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(71) Applicant *(for all designated States except US)*: **DSM IP Assets B.V.** [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **BRULS, Wilhelmus Gerardus Marie** [NL/NL]; Graaf Wolterhoenstraat 32, NL-6243 BE Geulle (NL). **BUIJSCH OP DEN, Francois Antoine Marie** [NL/NL]; Grispenstraat 31, NL-6367 HN Voerendaal (NL). **BLOM, Dirk Gijsbert** [NL/NL]; Gouverneur van Hövellstraat 13, NL-6131 KC Sittard (NL). **WELZEN, Leonardus Jacobus Johannus Wilhelmus** [NL/NL]; Staakijzerstraat 18, NL-6129 JC Urmond (NL).

(74) Agent: **DORRESTIJN, Antoon**; P.O. Box 4, NL-6100 AA Echt (NL).

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(54) **Title**: POLYMER COMPOSITION AND A SEALING BODY MADE OF THAT COMPOSITION

(57) **Abstract**: Polymer composition containing: A. A thermoplastic copolyester elastomer, B. a plastomer, C. a polyolefin polymer grafted with an ethylenically unsaturated compound, functionalized with a functional group.

POLYMER COMPOSITION AND A SEALING BODY MADE OF THAT COMPOSITION

The invention relates to a polymer composition and a sealing body made of that composition.

Sealing bodies are well known in the art and are often used for making a gas or liquid tight seal between two parts, for example between parts of an engine. Examples of sealing bodies include sealing rings, gaskets, etc. A specific example is a sealing body, being a part of a body plug assembly for cars. In car bodies relatively large openings exist to give access to hollow spaces in the car body, like for example hollow beams for reinforcement of the car body. The relatively large openings are used for supplying corrosion protective compounds into the hollow spaces at the inner walls of the hollow spaces and into the welds. After the supply of the corrosion protective compound the opening is closed with a so-called body plug. The body plug is usually made of a flexible, resilient polymer composition, so that it can be pushed into the opening, to close the opening. Because of the resilient nature of the polymer composition of the body plug a firm closure of the opening is obtained.

The closure however is not always firm enough. It is possible that after a certain period of time leakages develop between the plug and the car body. The leakages allow moisture to enter the hollow space, so that corrosion starts.

To solve this problem, a sealing body is used, which fits between the body plug and the car body. Generally the sealing body is an integral part of the body plug assembly. For the sealing body it is important that it adheres well at the car body and at the flexible, resilient polymer composition of the body plug itself. The adhesion between the sealing body and the body plug may be obtained at high temperatures, during a 2K injection molding process for producing the assembly of the body plug and the sealing body. The assembly of the body plug and the sealing body is most often installed after the application of the corrosion protective compound and before the painting of the car body. The painting process comprises a curing step for curing the paint at temperatures between 100 and 200 ºC. During this curing step adhesion between the sealing body and the car body develops.

It is important that the sealing body keeps its integrity at the high temperatures during the curing step, but that at the same time a good adhesion between the sealing body and the car body is obtained, also at the lower temperatures of about 100 -120 ºC. These are conflicting conditions, because to obtain a good adhesion, softening or even partial melting of the sealing body is desirable, while this

enhances deformation or even flowing away of the sealing body.

Surprisingly the conflicting conditions are met if for the production of the sealing body a polymer composition is used containing:

A. A thermoplastic copolyester elastomer,

B. a plastomer,

C. a polyolefin polymer grafted with an ethylenically unsaturated compound, functionalized with a functional group.

The assembly of the body plug and the sealing body provides a firm closure of the opening in the car body, because a good adhesion is obtained between the sealing body and the flexible and resilient polymer composition of the body plug as well as the sealing body and the eventually pretreated metal of the car body, also at a temperature in the curing step for curing the paint of about 100ºC. The sealing body also keeps very well its integrity during the curing step, even at a temperature of about 200 ºC.

A. Thermoplastic copolyester elastomer

The thermoplastic copolyester elastomers are thermoplastic polymers with elastomeric properties comprising polyester hard segments and soft segments derived from another polymer. The polyester hard segments in the copolyester elastomers are generally composed of monomer units derived from at least one alkylene diol and at least one aromatic or cycloaliphatic dicarboxylic acid.

The hard segments typically consist of a polyester having a melting temperature or glass temperature, where applicable, well above room temperature. Preferably the melting temperature or glass temperature is at least 150 °C, more preferably at least 170 °C even more preferably at least 190 °C. Still more preferably the melting temperature or glass temperature of the hard segments is in the range of 200 – 280 °C. The soft segments typically consist of segments of an amorphous polymer having a glass transition temperature well below room temperature. Preferably the glass temperature of the amorphous polymer is at most 0 °C, more preferably at most -10 °C or even at most -20 °C. Still more preferably the glass temperature of the soft segments is in the range of -20 – -60 °C, most preferably in the range of -30 – -60 °C.

Examples of copolyester elastomers include a copolyesterester elastomer, a copolycarbonateester elastomer or a copolyetherester elastomer; i.e. a

copolyester block copolymer with soft segments derived from a polyester, a polycarbonate or, respectively, a polyether. Copolyester elastomers are available, for example, under the trade name Arnitel, from DSM Engineering Plastics B.V. The Netherlands.

Suitable copolyesterester elastomers are described, for example, in EP-0102115-B1.

Copolyetherester elastomers have soft segments derived from at least one polyalkylene oxide glycol. Copolyetherester elastomers and the preparation and properties thereof are for example described in detail in Thermoplastic Elastomers, 2nd Ed., Chapter 8, Carl Hanser Verlag (1996) ISBN 1-56990-205-4, Handbook of Thermoplastics, Ed. O. Otabisi, Chapter 17, Marcel Dekker Inc., New York 1997, ISBN 0-8247-9797-3, and the Encyclopedia of Polymer Science and Engineering, Vol. 12, pp. 75-117 (1988), John Wiley and Sons, and the references mentioned therein.

The aromatic dicarboxylic acid in the hard segments of the polyetherester elastomer suitably is selected from the group consisting of terephthalic acid, isophthalic acid, phthalic acid, 2,6-naphthalenedicarboxylic acid and 4,4-diphenyldicarboxylic acid, and mixtures thereof. Preferably, the aromatic dicarboxylic acid comprises terephthalic acid, more preferably consists for at least 50 mole %, still more preferably at least 90 mole %, or even fully consists of terephthalic acid, relative to the total molar amount of dicarboxylic acid.

The alkylene diol in the hard segments of the polyetherester elastomer suitably is selected from the group consisting of ethylene glycol, propylene glycol, butylene glycol, 1,2-hexane diol, 1,6-hexamethylene diol, 1,4-butane diol, benzene dimethanol, cyclohexane diol, cyclohexane dimethanol, and mixtures thereof. Preferably, the alkylene diol comprises ethylene glycol and/or 1,4 butane diol, more preferably consists for at least 50 mole %, still more preferably at least 90 mole %, or even fully consists of ethylene glycol and/or 1,4 butane diol, relative to the total molar amount of alkylene diol.

The hard segments of the polyetherester elastomer most preferably comprise or even consist of polybutylene terephthalate segments.

Suitably, the polyalkylene oxide glycol is a homopolymer or copolymer on the basis of oxiranes, oxetanes and/or oxolanes. Examples of suitable oxiranes, where upon the polyalkylene oxide glycol may be based, are ethylene oxide and propylene oxide. The corresponding polyalkylene oxide glycol homopolymers are known by the names polyethylene glycol, polyethylene oxide, or polyethylene oxide

glycol (also abbreviated as PEG or PEO), and polypropylene glycol, polypropylene oxide or polypropylene oxide glycol (also abbreviated as PPG or PPO), respectively. An example of a suitable oxetane, where upon the polyalkylene oxide glycol may be based, is 1,3-propanediol. The corresponding polyalkylene oxide glycol homopolymer is known by the name of poly(trimethylene)glycol. An example of a very suitable oxolane, where upon the polyalkylene oxide glycol may be based, is tetrahydrofuran. If a polyetherester is used with soft blocks based on tetrahydrofuran the composition according to the invention shows an optimum in flexibility and strength. The corresponding polyalkylene oxide glycol homopolymer is known by the name of poly(tretramethylene)glycol (PTMG) or polytetrahydrofuran (PTHF). The polyalkylene oxide glycol copolymer can be random copolymers, block copolymers or mixed structures thereof. Suitable copolymers are, for example, ethylene oxide / polypropylene oxide block-copolymers, (or EO/PO block copolymer), in particular ethylene-oxide-terminated polypropylene oxide glycol.

The polyalkylene oxide can also be based on the etherification product of alkylene diols or mixtures of alkylene diols or low molecular weight poly alkylene oxide glycol or mixtures of the aforementioned glycols.

It is also possible that the thermoplastic elastomer is a copolycarbonateester elastomer. Suitable copolycarbonateester elastomers are described, for example, in EP-A-0846712 and EP-A-1964871. The hard segments is the copolycarbonate ester in principle may be the same as described above for the copolyesterester and copolyetherester elastomers. The soft segments suitably contain monomeric units of at least one alkylene carbonate The alkylene carbonate may be represented by the formula

$$-O-(CR_2)_x-O-C-$$

Where R =H, alkyl or aryl

X = 2 – 20.

Preferably the alkylenecarbonate is hexamethylene carbonate. It is also possible that the copolycarbonateester contains further units, derived from an alophatic diol, an aliphatic diol or lactone. A good example is butylene adipate. In case a lactone is used, preference is given to polycaprolactone.

B. Plastomer.

Plastomers are copolymers of ethylene with 1-butene, 1-hexene or 1-octene, manufactured with a metallocene catalyst or eventually another single site catalyst. Because of the plastomer very good sealing is obtained in a wide temperature range and for a long period of time. This is especially important for use in cars, where these demands are high. Preferably the plastomer has a density of at most 930 kg/m^3, more preferably of at most 910, even more preferably at most 890 kg/m^3 and most preferably at most 885 kg/m^3. In addition to the single site catalyst polymerised polyolefins the polymer composition may comprise other polymers, in particular polyolefins. These polyolefins can be polymerised with conventional polymerisation techniques with Ziegler-Natta or Phillips type catalysts. Furthermore the polymer composition may comprise polystyrene, acryl-butadiene-styrene, SEBS, SBR, EP(D)M rubbers as well as thermoplastic polyolefin elastmers and vulcanisates. The total amount of other polymers than the single site catalysed polyolefins in the polymer composition may range from 0 – 45 wt. % of the polymer composition. The proportion of the component B is preferably at least 50 wt%, preferably 55 wt% and more preferably at least 70%.

C. A polyolefin polymer grafted with an ethylenically unsaturated compound, functionalized with a functional group.

The polymer composition according to the invention contains a polyolefin polymer grafted with an ethylenically unsaturated functionalised compound, containing a functional group, also referred to as “grafted polyolefin polymer”.

As grafted polyolefin polymers in the composition according to the invention homo-and copolymers of one or more olefin monomers that are grafted with an ethylenically unsaturated functionalised compound may be used.

Examples of suitable polyolefin polymers are ethylene polymers, propylene polymers and styrene- butadiene-styrene block copolymers or the hydrogenated form hereof. Examples of suitable ethylene polymers are all thermoplastic homopolymers of ethylene and copolymers of ethylene with as comonomer one or more a-olefins with 3-10 C-atoms, in particular propylene, isobutene, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene which can be manufactured with the known catalysts such as for example Ziegler-Natta, Phillips and single site catalysts, preferably metallocene catalysts. The quantity of comonomer lies as a rule between 0 and 50 wt. %, and preferably between 5 and 35 wt. %. Such

polyethylenes are for instance known as high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE) and linear very low density polyethylene (VL(L)DPE). Also elastomers and plastomers are among the examples. Suitable polyethylenes have a density between 860 and 970 kg/m^3 .

Examples of suitable propylene polymers are homopolymers of propylene and copolymers of propylene with ethylene, in which the proportion of ethylene amounts to at most 30 wt% and preferably at most 25 wt%. Their Melt Flow Index (230°C, 2,16 kg) lies between 0.5 and 25 g/10min, more preferably between 1.0 and 10 g/10min. Preferably component C is based on the same monomeric units as componenet B. Even more preferably component C is obtained by grafting component B.

Suitable ethylenically unsaturated functionalised compounds are those that can be grafted on at least one of the above-mentioned suitable polyolefin polymers. These compounds contain a carbon-carbon double bond and can form a side branch on a polyolefin polymer by grafting thereon. The compounds have been functionalised, which means that they possess a functional group. The functional group is preferably able to form a chemical bond with an –OH group and/or an –COOH group and/or a -NH3 group. Examples of functional groups are carboxylic acids and esters, anhydrides and salts thereof. The functionalised compounds can also contain an epoxy ring, an amine group, an alkoxy silane group or an alcohol group. The compound can also be an ethylenically unsaturated oxazoline.

Examples of suitable ethylenically unsaturated functionalised compounds are the unsaturated carboxylic acids and esters and anhydrides and metallic or non-metallic salts thereof. Preferably the ethylenic unsaturation in the compound has been conjugated with a carbonyl group. Examples thereof are acrylic, methacrylic, maleic, fumaric, itaconic, crotonic, methyl crotonic, and cinnamic acid and esters, anhydrides and possible salts thereof. Of the compounds with at least one carbonyl group maleic anhydride is preferable.

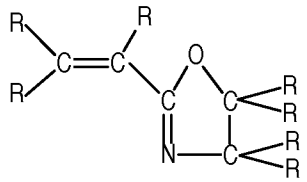
Examples of suitable ethylenically unsaturated functionalised compounds with at least one epoxy ring are for example glycidyl esters of unsaturated carboxylic acids, glycidyl ethers of unsaturated alcohols and of alkyl phenols and vinyl and allyl esters of epoxy carboxylic acids. Glycidyl methacrylate is specially suitable.

Examples of suitable ethylenically unsaturated functionalised compounds with at least one amine functionality are amine compounds with at least one ethylenically unsaturated group, for example allylamine, propenyl, butenyl, pentenyl and hexenyl amine, amine ethers, for example isopropenylphenyl ethylamine

ether. The amine group and the unsaturation should be situated relative to each other in such a position that they do not influence the grafting reaction to an undesirable degree. The amines can be unsubstituted but also substituted with for example alkyl and aryl groups, halogen, ether and thioether groups.

Examples of suitable ethylenically unsaturated functionalised compounds with at least one alcohol functionality are all compounds with a hydroxyl group whether or not etherified or esterified and an ethylenically unsaturated compound, for example allyl and vinyl ethers of alcohols such as ethyl alcohol and higher branched and unbranched alkyl alcohols, a well as allyl and vinyl esters of alcohol-substituted acids, preferably carboxylic acids and C_3-C_3 -C_8 alkenyl alcohols. The alcohols can further be substituted with for example alkyl and aryl groups, halogen, ether and thioether groups which do not influence the grafting reaction to an undesirable degree.

Examples of oxazoline compounds that are suitable as ethylenically unsaturated functionalised compounds in the framework of the invention are for example those with the following general formula



wherein each R independently of the other hydrogen, is a halogen, a C_1-C_{10} alkyl radical or a C_6-C_{14} aryl radical.

Preferably as functional groups dicarboxylic acid anhydride is used, most preferably maleic acid anhydride.

The quantity of the ethylenically unsaturated functionalised compound in the grafted polyolefin polymer may be between 0.05 and 1 mgeq per gram polyolefin polymer. Preferably the quantity of the ethylenically unsaturated functionalised compound in the grafted polyolefin polymer lies between 0.1 and 0.5 mgeq per gram polyolefin polymer and more preferably between 0.15 and 0.3 mgeq per gram polyolefin polymer. In this way a very good adhesion between the sealing body and metal is obtained.

The grafted polyolefin polymer can be prepared by reacting the polyolefin polymer with the ethylenically unsaturated functionalised compound

according to methods known per se for this purpose, for example as described in US patent 3,236,917, US patent 5,194,509 and US patent 4,950,541.

The composition may further comprise the usual additives, for example antioxidants, dyes or pigments, UV absorbers, hydrolytic stabilizers, anti-static agents, lubricants etc. The composition may comprise between 0 and 5 parts by weight of the additives at 100 parts by weight (pbw) of A + B + C, preferably between 1 and 3 parts by weight.

In a preferred embodiment polymer composition contains

5 - 80 pbw component A

85 – 20 pbw component B,

whereby A and B add up to 100 parts by weight (pbw),

0.1 - 20 pbw component C

Such a composition may be used for a wide variety of applications.

More preferably the composition consists of

5 - 45 pbw component A

85 - 55 pbw component B,

whereby A and B add up to 100 parts by weight,

0.1 - 20 pbw component C

0- 5 pbw of usual additives.

The invention also relates to a sealing body made of the polymer composition according to the invention.

The invention also refers to an assembly of a body plug and a sealing body, the sealing body made of the polymer composition according to the invention. Preferably also the body plug is made from the composition according to the invention, however the amount of component A is higher in the composition of the body plug than in the composition of the sealing body.

In the composition of the body plug the amount of component A is preferably between 60 and 90 and in the polymer composition for the sealing ring the amount of component A is preferably between 10 and 40 parts by weight, and component B is between 60 and 90 parts by weight, A and B add up to 100 parts.

The polymer composition of the invention is also very suitable for use as a carpet backing material, hot melt adhesive, boots, bellows, etc.

Examples.

Materials used.

Component A:
-Arnitel™ EM460, a thermoplastic copolyester elastomer, delivered by DSM, the Netherlands. The soft segments consist of polytetrahydrofuran.

Component B:
Exact™ 8210, a plastomer containing ethylene and 1-octene, having a density of 882 kg/m^3, delivered by DEX Plastomers, the Netherlands.

Component C:
Fusabond™ N525, an ethylene copolymer, grafted with 0.9 wt. % maleic acid anhydride, delivered by Dupont, the USA.

Preparation of polymer composition.
Dry blends where produced by mixing granulates of the components. The compositions are indicated in tables 1 and 2.
Part of the dry blends were directly processed into test plates as explained below, whereby mixing of the components took place in the injection moulding machine used for producing the test plates. Parts of the dry blends were pre-mixed. The pre-mixing took place by dosing the dry blend to a Werner and Pfleiderer ™ co-rotating twin screw kneader, having screw diameters of 30 mm. The final melt temperature in the kneader was 240 ºC. The melt was cooled down in a water bath and granulated.

Injection molding.

The dry blends and the pre-mixed compositions were injection molded by an Arburg ™ Allrounder injection molding machine into flat test plates with dimensions of 65mm x 65mm x 1mm.

Testing of sealing body adhesion towards metal.

In order to test the adhesion of the sealing body towards the metal car body after the painting process of the car, the model experiments as described below were carried out.

A stack was made by putting the test plates between two steel plates having about the same dimensions as the test plates. The stack was placed during 30 minutes in a pre-heated oven at 180 ºC and cooled down to room temperature again. Than the adhesion between the metal plates and the test plates was judged manually. Results are indicated in table 1.

Example I.

A composition containing components A, B and C as indicated in table 1 was dry blended in processed by injection molded into test plates. The adhesion of the test plates towards steel plates was determined.

Example II.

As example I, however the dry blend of the composition was pre-mixed before injection molding of the plates.

Comparative experiments A, B and C.

As examples I and II, however, the compositions did not contain component C.

Table 1					
Ex./Exp.	A	B	C	I	II
Composion					
Exact 8230	100		60	67	67
Arnitel EM460		100	40	25	25
Fusabond N525				8	8
dry-blend	Y			Y	
premixed		Y	Y		Y
adhesion	no	no	no	very good	very good

The results show, that because of the presence of component C in the sealing ring composition a good adhesion is obtained between the seal body material and the metal plates. Similar results could be obtained with rigid polymers, for example polyamides, polyethylene, polypropylene, thermoplastic vulcanisates etc.

CLAIMS

1. Polymer composition containing:
A. A thermoplastic copolyester elastomer,
B. a plastomer,
C. a polyolefin polymer grafted with an ethylenically unsaturated compound, functionalized with a functional group.

2. Polymer composition according to claim 1, wherein the thermoplastic copolyester elastomer is a polyetherester elastomer.

3. Polymer composition according to claim 2, wherein the polyetherester elastomer contains soft blocks based on tetrahydrofuran.

4. Polymer composition according to any one of claims 1 – 3, wherein component C is a polyolefin grafted with a maleic acid anhydride.

5. Polymer composition according to any one of claims 1 – 4, wherein the composition contains:
5 - 80 pbw component A
85 – 20 pbw component B,
whereby A and B add up to 100 parts by weight (pbw),
0.1 - 20 pbw component C.

6. Polymer composition according to claim 5, wherein the composition consists of
5 - 45 pbw component A
85 - 55 pbw component B,
whereby A and B add up to 100 parts by weight,
0.1 - 20 pbw component C
0- 5 pbw of usual additives.

7. Sealing body consisting of the polymer composition according to any one of claims 1 – 6.

8. Assembly of the sealing body of claim 7 and a body plug for a car, wherein the body plug is made from the composition according to any one of claims 1 -6, however the amount of component A in the polymer composition of the sealing ring is higher than the amount of component A in the polymer composition of the body plug.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/056138

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L67/02 C08L23/08
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)
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 practical, 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 2006/120191 A1 (TOTAL PETROCHEMICALS RES FELUY [BE]; MAZIERS ERIC [BE]) 16 November 2006 (2006-11-16) page 4, line 1 - page 5, line 2; claims	1-4,7-9
X	WO 02/055599 A2 (DSM NV [NL]; WILLEMS EDWIN [NL]; SADEGHI MOHAMMAD REZA [US]) 18 July 2002 (2002-07-18) page 4, line 31 - page 5, line 10; claims; examples 7-9	1-4,7-9
A	WO 00/52094 A1 (DOW CHEMICAL CO [US]) 8 September 2000 (2000-09-08) claims	1-4,7-10

☐ 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

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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Date of the actual completion of the international search	Date of mailing of the international search report
26 July 2011	04/08/2011

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Schlicke, Benedikt

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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