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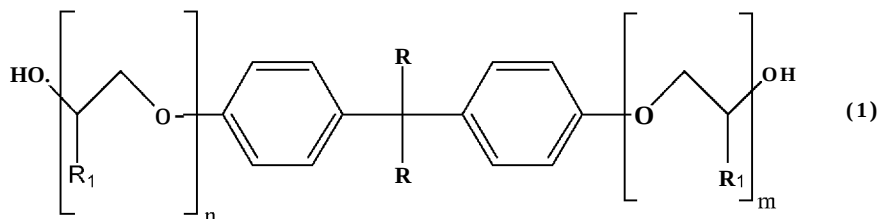
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## (54) Title: MULTI-COMPONENT RESIN SYSTEM



(57) Abstract: The invention relates to a multi-component resin system comprising (A) a hydroxyl functional unsaturated polyester resin comprising fumaric acid building blocks as unsaturated dicarboxylic acid building blocks and hydroxyl building blocks according to formula 1 in which  $n+m > 3$ , R is H or CH<sub>3</sub> and R<sub>1</sub> is H or CH<sub>3</sub> and having a hydroxyl value of from 40 up to and including 150 and an acid value  $< 4$ , an ethylenically unsaturated compound copolymerizable with (A) a polyisocyanate that has on average at least 1.9 isocyanate groups, and a radical initiator; and in which the molar ratio of [NCO]/[OH] in the resin system is from 2:1 up to and including 1:50.



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MULTI-COMPONENT RESIN SYSTEM

The present invention relates to a multi-component resin system comprising a hydroxyl functional unsaturated polyester, an ethylenically unsaturated compound copolymerizable with the hydroxyl functional unsaturated polyester, a  
5 polyisocyanate that has on average at least 1.9 isocyanate groups and a radical initiator.

Unsaturated polyester resins especially diluted in styrene are well known in the art. They are used in many applications such as for instance tanks, pipes,  
10 boats, relining, chemical anchoring, automotive applications etc.

In order to further improve the mechanical properties of unsaturated polyester resins for the more demanding applications, various hybrid systems have been developed. An example of such a hybrid system is the hybrid of the free radical co-polymerization of an hydroxyl functional polyester with an ethylenically unsaturated  
15 compound combined with the isocyanate (NCO)-hydroxyl (OH) polyaddition.

According to L. Valette and C.P.Hsu (Polymer vol 40 p 2059 (1999)) the mechanical properties can be greatly improved by this combination. This improvement in mechanical properties was also mentioned in the introduction part of US 5821296. According to D. Huajun, Z. Lianmeng, W. Jun, Y. Xiaoli, W. Xiang  
20 (Journal of Wuhan University of technology-mater. Sci. Ed P 627, (2009) DOI: 10.1 007/s1 1595-009-4627-2) these improvements in mechanical properties could be due to an increased toughness of the cured hybrid materials. N. Douglass and H. Nava (Composites Research Journal, p 24 ( 2007)) describe that these hybrid materials are resistant to various environments like water, alkaline and salt water. An example of  
25 using such a hybrid system for the resin transfer moulding process is described by A. Maazouz, J. Dupuy, G. Seytre (Polym. Eng. Sci. vol 40 p 690 (2000)).

However, although these hybrid systems can have excellent static mechanical properties which enables them to be used in many applications, improvement is still needed for other applications. An example of such an application  
30 area which still needs improvement is the windmill blade industry. In this industry there is besides high requirements on the static mechanical properties also a high requirement on the dynamic properties. An example thereof is the dynamic fatigue of a glass filled laminate. As the dynamic fatigue is generally linked to the life time under load conditions, improving the dynamic fatigue of a glass filled laminate will either  
35 improve the life time of current windmill blades or enable the construction of even

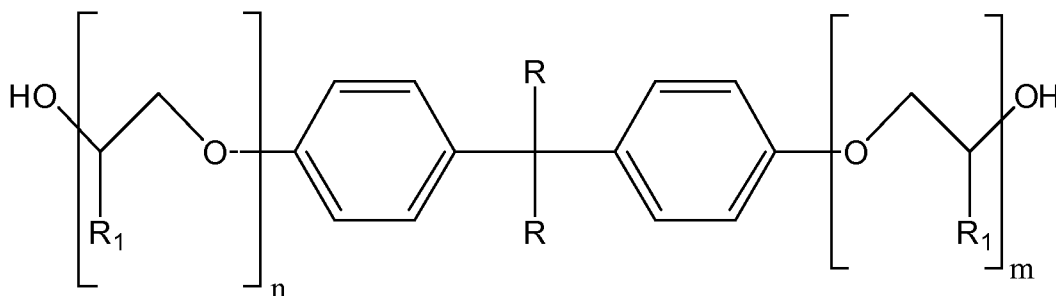
larger blades. As there is no link between the static mechanical properties and the dynamic fatigue, improving the static mechanical properties does not automatically result in improved dynamic mechanical properties. In fact improving the static properties can even result in a decrease in dynamic fatigue.

5                                      Consequently, especially for the windmill blade industry which uses glass filled laminates, there is still a need for unsaturated polyester resin compositions which can result in improved dynamic fatigue properties of glass fiber reinforced laminates whilst maintaining the static mechanical properties at a level suitable for construction purposes.

10                                     Accordingly, the object of the present invention is to be able to improve the dynamic fatigue of glass fiber reinforced laminates of cured unsaturated polyester resin compositions whilst maintaining other mechanical properties at a level sufficient to be suitable for composite applications.

15                                     This object has surprisingly been achieved in that the multi-component resin system comprises

(A) a hydroxyl functional unsaturated polyester resin comprising fumaric acid building blocks as unsaturated dicarboxylic acid building blocks and hydroxyl building blocks according to formula 1



20                                     in which  $n+m \geq 3$ , R is H or CH<sub>3</sub> and R<sub>1</sub> is H or CH<sub>3</sub> and having a hydroxyl value of from 40 up to and including 150 and an acid value < 4,

(B) an ethylenically unsaturated compound copolymerizable with (A),

(C) a polyisocyanate that has on average at least 1.9 isocyanate groups, and

25                                     (D) a radical initiator;

and in which the molar ratio of [NCO]/[OH] in the resin system is from 2:1 up to and including 1:50.

The simple fact that by using a composition according to the invention the dynamic fatigue is significantly improved is very surprising as none of the literature

cited above even mentions the possibility that by using such composition this could have an effect on the dynamic fatigue.

Preferably,  $n+m \geq 3.5$  and more preferably,  $n+m \geq 4$ .

Examples of hydroxyl building blocks groups according to formula 1 for the hydroxyl functional unsaturated polyester resin comprising fumaric acid building blocks are ethoxylated and/or propoxylated bisphenol A and ethoxylated and/or propoxylated bisphenol F compounds with various degrees of ethoxylation or propoxylation, like for example E03, E04, P03, P04, P05 and P08. Preferably, the degree of ethoxylation or propoxylation is less than 10 ( $n+m < 10$ ).

Preferably, propoxylated bisphenol A or F ( $R_1 = CH_3$ ), more preferably propoxylated bisphenol A ( $R_1 = CH_3$  and  $R = CH_3$ ) is used as hydroxyl building block according to formula (1).

Preferably, the amount of hydroxyl building blocks according to formula (1) in (A) is such that the molar amount of hydroxyl building blocks according to formula (1) in (A) relative to the total molar amount of hydroxyl building blocks in (A) is from 0.3 up to and including 1, more preferably from 0.5 up to and including 1 and even more preferably 1.

Preferably, the hydroxyl functional unsaturated polyester resin comprising fumaric acid building blocks as unsaturated dicarboxylic acid building blocks and hydroxyl building blocks according to formula 1 has an acid value lower than 3, more preferably lower than 2 and most preferably lower than 1 mg KOH/g resin. As used herein, the acid value of hydroxyl functional unsaturated polyester resin comprising fumaric acid building blocks as unsaturated dicarboxylic acid building blocks and hydroxyl building blocks according to formula 1 is determined titrimetrically according to ISO 2114-2000.

Preferably, the hydroxyl value of hydroxyl functional unsaturated polyester resin comprising fumaric acid building blocks as unsaturated dicarboxylic acid building blocks and hydroxyl building blocks according to formula 1 is higher than 50, more preferably higher than 60. Preferably the hydroxyl value is lower than 100 mg KOH/g resin. The hydroxyl value (OHV) (mg KOH/g of polyester) of the polyester is measured using ISO 4629-1978.

The hydroxyl functional unsaturated polyester resin comprising fumaric acid building blocks as unsaturated dicarboxylic acid building blocks and hydroxyl building blocks according to formula 1 has a molecular weight of at least 800 Dalton, more preferably of at least 900 Dalton and even more preferably of at least

1000 Dalton. The compound capable of undergoing radical copolymerization preferably has a molecular weight of at most 10.000 Dalton and more preferably at most 5000 Dalton. As used herein, the molecular weight of the resin is determined in tetrahydrofuran using gel permeation chromatography according to ISO 13885-1  
5 employing polystyrene standards and appropriate columns designed for the determination of the molecular weights.

Preferably, the molar ratio of  $[NCO]/[OH]$  in the resin system is from 1.5:1 up to and including 1:10, more preferably, from 1:1 up to and including 1:5.

The ethylenically unsaturated compound copolymerizable with A  
10 (compound B) can be any ethylenically unsaturated compound as long as it can copolymerize with A and are used for both reactivity as well as viscosity reasons. They are generally referred to as reactive diluents.

Preferably the hydroxyl functional unsaturated polyester resin (A) comprising fumaric acid building blocks as unsaturated dicarboxylic acid building  
15 blocks and hydroxyl building blocks according to formula 1 is diluted in an ethylenically unsaturated compound copolymerizable with (A). Examples of suitable reactive diluents are, for instance, alkenyl aromatic monomer, such as for example styrene and divinylbenzene vinyl toluene, t-butyl styrene, dialkyl itaconates, (meth)acrylates, vinyl ethers and vinyl amides but all other reactive monomers for use in the field of  
20 thermosetting resins as are known to the person skilled in the art can be used. Non-limited examples of reactive diluents are styrene, alpha-methyl styrene, chlorostyrene, vinyl toluene, divinyl benzene, methyl methacrylate, n-butyl methacrylate, cyclohexylmethacrylate, tert. butyl styrene, tert. butylacrylate, butanediol dimethacrylate, 2-hydroxypropyl methacrylate, 2-hydroxyethyl methacrylate, acetoacetoxyethyl  
25 methacrylate, PEG200 di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,3-butanediol di(meth)acrylate, 2,3-butanedioldi(meth)acrylate, 1,6-hexanediol di(meth)acrylate and its isomers, diethyleneglycol di(meth)acrylate, triethyleneglycol di(meth)acrylate, glycerol di(meth)acrylate, trimethylolpropane di(meth)acrylate, neopentyl glycol di(meth)acrylate, dipropyleneglycol di(meth)acrylate,  
30 tripropyleneglycol di(meth)acrylate, PPG250 di(meth)acrylate, tricyclodecane dimethylol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, tetraethylene glycol di(meth)acrylate and trimethylolpropanetri(meth)acrylate, dimethyl itaconate, diethyl itaconate, dibutyl itaconate and mixtures thereof. Preferably, the ethylenically unsaturated compound copolymerizable with (A) is selected from the group of styrene,  
35 substituted styrene, dialkyl itaconates and methacrylates.

Preferably the amount of ethylenically unsaturated compound copolymerizable with (A) is between 10 and 90 wt.% more preferably between 15 and 80 wt.% and even more preferably between 20 and 70 wt % based on the total amount of (A) and (B).

5                      Preferably the amount of hydroxyl functional unsaturated polyester (A) is between 10 and 90 wt.% more preferably between 20 and 85 wt.%, and even more preferably between 30 and 80 wt.% based on the total amount of (A) and (B).

                    The compound C comprises an isocyanate compound with an average functionality  $> 1.9$ , preferably with an average functionality  $\geq 2$ . Non-limiting  
10    examples of aromatic and/or aliphatic di isocyanates ( $f=2$ ) are toluene diisocyanate (TDI), 4,4'-methylene diphenyl diisocyanate (MDI), hexanediisocyanate (HDI), isophorone diisocyanate (IPDI). Non-limiting examples of aromatic and/or aliphatic tri-isocyanates ( $f=3$ ) are TDI trimers, HDI trimers, and polymeric MDI (pMDI) . Mixtures of the above mentioned isocyanates can be used as well. Preferred aromatic and/or  
15    aliphatic di and/or tri- isocyanates are toluene diisocyanate (TDI), 4,4'-methylene diphenyl diisocyanate (MDI), hexanediisocyanate (HDI), isophorone diisocyanate (IPDI) TDI trimers, HDI trimers, and polymeric MDI (pMDI), especially MDI and polymeric MDI are preferred. Polymeric MDI usually has an average functionality from 2 to 3 and may comprise triisocyanates next to for example diisocyanate. In a preferred embodiment  
20    of the invention, the isocyanate compound with an average functionality of at least 1.9 comprises aromatic and/or aliphatic diisocyanates.

                    The radical initiator in the multi-component system according to the invention can be any radical initiator or initiation system, such as for example azo compounds, photo-initiators and peroxide comprising systems. Preferably the radical  
25    initiating system comprises a peroxide in which embodiment the radical initiator is a peroxide.

                    The peroxide can in principle be any peroxide and the type will depend on for instance the temperature of cure. At high temperatures the thermal decomposition of the peroxide in the initiating system can be sufficient for an efficient  
30    cure depending on the peroxide decomposition temperature. At lower temperatures generally the peroxide is used in combination with a peroxide decomposition accelerator. Also the accelerator depends on the type of peroxide used and can be any peroxide decomposition accelerator known to the man skilled in the art. Suitable examples are for instance transition metal salts, complexes and cocktails of these salt  
35    or complexes with various ligands such as for instance based on cobalt, copper, iron

and manganese. In case peranhydrides are used, the peroxide decomposition accelerators are often selected from the group of tertiary aromatic amines.

Preferably the peroxide is selected from the group of peresters, perketals, percarbonates, hydroperoxides and peranhydrides.

5                   The amount of peroxide can be varied within wide ranges, in general less than 20 wt.%, and preferably less than 10 wt.% (relative to the total amount of A and B).

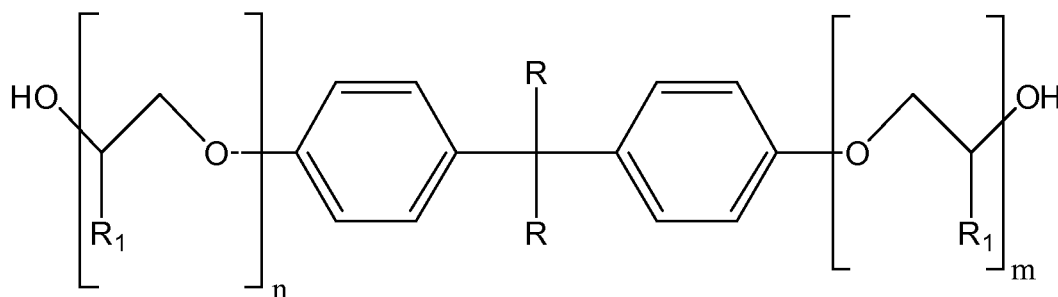
As used herein, multi-component resin systems means that the different compounds of the system are present in at least three spatially separated  
10                   components in order to prevent premature polymerization of the compounds prior to the use of the multicomponent resin system to obtain the hybrid cured resin network. The multicomponent resin system according to the invention comprises at least three components. In one embodiment, the multicomponent resin system comprises at least three components, whereby a first component consists of a resin composition  
15                   comprising the hydroxyl functional unsaturated polyester (A) and the ethylenically unsaturated compound (B); a second component B consists of a composition comprising the radical initiator (D) and a third component comprises the polyisocyanate (C). The use of the three component resin system according to the invention requires mixing of the three components to obtain a hybrid cured resin network.

20                   The multi-component resin system may further comprise a radical inhibitor which retards the peroxide initiated radical copolymerization of the unsaturated polyester resin with the reactive diluent. These radical inhibitors are preferably chosen from the group of phenolic compounds, hydroquinones, catechols, benzoquinones stable radicals and/or phenothiazines. The amount of radical inhibitor that can be  
25                   added may vary within rather wide ranges, and may be chosen as a first indication of the pot-life as is desired to be achieved.

Suitable examples of radical inhibitors that can be used in the resin compositions according to the invention are, for instance, 2-methoxyphenol, 4-methoxyphenol, 2,6-di-t-butyl-4-methylphenol, 2,6-di-t-butylphenol,  
30                   2,4,6-trimethyl-phenol, 2,4,6-tris-dimethylaminomethyl phenol, 4,4'-thio-bis(3-methyl-6-t-butylphenol), 4,4'-isopropylidene diphenol, 2,4-di-t-butylphenol, 6,6'-di-t-butyl-2,2'-methylene di-p-cresol, hydroquinone, 2-methylhydroquinone, 2-t-butylhydroquinone, 2,5-di-t-butylhydroquinone, 2,6-di-t-butylhydroquinone, 2,6-dimethylhydroquinone, 2,3,5-trimethylhydroquinone,  
35                   catechol, 4-t-butylcatechol, 4,6-di-t-butylcatechol, benzoquinone,

2,3,5,6-tetrachloro-1,4-benzoquinone, methylbenzoquinone, 2,6-dimethylbenzoquinone, naphthoquinone, 1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidine-4-ol (a compound also referred to as TEMPOL), 1-oxyl-2,2,6,6-tetramethylpiperidine-4-one (a compound also referred to as TEMPON),  
 5 1-oxyl-2,2,6,6-tetramethyl-4-carboxyl-piperidine (a compound also referred to as 4-carboxy-TEMPO), 1-oxyl-2,2,5,5-tetramethylpyrrolidine, 1-oxyl-2,2,5,5-tetramethyl-3-carboxylpyrrolidine (also called 3-carboxy-PROXYL), galvinoxyl, aluminium-N-nitrosophenyl hydroxylamine, diethylhydroxylamine, phenothiazine and/or derivatives or combinations of any of these compounds.

10 According to another embodiment of the invention, the multi-component resin system further comprises (E) a hydroxyl functional saturated polyester resin comprising cyclohexane dicarboxylic acid building blocks as saturated dicarboxylic acid building blocks and preferably hydroxyl building blocks according to formula 1



15 in which  $n+m \geq 3$ , R is H or CH<sub>3</sub> and R<sub>1</sub> is H or CH<sub>3</sub>

and having a hydroxyl value of from 40 up to and including 150 and an acid value < 4.

For clarity reasons, it is to be noted that when E is present, the amount of hydroxyls in E should be taken into account for the determination of [OH].

20 Preferably, the molar amount of compound A relative to the molar amount of compound E is from 10:1 up to and including 1:10, more preferably from 5:1 up to and including 1:5 and even more preferably from 2:1 up to 1:2.

Preferably, the molar amount of compound A relative to the molar amount of compound E is from 10:1 up to and including 1:10, more preferably from 5:1 up to and including 1:5 and even more preferably from 2:1 up to 1:2.

25 Preferably, the amount of hydroxyl building blocks according to formula (1) in (E) is such that the molar amount of hydroxyl building blocks according to formula (1) in (E) relative to the total molar amount of hydroxyl building blocks in (E) is

from 0.3 up to and including 1, more preferably from 0.5 up to and including 1 and even more preferably 1.

Preferably, the amount of cyclohexane dicarboxylic acid building blocks in (E) is such that the molar amount of cyclohexane dicarboxylic acid building blocks in (E) relative to the total molar amount of saturated dicarboxylic acid building blocks in (E) is from 0.3 up to and including 1, more preferably from 0.5 up to and including 1 and even more preferably 1.

Compounds A and E can be prepared separately but it is also possible to prepare such mixtures via a one pot synthesis procedure. According to a preferred embodiment, compounds (A) and (E) have been prepared simultaneously by mixing two equivalents of diol with 0.25 to 0.75, preferably 0.5 equivalent of fumaric acid and with 0.75 to 0.25, preferably 0.5 equivalent of cyclohexane dicarboxylic acid.

The invention further relates to systems comprising fibrous reinforcement. The fibrous reinforcement can be any type of fibers, preferably glass or carbon fibers are used, more preferably glass fibers are used. The amount of fibrous reinforcement is preferably from 5 to 90 wt.%, more preferably from 5 to 50 wt.% (relative to the total amount of A, B, C and D).

Besides fibers also other materials can be present in the resin system according to the invention like for instance pigments, fillers, low profile additives etc

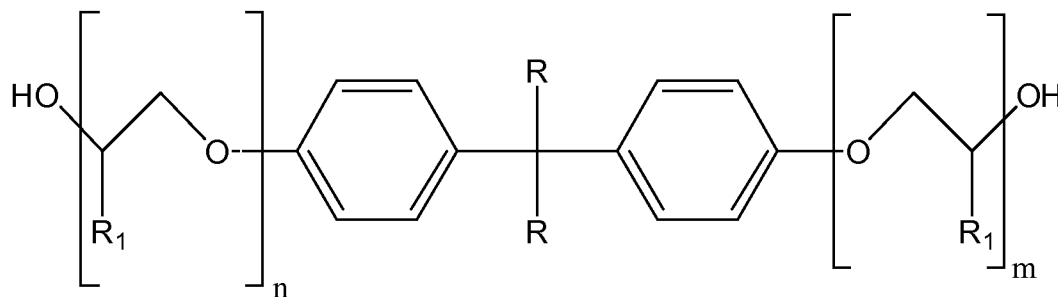
According to another embodiment of the invention, the multi-component resin system further comprises (F) a rubber which (i) is soluble in the mixture of (A) and (B), (ii) contains functional groups of which at least a part are, upon curing of the composition, able to react with at least (A), (B) and/or (C) and (iii) is, upon curing of the composition, phase separated from the cured composition.

In the context of the invention soluble means a solubility higher than 0.1 g per 100g mixture of (A) and (B). Phase separation upon cure can be easily detected visually as phase separation results in an opaque cured composition. In case due to fillers, fibers pigments etc the resins formulation is not transparent, phase separation can be detected as 2 distinct glass transition temperatures ( $T_g$ ) will appear in the DMTA of the cured material.

Preferably, the amount of rubber is between 1 and 30 wt.% (relative to the total amount of (A) and (B)). Preferably the amount of rubber is less than 25 wt.%, more preferably less than 20 wt.% and even more preferably less than 15 wt.%. Preferably the amount of rubber is more than 2 wt. %, more preferably more than 3 wt.%.

The invention further relates to a resin composition comprising

- (A) a hydroxyl functional unsaturated polyester resin comprising fumaric acid building blocks as unsaturated dicarboxylic acid building blocks and hydroxyl building blocks according to formula 1



5

in which  $n+m \geq 3$ , R is H or CH<sub>3</sub> and R<sub>1</sub> is H or CH<sub>3</sub>

and having a hydroxyl value of from 40 up to and including 150 and an acid value <4 and

- (B) an ethylenically unsaturated compound copolymerizable with (A)

10

Preferably the acid value is lower than 3, more preferably lower than 2 more preferably lower than 1 mg KOH/ g resin.

The present invention further relates to a process for curing a resin composition comprising (A) a hydroxyl functional unsaturated polyester resin

15

comprising fumaric acid building blocks as unsaturated dicarboxylic acid building blocks and hydroxyl building blocks according to formula 1 as defined above and

having a hydroxyl value of from 40 up to and including 150 and an acid value < 4, (B)

an ethylenically unsaturated compound copolymerizable with (A), with a peroxide and an isocyanate, wherein the curing is performed by mixing the components from the multi-component system as described above. Preferably, the curing is effected at a

20

temperature in the range of from -20 to +200 °C, preferably in the range of from -20 to +150 °C, more preferably in the range of from -10 to +80 °C and even more preferably at room temperature (from 20 up to and including 25 °C).

According to a preferred embodiment, the process for curing a resin composition comprising (A) a hydroxyl functional unsaturated polyester resin

25

comprising fumaric acid building blocks as unsaturated dicarboxylic acid building blocks and hydroxyl building blocks according to formula 1 as defined above and

having a hydroxyl value of from 40 up to and including 150 and an acid value < 4, (B)

an ethylenically unsaturated compound copolymerizable with (A), with a peroxide and an isocyanate is by preparing a resin composition comprising (A) a hydroxyl functional

unsaturated polyester resin comprising fumaric acid building blocks as unsaturated dicarboxylic acid building blocks and hydroxyl building blocks according to formula 1 as defined above and having a hydroxyl value of from 40 up to and including 150 and an acid value  $< 4$ , (B) an ethylenically unsaturated compound copolymerizable with (A) according to the invention, and by mixing the isocyanate and a peroxide to the so obtained resin composition.

Besides the windmill blade industry, the multi component resin systems according to the invention can also advantageously be applied in for example tanks, pipes, boats, relining, chemical anchoring, automotive applications, roofing, flooring, boats. The invention also relates to the cured objects or structural parts obtained by mixing the components from the multi-component system according to the invention.

The present invention further relates to a process for the preparation of fiber reinforced composite articles comprising mixing the components of the multi-component system as described above; impregnating fibers with this mixture and allowing the resin composition to cure. According to a preferred embodiment, the process of fiber impregnation is performed via vacuum infusion. As fibers both organic as well as inorganic fibers can be used. Preferred inorganic fibers are glass fibers and carbon fibers. Most preferred inorganic fibers are glass fibers. The invention further relates to method for increasing the dynamic fatigue of a fibre-reinforced composite article prepared by mixing the components of a multi-component system to obtain a mixture, impregnating fibres with said mixture and allowing the mixture to cure; wherein the multi-component system is as described above.

The invention is now demonstrated by means of a series of examples and comparative examples. All examples are supportive of the scope of claims. The invention, however, is not restricted to the specific embodiments as shown in the examples.

#### EXPERIMENTAL

Tensile tests were performed according to ISO 527-2.

K1c tests were performed using a Zwick Z010-I according to ISO 17281 .

Dynamic Fatigue was tested using A Zwick Rel1 100kN fatigue tester  
Force controlled tensile fatigue tests were performed using A Zwick Rel1 100kN fatigue tester equipped with a 100kN load cell using 50kN grips. Tests were

performed at ambient temperature. The frequency of the sinusoidal fatigue cycles was 5Hz. The applied ratio (R) between min. fatigue load and max. fatigue load is  $R=0.1$  (tensile-tensile fatigue).

5 The sample thickness is about 4.5mm. The geometry of the samples is curved (dogbone shaped). Total radius of the curve is 362.5mm. The width of the sample at the small part in the centre is 10mm and the width at the gripping part is 20mm. The total sample length is 240mm. The length of the clamping part on each side is 60mm. Aluminium end tabs  $L*W*T=60*20*2$ mm were glued on the clamping parts for optimal gripping. The mid sample length in between the tabs is  $\pm 120$ mm. The grip-to-  
10 grip distance at the tests is 130mm.

Prior to the fatigue tests the samples are loaded up to 0.30% strain to measure the tensile modulus, necessary to determine the fatigue loads at the requested strain-range. Strain was measured by using a MultiXtense Extensometer with  $l_0 = 50$ mm.

15 Force controlled tensile fatigue tests till break with a frequency of 5Hz at 25°C were performed. The number of fatigue cycles up to fracture of the samples was measured.

Dynamic Mechanical Analysis was performed according to ASTM D5026 using a Rheometrics RSA-III employing a 1Hz frequency over a temperature  
20 range from -130°C-250°C with a heating ramp of 5°C/min using 0.2 mm thick samples

#### Laminates and neat resin casting

Laminates were prepared using vacuum infusion. Employed glass fiber package consisted of 4 layers of Combi 1250 E-glass (Devoid: L 1200/G50F-E07-  
25 A), which were stacked in mirror image (UD facing to the middle). This package is covered on both sides with one layer Biax 806 +/-45° E-glass (DB 810-E05-A). On top of the glass fiber package, peel-ply and a bleeder foil are employed to facilitate demoulding and resin transport. Infusion was performed along the fiber direction. Initial applied vacuum was 90%, which was reduced to 60 % (400 mbar) once the pack was  
30 filled and maintained at this vacuum for 25 min before the inlet was closed and the laminate was allowed to cure. After curing overnight at room temperature the laminates were post-cured for 15 hrs at 80°C. The resulting laminates had a glass content around 72 wt%.

4 mm thick neat resin castings were prepared by casting the resin  
35 formulations between two hardened borosilicate glass plates that are separated by a U-

shaped 4mm EPDM rubber. After curing overnight at room temperature, the castings were post-cured 15 hrs at 80°C.

#### Resin synthesis

##### 5 Resin 1

866.5 g of tetrapropoxylated bisphenol A (BPA(PO)<sub>4</sub>), 113.1 g of fumaric acid (FA) and 0.131 g of tempol were charged in a vessel equipped with a stirrer, reflux condenser, a temperature measurement device and inert gas inlet. The reaction mixture was heated slowly to 210°C and kept at 210°C until the acid value  
10 reached a value below 5 mgKOH/g resin. After cooling down to 200°C, 1.47 g of triphenyl ethylphosphonium bromide and 10g of propylenecarbonate were added subsequently and the reaction mixture was kept at 200°C until the acid value was below 1.5 mg KOH/g resin. Next vacuum was applied for 1 hr and the reaction mixture was cooled down to 90°C. The reaction mixture was added to a mixture of 328.43 g of  
15 styrene and 0.196 g of tempol maintaining a temperature below 80°C yielding resin 1 with a viscosity at 23°C of 684 mPa\*s, an acid value of 0.7 mg KOH/g resin and a solid content of 74wt%.

##### Comparitive resin A

20 64,6 g of dipropoxylated bisphenol A (BPA(PO)<sub>2</sub>), 534.9 g of diethoxylated bisphenol A (BPA(EO)<sub>2</sub>) and 113 g of fumaric acid (FA) were charged in a vessel equipped with a stirrer, reflux condenser, a temperature measurement device and inert gas inlet. The mixture was heated slowly to 100°C to melt all raw materials. After melting, the mixture was heated to 210°C. At 210°C the mixture was kept under  
25 reduced pressure until the acid value reached a value below 2.3 mg KOH/g resin. Then the vacuum was relieved with inert gas, and the mixture was cooled down to 150°C. The reaction mixture was added to a mixture of 328.4 g of styrene and 0.05 g of mono tert-butyl hydroquinone, 0.05 g of a copper naphthenate solution (8% Cu) and 0.104 g of 2-methylhydroquinone maintaining a temperature below 80° C, yielding resin A with  
30 a viscosity at 23°C of 556 mPa\*s, an acid value of 1.6 mg KOH/g resin and a solid content of 67.8wt%.

Example 1 and comparative experiment AExample 1

400 g of resin 1, 60.0 g of styrene, 4.88 g of N,N-Dimethyl-1-naphthylamine and 0.53 g of BYK A-555 were added to a beaker and homogenized  
5 with a stirrer. To this mixture, 70.8 g of polymeric methylene diphenyldiisocyanate (pMDI) and 9.2 g of Perkadox CH-50L (Akzo Nobel) were added. This mixture was again homogenized and subsequently degassed to eliminate entrapped air.

Comparative experiment A

10 272.7 g of resin A, 27.23 g of styrene, 3.0 g of NL64-1 OP and 0.34 g of BYK A-555 were added to a beaker and homogenized with a stirrer. To this mixture 69.0 g of polymeric methylene diphenyldiisocyanate (pMDI) and 3.0 g of Perkadox CH-50L were added. This mixture was again homogenized and subsequently degassed to eliminate entrapped air.

15 Castings and laminates were prepared of these resin formulations and the mechanical results are shown in table 1

Table 1

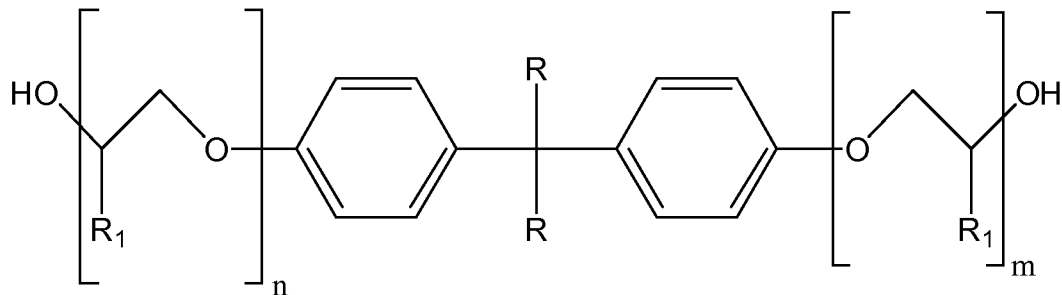
|                                   | Example 1    | Comparative A |
|-----------------------------------|--------------|---------------|
| Castings                          |              |               |
| Tensile E' (MPa)                  | 2920         | 3070          |
| Yieldstress<br>$\sigma$ max (MPa) | 70.2         | 83.8          |
| $\epsilon$ @ break (%)            | 6.7          | 7.5           |
| Tg (E'') (°C)                     | 84           | 127           |
| K1c (MPa*m <sup>0.5</sup> )       | 0.99         | 0.92          |
| Laminates                         |              |               |
| Fatigue @ strain range 0,72%      |              |               |
| # of cycles to failure            | $2.8 * 10^6$ | $1.7 * 10^5$  |
| Absolute stress (MPa)             | 261          | 307           |
| Fatigue @ absolute stress         |              |               |
| Absolute stress (MPa)             | 261          | 253           |
| # of cycles to failure            | $2.8 * 10^6$ | $6.8 * 10^5$  |
| Absolute stress (MPa)             | 291          | 293           |
| # of cycles to failure            | $2.1 * 10^6$ | $2.9 * 10^5$  |
|                                   |              |               |

The table demonstrates both cured resin systems have static mechanical properties at a level that make both resin systems suitable for construction purposes. This table also clearly demonstrates that although the static performance of the formulation according to the invention (example 1) is in fact even (slightly) lower (comparative A) regarding tensile strength, elongation @ break and yield stress, the fatigue properties of the laminate according to the invention are surprisingly significantly improved. In both cases, either using the same strain range or using the same absolute stress the life time of the laminate according to the invention is 5-10 times longer.

CLAIMS

1. Multi-component resin system comprising

(A) a hydroxyl functional unsaturated polyester resin comprising fumaric acid building blocks as unsaturated dicarboxylic acid building blocks and hydroxyl building blocks according to formula 1



in which  $n+m \geq 3$ , R is H or CH<sub>3</sub> and R<sub>1</sub> is H or CH<sub>3</sub>

and having a hydroxyl value of from 40 up to and including 150 and an acid value < 4,

(B) an ethylenically unsaturated compound copolymerizable with (A)

(C) a polyisocyanate that has on average at least 1.9 isocyanate groups, and

(D) a radical initiator;

and in which the molar ratio of [NCO]/[OH] in the resin system is from 2:1 up to and including 1:50.

2. Multi-component resin system according to claim 1, wherein  $n+m \geq 4$ .

3. Multi-component resin system according to any of claims 1-2, wherein R<sub>1</sub>=CH<sub>3</sub>.

4. Multi-component resin system according to any of claims 1-3, wherein R<sub>1</sub>=CH<sub>3</sub>

5. Multi-component resin system according to any of claims 1-4 wherein the molar ratio of [NCO]/[OH] in the resin system is from 1.5:1 up to and including 1:10 .

6. Multi-component resin system according to any of the preceding claims, wherein the polyisocyanate has an average functionality  $\geq 2$ .

7. Multi-component resin system comprising according to any of the claims wherein the composition further comprises (E) a hydroxyl functional saturated polyester resin comprising cyclohexane dicarboxylic acid building blocks as

saturated dicarboxylic acid building blocks and having a hydroxyl value of from 40 up to and including 150.

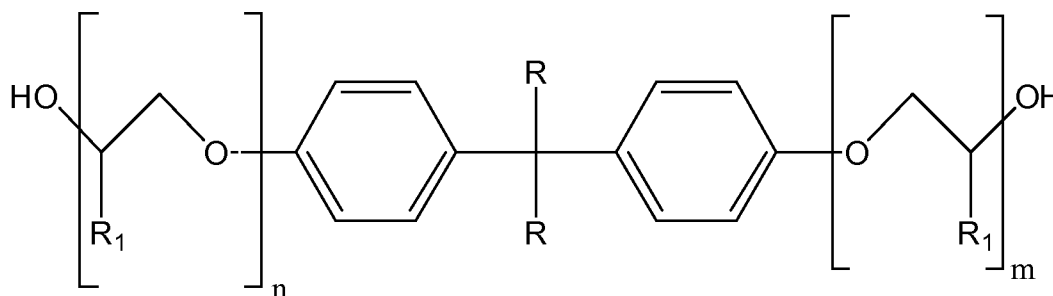
8. Multi-component resin system according to claim 7, wherein the molar amount of compound A relative to the molar amount of compound E is from 10:1 up to and including 1:10.

9. Multi-component resin system according to any of the preceding claims, wherein the resin system further comprises fibrous reinforcement.

10. Multi-component resin system according to any of claims 1-9, wherein the resin system further comprises (F) a rubber which (i) is soluble in the mixture of (A) and (B), (ii) contains functional groups of which at least a part are, upon curing of the composition, able to react with at least (A), (B) and/or (C) and (iii) is, upon curing of the composition, phase separated from the cured composition.

11. Resin composition comprising

(A) a hydroxyl functional unsaturated polyester resin comprising fumaric acid building blocks as unsaturated dicarboxylic acid building blocks and hydroxyl building blocks according to formula 1



in which  $n+m \geq 3$ , R is H or CH<sub>3</sub> and R<sub>1</sub> is H or CH<sub>3</sub>

and having a hydroxyl value of from 40 up to and including 150 and an acid value < 4 and

(B) an ethylenically unsaturated compound copolymerizable with (A).

12. Cured objects or structural parts obtained by mixing the components of the multi-component system according to any of claims 1-10.

13. Use of the multi component system according to any of claims 1-10, in any one of the areas of chemical anchoring, construction, roofing, flooring, windmill blades, containers, tanks, pipes, automotive parts or boats.

14. Use of the multi component system according to any of claims 1-10 for producing windmill blades.

15. Process for increasing the dynamic fatigue of a fiber-reinforced composite article prepared by mixing the components of a multi-component system according to any of claims 1-10 to obtain a mixture, impregnating fibers with said mixture and allowing the mixture to cure.
- 5 16. Process according to claim 15 in which the fibers are glass fibers.
17. Process according to claim 15 or 16 in which the impregnation is performed via vacuum infusion.

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2012/074512

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|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------|
| A. CLASSIFICATION OF SUBJECT MATTER<br>INV. C08G18/68 C08G63/676 C08F283/01 C08G18/76<br>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)<br>C08G C08F                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                          |                                                                                                             |
| 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)<br>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.                                                                                       |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | US 5 393 829 A (VERLEG RONALD L [NL] ET AL) 28 February 1995 (1995-02-28)<br>claims 1-23<br>examples 1-7 | 1-15                                                                                                        |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | US 2007/029042 A1 (ENDO TAKAYUKI [JP] ET AL) 8 February 2007 (2007-02-08)<br>claims 1-4<br>examples 1-9  | 1-15                                                                                                        |
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| <div style="display: flex; justify-content: space-between;"> <div> <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.         </div> <div> <input checked="" type="checkbox"/> See patent family annex.         </div> </div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                          |                                                                                                             |
| <div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div> |                                                                                                          |                                                                                                             |
| Date of the actual completion of the international search<br><br><div style="text-align: center;">6 February 2013</div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                                          | Date of mailing of the international search report<br><br><div style="text-align: center;">28/02/2013</div> |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                          | Authorized officer<br><br><div style="text-align: center;">Pouille, Delphine</div>                          |

## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2012/074512

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                                                         | Relevant to claim No. |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | <p>MAAZOUZ A ET AL: "Polyurethane and unsaturated polyester hybrid networks : Chemorheological and dielectric study for the resin transfer molding process (RTM) ", POLYMER ENGINEERING AND SCIENCE, BROOKFIELD CENTER, US, vol . 40, no. 3, 1 January 2000 (2000-01-01) , pages 690-701 , XP002671352 , ISSN: 0032-3888 cited in the application Raw Materials; page 691</p> <p>-----</p> | 1-15                  |

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Information on patent family members

International application No

PCT/EP2012/074512

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date           |
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