wt%	total urethane & urea after curing, wt%	total prepoly. in the adhesive	total urethane after adhesive curing	total urea in the adhesive after curing	total urethane & urea in the adhesive after curing
A	2.22	1.30	3.52	(1) 51.4	1.14	0.67	1.81
B	2.36	1.30	3.66	(2) 51.4	1.21	0.67	1.88
C	4.52	1.30	5.83	(3) 51.4	2.33	0.67	2.99
D	2.73	1.59	4.32	(4) 62.4	1.70	0.99	2.70
E	5.43	2.92	8.35	(5) 57.4	3.12	1.68	4.79
E	5.43	2.92	8.35	(6) 56.4	3.06	1.65	4.71
F	5.82	2.07	7.90	(7) 53.8	3.13	1.11	4.25
G	7.35	2.07	9.42	(8) 52.4	3.85	1.09	4.93
F	5.82	2.07	7.90	(9) 51.5	3.00	1.09	4.09

Adhesive formulation

Table 4 shows the formulation details of the formulated adhesives. Because of the low basic viscosity of the prepolymer, the adhesive formulations which use the prepolymers D, E and F need no plasticizer.

Table 4: Adhesive formulation details

	Comp.	Comp.	Comp.	Comp.	Comp.	Comp.	Inv.	Comp.	Inv.
	1	2	3	4	5	6	7	8	9
polyol	PPO	PPO	PPO	PPO	PPO/ PCL	PPO/ PCL	PTHF	PTHF/ PLC	PTHF
NCO Type	MDI	MDI	MDI	HDI	HDI	HDI	HDI	MDI	HDI
P ^I , wt%	12.5	9.9	6.6	<0.5	0	0.7	0	5.7	3.47
	%	%	%	%	%	%	%	%	%
(A)	51.4	---	---	---	---	---	---	---	---
(B)	---	51.4	---	---	---	---	---	---	---
(C)	---	---	51.4	---	---	---	---	---	---
(D)	---	---	---	62.4	---	---	---	---	---
(E)	---	---	---	---	57.4	56.8	---	---	---
(F)	---	---	---	---	---	---	53.8	---	51.5
(G)	---	---	---	---	---	---	---	52.4	---
PRINTEX 30	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	18.0
POLESTAR R200	21.0	21.0	20.0	16.0	21.0	21.0	24.0	20.4	22.0
HDK 20H	0.5	0.5	0.5	16.0	---	---	---	---	2.0
CARBITAL 140	5.0	5.0	4.1	5.0	5.0	5.0	5.0	5.0	2.0
DESMODUR N3300	1.0	1.0	1.0	---	---	---	---	---	---
VESTINOL 9	4.1	4.1	6.0	---	---	---	---	5.0	2.0
Cat2010	0.9	0.9	0.9	0.5	---	1.0	1.0	1.0	2.0
BiCat 8108M	---	---	---	---	0.5	---	---	---	---
DMDEE	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.5
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.00	100.0

1. P=plasticizer

5 Adhesive Preparation:

Combine prepolymer, carbon black, pyrogenic silica, uncoated Kaoline, coated Kaoline, plasticizer and isocyanate to a planetary mixer and mix for 10 min under nitrogen at 30°C. Then set vacuum and let the mixture mix for additional 30 min at 30°C. If the mixture is homogeneous add catalyst (1) and catalyst (2) to the mixture and let it mix for 10 min at 30°C under nitrogen. Then set vacuum and let the mixture mix for additional 20 min.

TEST RESULTS

Applied methods

Tensile strength, e-modulus, elongation according to DIN 53504

Tear Resistance following DIN ISO 34-1

- 5 Lab shear strength following DIN EN 1465: substrate: e-coated steel, bonding area: 10*25 mm, adhesive layer thickness: 2 mm

Prepolymer results

- 10 Table 5 presents the test data for the prepolymer itself. The prepolymers which use HDI over MDI show a significant reduction in viscosity as compared to the other formulations and therefore can be used without adding plasticizer, either to the prepolymer or the adhesive formulation.

Table 5: Test results for the prepolymers

	NCO [%]	NCO	NCO/OH	GPC [Mn]	GPC [Mw]	GPC PDI	GPC: sample recovery [Mn > 1000] %	Viscosity 23°C: Newtonian [Pas]	Diisobutylphthalate Conc. [%]
(A)	1.821	MDI	2.2:1.0	17400	44400	2.6	75.8	132	15
(B)	1.922	MDI	2.1 :1.0	8800	11400	1.3	81.1	19	10
(C)	2.651	MDI	2.0:1.0	12400	29900	2.4	74.9	77	15
(D)	2.23	HDI	2.2:1.0	7700	27300	3.5	91.1	103	0
(E)	4.014	HDI	2.1:1.0	4400	13600	3.1	95.3	26	0
(F)	2.955	HDI	1.7:1	5400	11500	2.1	95.3	71	0
(G)	3.025	MDI	1.7:1	5400	16700	3.1	93.7	1298	0

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Adhesive test results

Table 6 shows the test data for the prepared adhesive formulations. The following can be concluded:

- 20 ■ All inventive formulations meet an elastic modulus of above 20 MPa

- The inventive formulations combine high elastic modulus with high bulk elongation of above 200%
 - The highest elastic moduli above 30 MPa are achieved by using aliphatic- (e.g. HDI) over aromatic (e.g. MDI) diisocyanates
- 5▪ The use of PTMEG based polyether polyols over PPO further very significantly increases the bulk elongation and the tear strength
- Purely PPO based prepolymers do not meet the elastic modulus requirement
 - Inventive formulations show high lap shear strength combined with cohesive failure mode

10 Table 6: Adhesive physical and mechanical data

	Comp	Comp	Comp	Comp	Comp	Comp	Inv.	Comp.	Inv.
Formulation	1	2	3	4	5	6	7	8	9
polyol	PPO	PPO	PPO	PPO	PPO/ PCL	PPO/ PCL	PTHF	PTHF/ PCL	PTHF
NCO Type	MDI	MDI	MDI	HDI	HDI	HDI	HDI	MDI	HDI
Tensile strength [MPa]	7.5	5.3	7.3	7.7	10.8	10.8	19.1	13.8	16.1
Elongation at break [%]	210	666	301	173	273	251	424	303	467
E-modulus [MPa]	10.3	7.7	7.4	11.5	39.2	41.8	44.3	25.8	28.3
Tear resistance [N/mm]	9.3	31.2	9.5	8.3	20.8	24.3	38.9	21.3	46.6
Lap Shear Strength after 24 h RT [MPa]	---	---	---	---	2.6	0.4	---	---	0.4
Lap Shear Strength after 7d RT [MPa]	---	---	---	---	8.1	7.5	---	---	9.5
Lap Shear Strength after 14d RT [MPa]	---	---	---	---	7.8	8.1	---	---	13.6

Table 7 presents the limits for the bulk adhesive data and the prepolymer composition.

Table 7: Requirements for bulk properties

Tensile strength [MPa]	>15
Elongation at break [%]	>350
E-Modulus [MPa]	> 28
Tear resistance [N/mm]	> 30

CLAIMS

1. A one-component structural adhesive comprising an isocyanate-terminated prepolymer comprising polymerized residues of: (a) 40 to 95 wt% of a polytetramethylene ether glycol; and (b) 5 to 60 wt% of an aliphatic diisocyanate.
- 5 2. The one-component structural adhesive of claim 1 in which the aliphatic diisocyanate is hexamethylene diisocyanate.
3. The one-component structural adhesive of claim 2 in which the polytetramethylene ether glycol has M_n from 500 to 3000.
4. The one-component structural adhesive of claim 3 having from 55 to 90 wt%
10 of a polytetramethylene ether glycol; and (b) 10 to 45 wt% of an aliphatic diisocyanate.
5. A method for bonding coated or painted parts made of fiber-reinforced plastics; said method comprising applying a one-component structural adhesive comprising an isocyanate-terminated prepolymer comprising polymerized residues of: (a) 40 to 95 wt%
15 of a polytetramethylene ether glycol; and (b) 5 to 60 wt% of an aliphatic diisocyanate to said parts.
6. The method of claim 5 in which the aliphatic diisocyanate is hexamethylene diisocyanate.
7. The method of claim 6 in which the polytetramethylene ether glycol has M_n from 500 to 3000.
- 20 8. The method of claim 7 having from 55 to 90 wt% of a polytetramethylene ether glycol; and (b) 10 to 45 wt% of an aliphatic diisocyanate.
9. The method of claim 8 in which the fiber reinforced plastic is an epoxy composite.
10. The method of claim 9 in which adhesive further comprises from 7 to 40
25 wt% carbon black.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/48 C08G18/66 C08G18/73 C08G18/30 C09J175/08
ADD.

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)
C08G C09J

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/091842 A2 (DOW GLOBAL TECHNOLOGIES LLC [US]; LUTZ ANDREAS [CH]; SCHNEIDER DANIEL) 5 July 2012 (2012-07-05) claims 1, 12 examples page 2, line 27 - line 35 page 12, line 13 - line 31 page 13, line 28 - line 32 -----	1-10
A	US 5 288 797 A (KHALIL HAMDY [CA] ET AL) 22 February 1994 (1994-02-22) cited in the application claims 1-3 examples column 5, line 64 - column 6, line 4 column 9, line 31 - line 37 -----	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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