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(54) Title: ADHESIVE COMPOSITION WITH GROUND RUBBER

(57) Abstract: A new adhesive composition containing ground rubber and having unique properties in automotive related applications.
The method of making such new adhesive composition.



ADHESIVE COMPOSITION WITH GROUND RUBBER

The present invention relates to a new adhesive composition having unique properties in automotive related applications.

Epoxy resin-containing adhesives are widely used in automotive industries. When
5 the adhesive composition has a Young's modulus value above 1000-1500 MPa, some
modification to the adhesive composition is needed in order to achieve acceptable cohesive
failure and to avoid distortion of the vehicle materials such as aluminum closure. These
modifications can create an apparent increase in toughness due to keeping the crack
propagation away from the substrate interface. Typically, for one component epoxy
10 adhesive compositions, a target of a Young's modulus of less than 1000 Mpa and preferably
around 500 MPa is desired as shown in prior art compositions such as those taught in
WO2013151835A1, incorporated herein by reference in its entirety.

Invariably as the adhesive composition is modified with inorganic filler to improve
failure mode and other properties, more rubber may be required to offset a loss of toughness
15 due to the inorganic filler addition. This increases cost and lowers cross link density which
is not ideal for corrosion resistance. Common methods to achieve good failure mode
include the use of talc and chlorite fillers. Cashew nutshell oil can also be used but it has
the same issues as talc. Blowing agents may also be used but with many negative side-
effects. Because of the difficulty of maintaining desired impact peel performance, many
20 benefits of higher filler loadings are avoided when formulating high impact peel performing
epoxy containing adhesive compositions. The benefits of fillers in epoxy adhesive
compositions include superior rheology control and improved corrosion resistance.
Inorganic filler loadings typically improve corrosion resistance due to blocking the ingress
of moisture into the bond line. However, filler loadings of 20 to 40 % by volume of the
25 composition are avoided due to the negative effect on impact peel performance.

It is surprising to find that ground rubber can induce good cohesive failure mode and
many other good properties to the adhesive compositions without the negative effects of talc
and chlorite fillers. A typical adhesive composition of the present invention will have a
Young's modulus of less than 1000 MPa. Ground rubber is produced by grinding scrap
30 tires into relatively uniform rubber particle sizes. Because it is produced from scrap tires,
the cost of such ground rubber is low.

The new ground rubber containing adhesive composition has potential application for steel and aluminum closures bonding as well as body structure bonding in general.

The present invention provides an adhesive composition comprising ground rubber to improve cohesive failure and other properties of the composition. Like an ordinary base
5 adhesive composition (commercially existing adhesive composition of similar functionalities as the composition of the present invention), it will contain such conventional components such as: epoxy resin(s), curing agent such as dicyandiamide, catalyst such as blocked tertiary amine or urea, fumed silica, tougheners such as urethane rubbers, optionally auxiliary tougheners such as carboxyl terminated butadiene-acrylonitrile
10 (CTBN) epoxy adducts and/or ethylene/butylenes oxide di block copolymer, epoxy silane and other fillers such as calcium carbonate, calcium oxide, calcium metasilicate etc. Instead of using talc and chlorites to maximize T-Peel failure mode and impact performance, ground rubber is used without or with lowered amounts of talc and chlorites in the same adhesive compositions. The use of ground rubber in the place of traditionally used
15 inorganic fillers not only resulted in better composition performances but also significantly reduced the cost of making adhesive compositions. Some commercial examples of the base adhesive compositions, into which modification can be made with ground rubber, include BETAMATE™ Series 1486, 1090G, 1485, 1696, 1822 available from The Dow Chemical Company.

20 The adhesive composition of the present invention comprises 1 to 40 wt% of ground rubber based on the total weight of the adhesive composition. In one preferred embodiment, the ground rubber used is a free flowing black powder produced from recycled rubber material as defined by ASTM D 5603-01 Grades 1, 2, 3, and 4. While any kind of ground rubber may be used, it is preferred that the ground rubber has a density between 1-5
25 g/cc, preferably between 1.1 to 1.25 g/cc and most preferably between 1.12 to 1.15 g/cc. The size of such ground rubber should be kept on average of no more than 250 microns, preferably no more than 200 microns and most preferably no more than 185 microns. In one preferred embodiment, Lehigh™ MD-184-TR, commercially available from LT Lehigh Technologies, is used as shown in the Examples.

30 In a preferred embodiment, ground rubber is added while making the base adhesive composition via a simple “add and mix” and in the place of talc and chlorites or with reduced amounts of talc and chlorites typically used for the base adhesive compositions. After addition of the ground rubber, the adhesive composition typically will comprise 1 to

- 40 wt%, preferably 5 to 35 wt% and more preferably 25 to 35 wt%, of the ground rubber, all based on the total weight of the adhesive composition. The composition also contains a reduced amount of talc and chlorites in the amount of 0 to 30 wt%, preferably, 0 to 10 wt%, and more preferably 0 to 5 wt%. In one preferred embodiment, after the addition of ground
- 5 rubber, no talc and chlorites fillers are needed in the adhesive composition. In another preferred embodiment, after the addition of ground rubber, the adhesive composition is substantially free of talc and chlorites fillers. Depending on different applications, some routine adjustment of volume and weight percentage of ground rubber in an adhesive composition may be needed with the general guidance as described above.
- 10 While the present invention focused on ground rubber, other rubbers such as liquid rubbers should provide essentially the same benefits to the adhesive composition as ground rubber albeit more expensive.

Examples

- 15 The present invention can be further demonstrated with the following non-limiting examples.

Table 1 illustrates the various raw material components used in the making the examples to demonstrate the present invention.

Table 1 Raw Materials

	Supplier	Chemistry/Function
DER™ 330	Olin Corp.	Liquid diglycidyl ether of Bisphenol A (DGEBA) resin
DER 331	Olin Corp	Liquid DGEBA resin
DER 661	Olin Corp.	Solid DGEBA resin
FORTEGRA™ 202	Olin Corp.	Diblock copolymer toughener
Urethane 2	Prepared according to US 8,404,787 B2: Example 2	Toughener
Lehigh MD-184-TR	LT Lehigh TECHNOLOGIES	Ground rubber used as filler - micronized rubber powder from tires
Silane A 187	Momentive	Epoxy silane used as surfactant
Amicure CG 1200	Airproducts	Dicyandiamide, a curing agent
EPCAT 50	Prepared according to US 2013/0090431 A1: Example 5	Catalyst
PolyCal OS325	Mississippi Lime	Calcium oxide used as water scavenger
Cab-O-Sil TS 720	Cabot	Fumed silica used as rheology modifier
Atomite	HuBer	Calcium Carbonate as filler
Nyglos 8	Nyco	Wollastonite as filler
Nyad 200	Nyco	Wollastonite as filler
Elftex S7100	Cabot	Carbon Black as pigment
Sierralite 252	Luzenac America Inc	Filler
BETAMATE™4601	The Dow Chemical Company	High modulus adhesive
Epoxy Amine Adduct	Described in WO2013/151835A1	Flexibilizer Epoxy Resin. Reaction of Jeffamine D2000 and DER 331
Kaneka MX150	Kaneka	Core Shell Rubber in Epoxy Resin
Rheotix 240	Byk	Organic Thixotrope, viscosity modification

A total of five samples were prepared to demonstrate the unique properties of the present invention as shown in Table 2. Sample F was prepared as a comparative example which is a prior art composition disclosed as Example 1 of WO2013151835A1.

Table 2. Preparation of samples (in grams)

Raw Materials	A	B	C	D	E
DER 331	45.7	42.6			26.4
DER 330	2.6	1.7			
DER 661	5.5	3.7			
LT Lehigh MD-184-TR	25	30	25	35	
Urethane 2		8			16
Fortegra 202	8	0			
Epoxy Amine Adduct					15
Kaneka MX150					8.25
Silane A-187	0.2	0.2			
Amicure CG 1200	4.8	4.7			3.4
EPCAT 50	0.4	0.4			0.95
Atomite					11
Nyad 200					2
PolyCal OS325	6	6			7
Sierralite 252					3
Elftex S7100	0.5	0.5			
Rheotix 240					3
Cab-O-Sil TS720	2	2			4
BETAMATE™ 4601		-	75	65	
Total	100.7	99.8	100	100	100

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Testing methods and Performance Observations

The samples were subjected to some mechanical performance tests and the test results are provided below.

Mechanical testing

LSS is conducted per ISO 4587

Impact Peel is conducted per ISO11343

T-Peel Test is conducted per ASTM D 1876

5 Tensile Strength and Young's Modulus per ASTM D638

Failure Mode is conducted visually to gauge the transition from adhesive failure to cohesive failure mode of the applied adhesive to a substrate. CF is cohesive failure mode.

10 The results are shown below in Table 3.

Table 3. Testing results of the Samples

FORMULA	A	B	C	D	E
LSS ¹ , Mpa	15.4	16	16.1	14.3	15.6
T-Peel ¹ , N/mm	7	6.7	7	6.3	7.5
Failure Mode	CF	CF	CF	CF	CF
RT Impact Peel ¹ , N/mm	9.7	19.4	17.5	17.5	27.7
1.6 mm Plate Steel, ² LSS Mpa	19.9	20.1	20.8	13.9	21.6

¹1.8 mm thick CRS, ¹10 Min 171° C Bake,

²10 Min 171° C Bake

An additional "Bend Test" was also performed with all the samples to evaluate the reduction of distortion of the materials. A 0.62 mm thick 5052H32 aluminum alloy obtained from Advanced Coatings Technology was used as the substrate for such Bend

15 Test. The substrate was first solvent wiped with acetone. The test substrate was cut into strips of 24 mm wide and 350 mm long coupons. A 2 mm deep skive was used to apply adhesive composition of the present invention evenly over 325 mm length leaving 25 mm at one end free of adhesives. Before baking, all coupons laid flat on the bench top. The coupons were cured 10 minutes at 171°C. After baking and cooling down of 24 hours, the

20 uncoated end was clamped to the bench top and the other end of the coupon was measured for height between the bench top and the unclamped end. Due to the thermal expansion differences of the adhesive and the metal, coupons exhibit a radius of curvature from the stresses occurring during cool down. The lower the radius of curvature the less distortion

one is likely to experience in an aluminum closure. The results of such Bend Test are summarized in Table 4.

Table 4. Bend Test results

Example	Parts Ground Rubber MD184 (wt.%)	Deflection mm	Tensile MPa	Young's Modulus MPa	Elongation %
A	25	54			
B	30	45			
C	25	50			
D	35	20	13.5	829	5
BETAMATE™4601	0	93	65	3100	5
E	0	40	18.7	931	17

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Summary of Observations for Tables 3 and 4

Example A shows how a low performance hem flange adhesive composition might perform with a respectable impact peel of 9.7 N/mm, when containing the ground rubber tire material MD-184 TR.

10 Example B is an example with LSS, T-Peel and impact sufficient to meet most automotive hem flange adhesive specifications, when containing the ground rubber tire material MD-184 TR.

Examples C and D is compared to BETAMATE™ 4601 which shows the dramatic effect on modulus and deflection decrease that occurs to BETAMATE™ 4601 when
15 incorporating ground rubber material MD-184 TR. BETAMATE™4601 is regarded as one of the highest modulus adhesives, perhaps the highest, in the automotive market with good impact peel performance. Excessive distortion of aluminum closures using adhesives with high modulus was observed.

Example E is a comparative sample prepared in accordance to WO2013151835A1.
20 It has excellent overall properties and is expected to perform well reducing distortion of

parts however it is also an inherently expensive formula. The examples B, C, D all have similar deflection values compared to E and the modulus of Example D is also comparable to that of Example E.

WHAT IS CLAIMED IS:

1. An epoxy resin containing adhesive composition comprising 1 to 40 wt% of a
5 ground rubber and 0 to 20 wt% of talc and chlorites.
2. The adhesive composition of Claim 1 comprising 25 to 35 wt% of a ground rubber
and 0 to 10 wt% of talc and chlorites.
- 10 3. An epoxy resin containing adhesive composition comprising 1 to 40 wt% of a
ground rubber and substantially free of talc and chlorites.
4. The adhesive composition of either Claims 1 or 3, further comprising a curing agent,
a catalyst, fumed silica, a toughener, and an optionally auxiliary toughener, epoxy silane
15 and fillers.
5. The adhesive composition of claim 4 wherein the adhesive composition has a
Young's modulus of no more than 1000 MPa.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/048871

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09J163/00
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)
C09D C08L 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	US 6 521 706 B1 (DESAI UMESH C [US] ET AL) 18 February 2003 (2003-02-18) tables 1,2 examples A,B,C, E,F,H claims 1-13	1-5
X	----- US 2007/048445 A1 (DIMARIO JOSEPH [US]) 1 March 2007 (2007-03-01) tables 4,5 examples A,B,C, E,F,H claims 10-16	1-5
X	----- US 2007/048504 A1 (DIMARIO JOSEPH [US]) 1 March 2007 (2007-03-01) tables 4,5 examples A,B,C, E,F,H ----- -/-	1-5



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 2012/142817 A1 (SWARUP SHANTI [US] ET AL) 7 June 2012 (2012-06-07) table 1 claims 1-19 -----	1-5
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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