(12) UK Patent (19) GB (11) 2548918 (13) B

(45) Date of B Publication **15.07.2020**

(54) Title of the Invention: Anaerobically curable (meth)acrylate compositions

(51) INT CL: ***C08F 20/18*** (2006.01) ***C08K 5/14*** (2006.01) ***C08L 33/08*** (2006.01) ***C08L 33/10*** (2006.01) ***C08L 33/12*** (2006.01) ***C08L 33/14*** (2006.01) ***C09J 133/08*** (2006.01) ***C09J 133/10*** (2006.01) ***C09J 133/12*** (2006.01) ***C09J 133/14*** (2006.01)

(21) Application No:	**1605618.6**
(22) Date of Filing:	**01.04.2016**
(43) Date of A Publication	**04.10.2017**

(56) Documents Cited:

US 7728092 B1
US 6596808 B1
US 6433091 B1
US 20100179078 A1
US 20100116435 A1

(58) Field of Search:
As for published application 2548918 A viz:
INT CL **C08F, C08L, C09J**
Other: **EPODOC, WPI, GOOGLE (RTM)**
updated as appropriate

Additional Fields
INT CL **C08F, C08L, C09D, C09J**
Other: **None**

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Figure 1

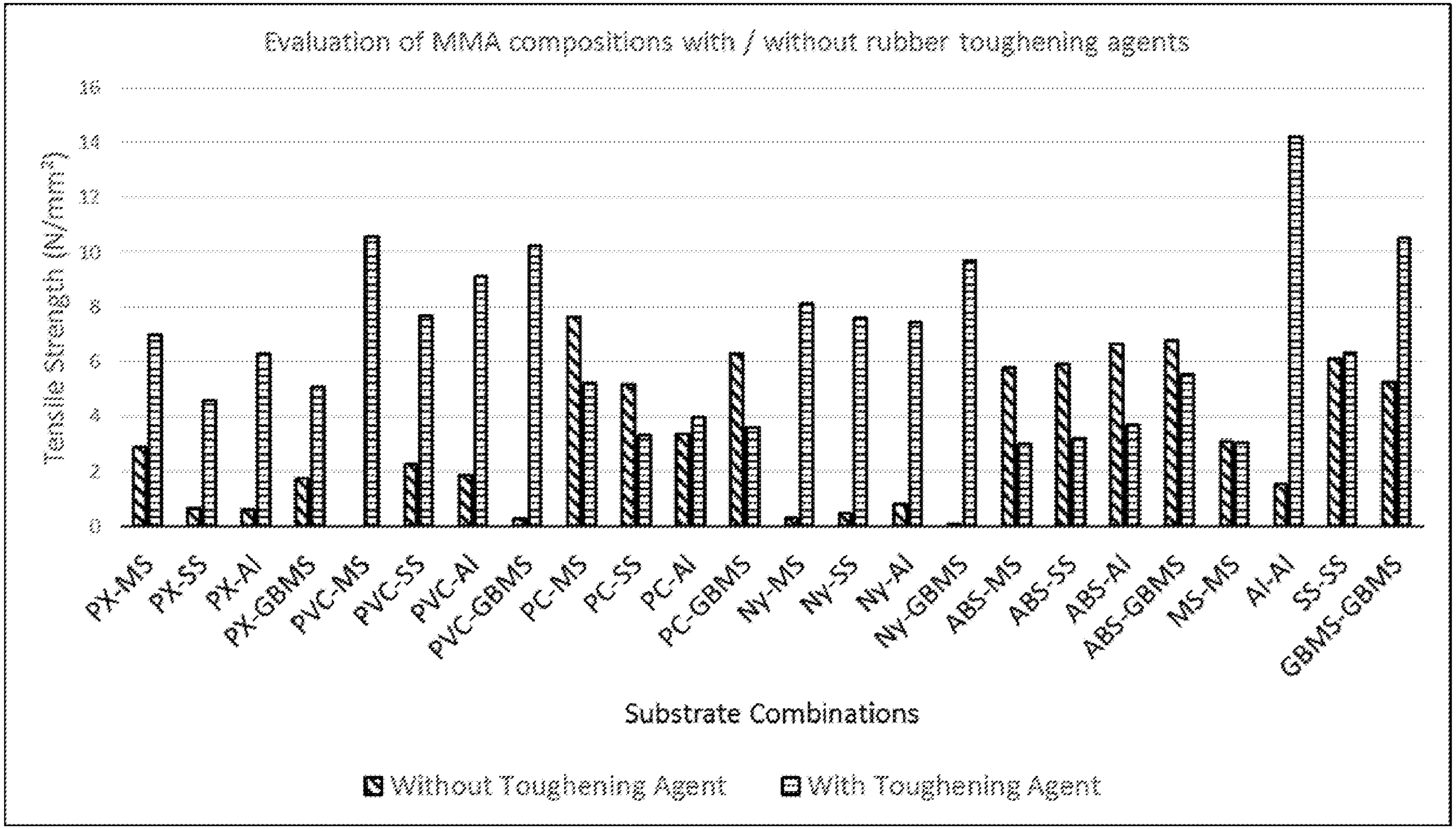
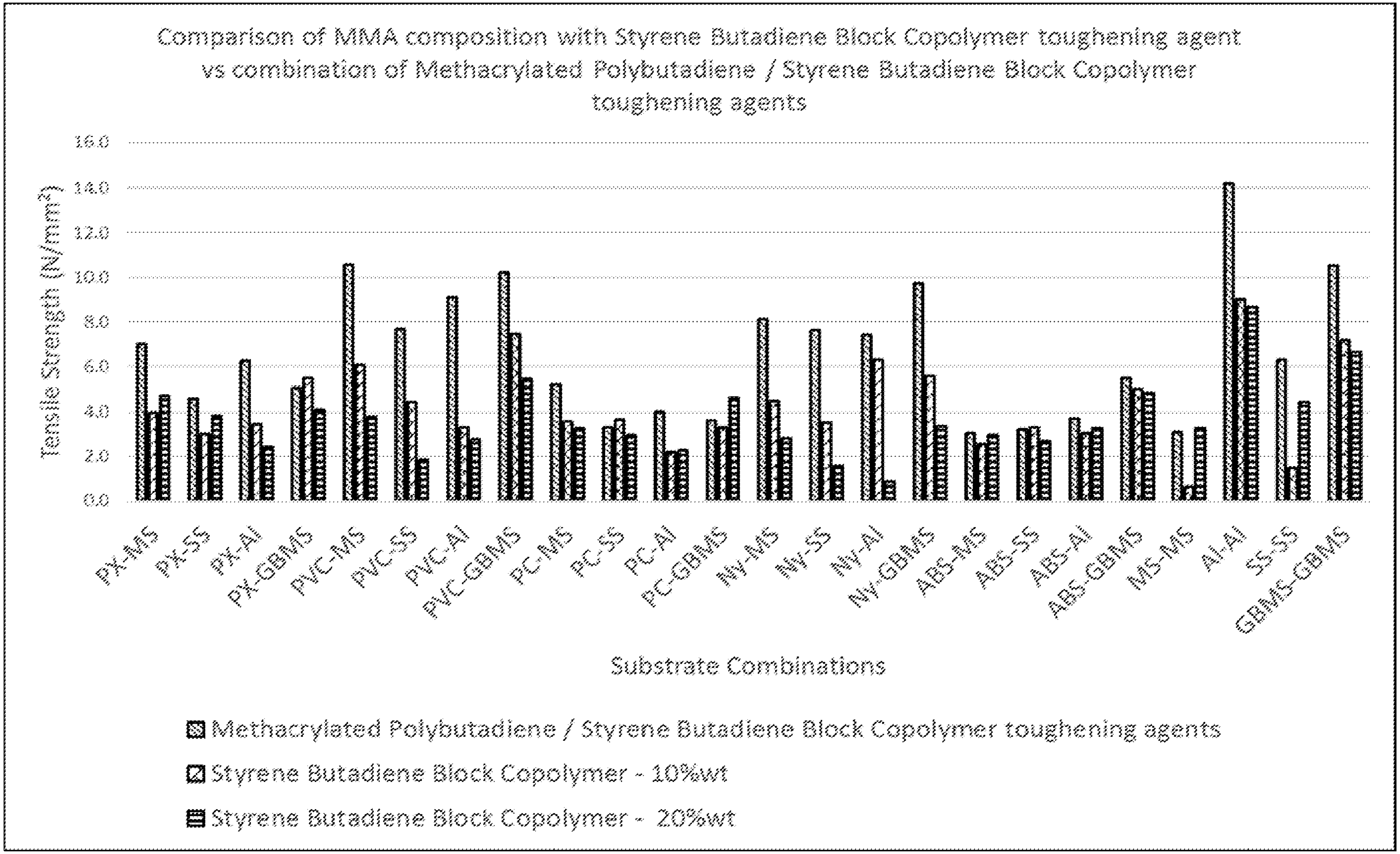

Evaluation of MMA compositions with / without rubber toughening agents
Tensile Strength (N/mm²)
0
2
4
6
8
10
12
14
16
PX-MS
PX-SS
PX-Al
PX-GBMS
PVC-MS
PVC-SS
PVC-Al
PVC-GBMS
PC-MS
PC-SS
PC-Al
PC-GBMS
Ny-MS
Ny-SS
Ny-Al
Ny-GBMS
ABS-MS
ABS-SS
ABS-Al
ABS-GBMS
MS-MS
Al-Al
SS-SS
GBMS-GBMS
Substrate Combinations
▨ Without Toughening Agent
▦ With Toughening Agent

Figure 2


Comparison of MMA composition with Styrene Butadiene Block Copolymer toughening agent vs combination of Methacrylated Polybutadiene / Styrene Butadiene Block Copolymer toughening agents
Tensile Strength (N/mm^2)
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
PX-MS
PX-SS
PX-Al
PX-GBMS
PVC-MS
PVC-SS
PVC-Al
PVC-GBMS
PC-MS
PC-SS
PC-Al
PC-GBMS
Ny-MS
Ny-SS
Ny-Al
Ny-GBMS
ABS-MS
ABS-SS
ABS-Al
ABS-GBMS
MS-MS
Al-Al
SS-SS
GBMS-GBMS
Substrate Combinations
▨ Methacrylated Polybutadiene / Styrene Butadiene Block Copolymer toughening agents
▨ Styrene Butadiene Block Copolymer - 10%wt
▤ Styrene Butadiene Block Copolymer - 20%wt

23 05 16

Figure 3

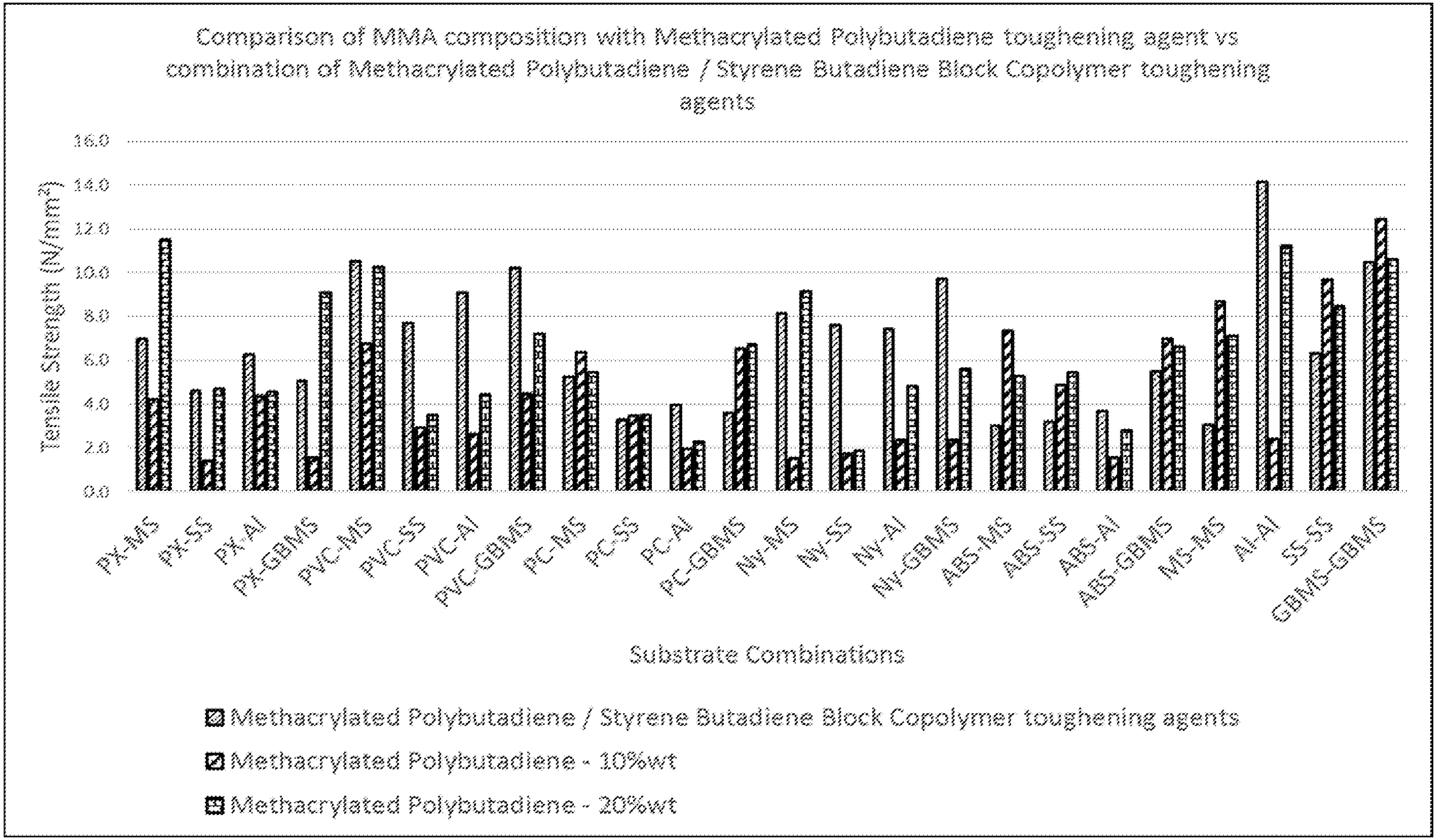
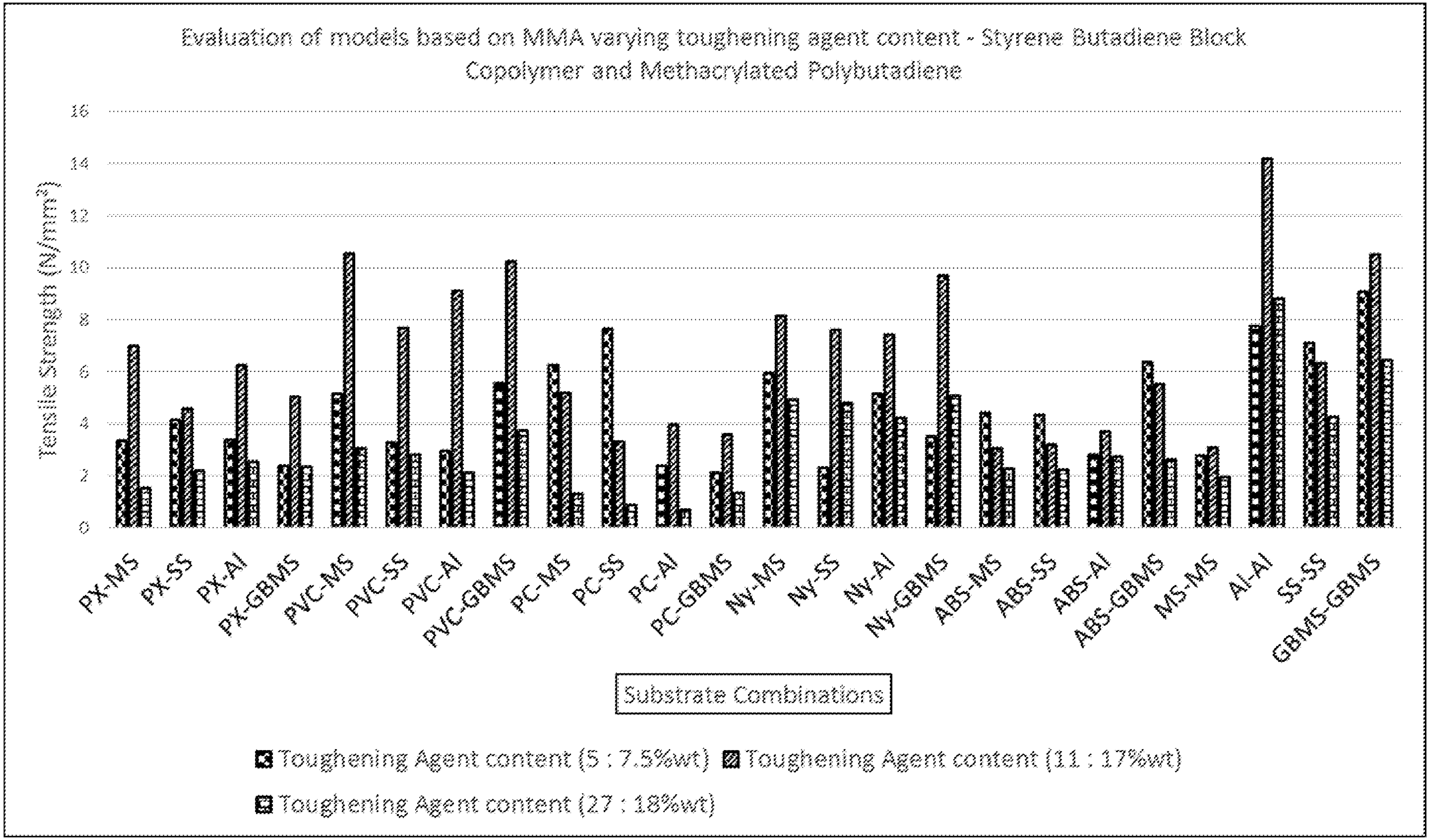


Figure 4


Evaluation of models based on MMA varying toughening agent content - Styrene Butadiene Block Copolymer and Methacrylated Polybutadiene
Tensile Strength (N/mm²)
16
14
12
10
8
6
4
2
0
PX-MS
PX-SS
PX-Al
PX-GBMS
PVC-MS
PVC-SS
PVC-Al
PVC-GBMS
PC-MS
PC-SS
PC-Al
PC-GBMS
Ny-MS
Ny-SS
Ny-Al
Ny-GBMS
ABS-MS
ABS-SS
ABS-Al
ABS-GBMS
MS-MS
Al-Al
SS-SS
GBMS-GBMS
Substrate Combinations
Toughening Agent content (5 : 7.5%wt)
Toughening Agent content (11 : 17%wt)
Toughening Agent content (27 : 18%wt)

23 05 16

Figure 5

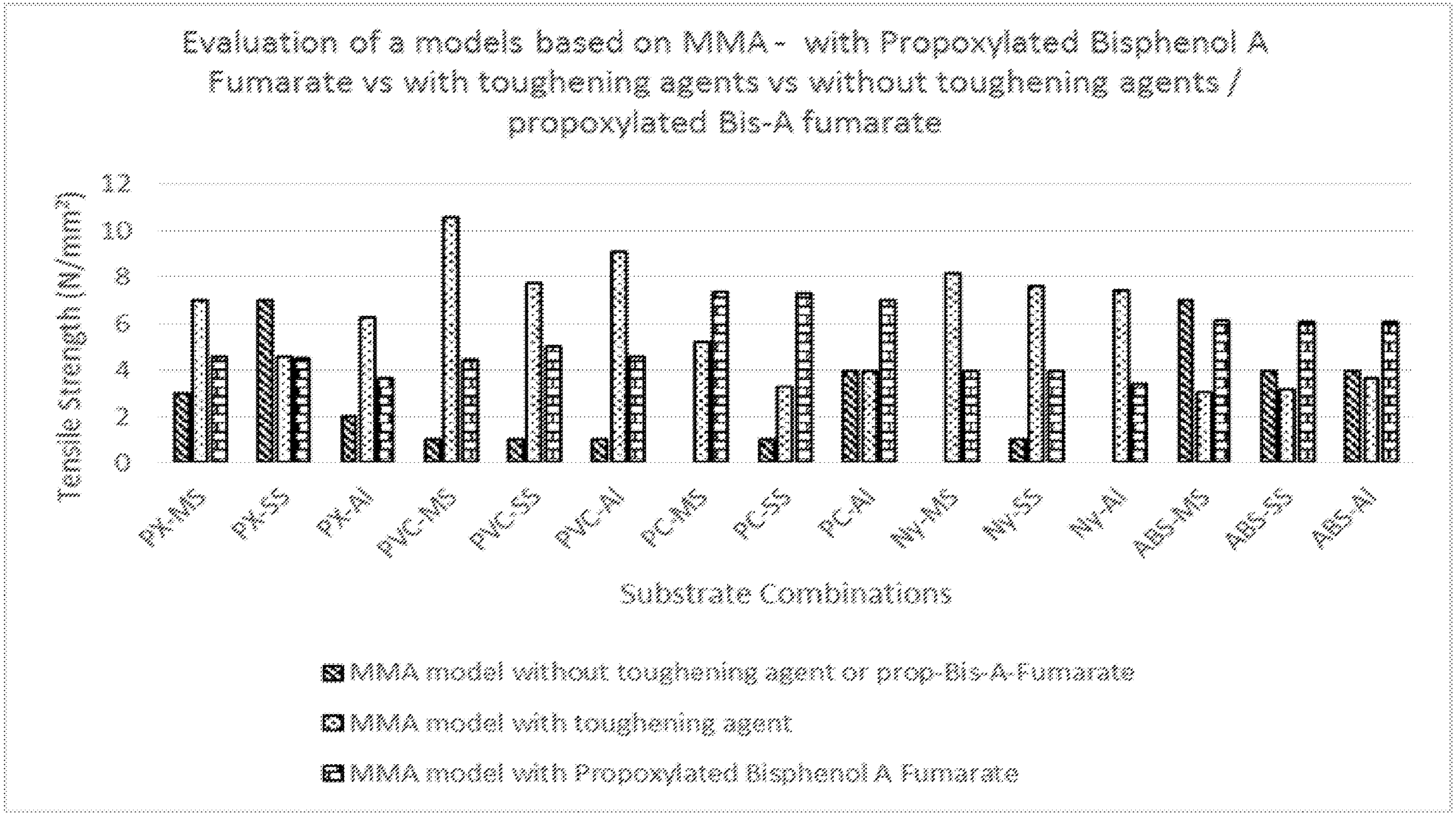
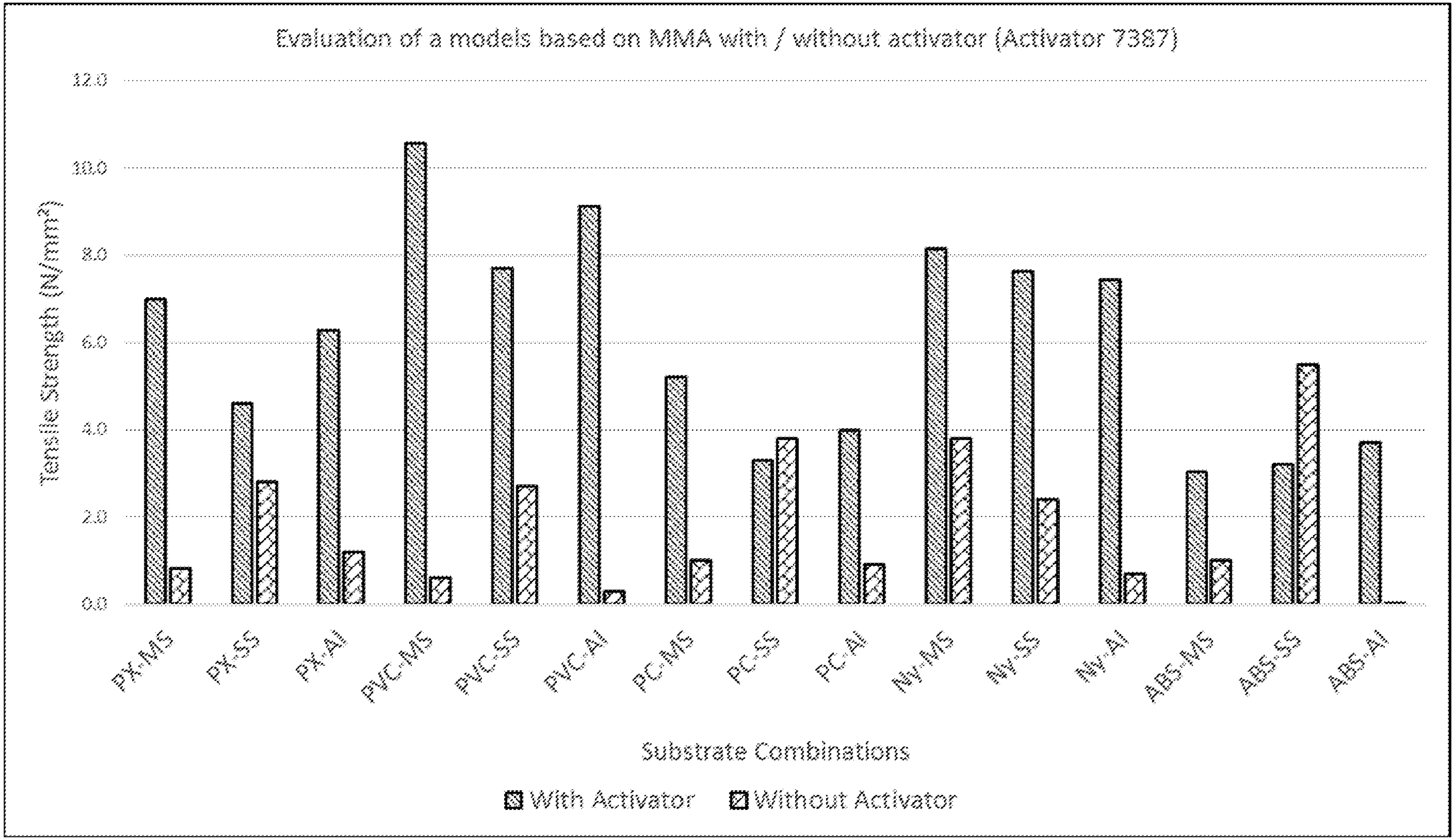


Figure 6


Evaluation of a models based on MMA with / without activator (Activator 7387)
Tensile Strength (N/mm²)
12.0
10.0
8.0
6.0
4.0
2.0
0.0
PX-MS
PX-SS
PX-Al
PVC-MS
PVC-SS
PVC-Al
PC-MS
PC-SS
PC-Al
Ny-MS
Ny-SS
Ny-Al
ABS-MS
ABS-SS
ABS-Al
Substrate Combinations
▨ With Activator
▨ Without Activator

Title

Anaerobically curable (meth)acrylate compositions

Background

Field

[0001] The present invention relates to anaerobically curable compositions, methods of bonding using anaerobically curable compositions, assemblies bonded using anaerobically curable compositions and cure products of anaerobically curable compositions.

Brief Description of Related Technology

[0002] Anaerobically curable compositions generally are well known. See e.g. R.D. Rich, "Anaerobic Adhesives" in Handbook of Adhesive Technology, 29, 467-79, A. Pizzi and K.L. Mittal, eds., Marcel Dekker, Inc., New York (1994), and references cited therein. Their uses are legion and new applications continue to be developed.

[0003] Anaerobic adhesive systems are those which are stable in the presence of oxygen, but which polymerize in the absence of oxygen. Polymerization is initiated by the presence of free radicals, often generated from peroxy compounds. Anaerobic adhesive compositions are well known for their ability to remain in a liquid, unpolymerized state in the presence of oxygen and to cure to a solid state upon the exclusion of oxygen. As a result of their ability to cure in a substantially oxygen-free environment, anaerobically curable compositions are widely used as adhesives, sealants, and for bonding materials with closely mated surfaces.

[0004] Oftentimes anaerobic adhesive systems comprise resin monomers terminated with polymerizable acrylate ester such as methacrylate, ethylacrylate and chloroacrylate esters [e.g., polyethylene glycol dimethacrylate and urethane-acrylates (e.g., U.S. Patent No. 3,425,988 (Gorman)] derived according to known urethane chemistry. Other ingredients typically present in anaerobically curable adhesive compositions include initiators, such as an organic hydroperoxide for example cumene hydroperoxide, tertiary butyl hydroperoxide and the like, accelerators to increase the rate at which the composition cures, and stabilizers such as quinone or hydroquinone, which are included to help prevent premature polymerization of the adhesive due to decomposition of peroxy compounds.

[0005] Desirable cure-inducing compositions to induce and accelerate anaerobic cure may include one or more of saccharin, toluidines, such as N,N-diethyl-p-toluidine ("DE-p-T") and N,N-dimethyl-o-toluidine ("DM-o-T"), and acetyl phenyl hydrazine ("APH") with maleic acid. See e.g. U.S. Patent Nos. 3,218,305 (Krieble), 4,180,640 (Melody), 4,287,330 (Rich) and 4,321,349 (Rich).

[0006] Saccharin and APH are used as standard cure accelerator components in anaerobic adhesive cure systems. Indeed, many of the LOCTITE®-brand anaerobic adhesive products currently available from Henkel Corporation use either saccharin alone or both saccharin and APH.

[0007] Anaerobically curable adhesive compositions also commonly include chelators such as ethylenediamine tetraacetic acid ("EDTA") which are employed to sequester metal ions.

[0008] For some applications, bonding using an anaerobic composition is troublesome. For example, conventional anaerobically curable compositions are ineffective for bonding some substrates, such as passive ones like plastics and some alloys. For such applications two-part compositions may be formulated. Formulating the compositions as two-part compositions allows a greater degree of freedom in selection of components. For example, it may be possible to place a cure initiator in one part of a two-part composition. When the two parts of the composition are brought together under suitable anaerobic conditions the composition cures.

[0009] It is also possible to use an activator for substrates that are difficult to bond utilising anaerobically curable compositions. Where two substrates are to be bonded together, an activator may be applied to at least one of the substrates. So for example, when bonding two substrates together, where at least one of those substrates is a difficult to bond substrate, an activator may be applied to either substrate, though desirably it is applied to the difficult to bond substrate. Where there is more than one substrate, and for example where there is more than one difficult to bond substrate, it is desirable that the activator is applied to each substrate.

[0010] It is desirable to provide alternative systems for bonding and methods of bonding utilising anaerobically curable compositions.

Summary

[0011] In one aspect the present invention provides an anaerobically curable composition as set out in the claims. Preferred embodiments are described in the dependent claims.

[0012] The present disclosure provides an anaerobically curable composition comprising:

(a) at least one (meth)acrylate component;

(b) an anaerobic cure inducing component; and

(c) a toughening agent selected comprising a combination of a styrene butadiene block copolymer and methacrylate functionalised polybutadiene wherein the methacrylate functionalised polybutadiene is present in an amount of from 8 to 16 wt% based on the total weight of the composition, and wherein the styrene butadiene is present in an amount of from 14 to 18 wt% based on the total weight of the composition, and wherein the weight ratio of the methacrylate functionalised polybutadiene to the styrene butadiene block copolymer is about 2:3.

[0013] Advantageously, compositions of the present invention have applications in metal-metal bonding and metal-plastic bonding, for example as threadlocking compositions, for securing for example nuts and bolts. The product cures when confined in the absence of air between close fitting surfaces such as close fitting metal surfaces. It protects threads from rust and corrosion and prevents loosening from shock and vibration.

[0014] The styrene butadiene block copolymer and methacrylate functionalised polybutadiene may be added together, for example mixed together and then added, or independently added. It does not matter in what order they are added to form a composition of the invention, for example whether or not they are added at the same time.

[0015] The toughening agent is a combination of a styrene butadiene block copolymer and methacrylate functionalised polybutadiene. Advantageously, the presence of the toughening agent ensures the compositions of the invention have excellent tensile strength performance on a variety of substrates. The compositions of the invention are particularly effective at bonding passive substrates, for example bonding passive substrates to metallic substrates.

[0016] Suitably, when the toughening agent is a combination of a styrene butadiene block copolymer and methacrylate functionalised polybutadiene, the ratio by weight of the methacrylate functionalised polybutadiene to the styrene butadiene block copolymer is 2:3. When the ratio is about 2:3, enhanced tensile strength performance was observed, particularly for bonding polymethyl methacrylate, polyvinyl chloride and polyamide substrates to steel substrates. Furthermore, when the ratio is about 2:3, the compositions of the invention proved particularly effective at bonding aluminium substrates.

[0017] The methacrylate functionalised polybutadiene may be selected from the group consisting of methacrylate (vinyl) terminated polybutadiene and butadiene-acrylonitrile polymer.

[0018] Suitably, the methacrylate functionalised polybutadiene has a number average molecular weight of from 3,000 to 5,500. Optionally, the methacrylate functionalised polybutadiene has a number average molecular weight of about 4,500.

[0019] Suitably, the methacrylate functionalised polybutadiene is methacrylate (vinyl) terminated polybutadiene. It may have a number average molecular weight of from 3,000 to 5,500, for example the number average molecular weight may be 4,500, such as 4,450. Advantageously, compositions of the invention comprising methacrylate (vinyl) terminated polybutadiene with a number average molecular weight of about 4,500 proved particularly effective at bonding a wide variety of substrates, particularly bonding passive substrates to metallic substrates.

[0020] Suitably, the anaerobically curable composition of the invention further comprises a transition metal.

[0021] The transition metal may be selected from copper, iron, vanadium, cobalt, chromium, silver and manganese, or combinations thereof.

[0022] Suitably, the transition metal is in salt form. Optionally the salt is selected from cobalt (II) naphthenate, copper carbonate, copper (II) acetylacetonate, silver nitrate, vanadium nitrate, vanadium (III) acetylacetonate and combinations thereof.

[0023] Another aspect of the present invention provides for use of an anaerobically curable composition as set out in the claims.

[0024] The present disclosure provides for use of an anaerobically curable composition as set out in the claims.

[0025] Suitably, the first substrate may be a passive substrate, for example a plastic substrate.

[0026] The plastic substrate may optionally be selected from: acrylonitrile butadiene styrene (“ABS”), polycarbonate (“PC”), polycarbonate/acrylonitrile butadiene styrene (“PCABS“), polyarylamides, polyamides such as nylon, including nylon 6’6 ((“Ny”), (poly[imino(1,6-dioxohexamethylene) iminohexamethylene])), acrylic plastic, polyvinyl chloride (“PVC”) and polymethyl methacrylate (“PMMA”).

[0027] The second substrate may be metallic. For example, the second substrate may be steel, including mild steel and stainless steel, brass including clock brass, bronze, or zinc, aluminium, iron, copper, beryllium, cobalt, manganese, nickel, cadmium, gold, silver or alloys thereof. Suitably, the second substrate may be an active substrate, containing trace amounts of a transition metal.

[0028] The compositions of the invention proved particularly effective at bonding PMMA to each of mild steel, stainless steel and aluminium substrates. Advantageously, said compositions also demonstrated excellent tensile strengths for

PVC bonding to each of mild steel, stainless steel and aluminium. Similarly, excellent tensile strengths were observed when the compositions of the invention were employed to bond polyamide 6'6 (i.e. nylon 6'6) substrates to each of mild steel, stainless steel and aluminium.

[0029] Compositions comprising propoxylated bisphenol A fumarate polyester in addition to compositions comprising a combination of a styrene butadiene block copolymer and methacrylate functionalised polybutadiene, proved particularly effective at bonding polycarbonate substrates to each of stainless steel and aluminium substrates.

[0030] A further aspect of the present invention provides a method of bonding together two substrates as set out in the claims.

[0031] A further aspect of the present disclosure provides a method of bonding together two substrates comprising the steps of:

applying an anaerobically curable composition comprising:

(a) at least one (meth)acrylate component;

(b) an anaerobic cure inducing component; and

(c) a toughening agent comprising a combination of a styrene butadiene block copolymer and methacrylate functionalised polybutadiene wherein the methacrylate functionalised polybutadiene is present in an amount of from 8 to 16 wt% based on the total weight of the composition, and wherein the styrene butadiene is present in an amount of from 14 to 18 wt% based on the total weight of the composition, and wherein the weight ratio of the methacrylate functionalised polybutadiene to the styrene butadiene block copolymer is about 2:3, to at least one of the substrates and mating together the substrates for a time sufficient to permit an adhesive bond to form from the (meth)acrylate composition between the mated substrates.

[0032] Advantageously, this method proved particularly effective at bonding a wide variety of substrates, for example bonding passive substrates such as plastic substrates to metallic substrates.

[0033] A still further aspect of the present invention provides an assembly comprising two substrates bonded together by a cure product of an anaerobically curable composition, as set out in the claims.

[0034] The present disclosure also provides an assembly comprising two substrates bonded together by the cure product of an anaerobically curable composition comprising:

(a) at least one (meth)acrylate component;

(b) an anaerobic cure inducing component; and

(c) a toughening agent comprising a combination of a styrene butadiene block copolymer and methacrylate functionalised polybutadiene wherein the methacrylate functionalised polybutadiene is present in an amount of from 8 to 16 wt% based on the total weight of the composition, and wherein the styrene butadiene is present in an amount of from 14 to 18 wt% based on the total weight of the composition, and wherein the weight ratio of the methacrylate functionalised polybutadiene to the styrene butadiene block copolymer is about 2:3.

[0035] Another aspect of the present invention provides a method of anaerobically curing a (meth)acrylate composition as set out in the claims.

[0036] The present disclosure also provides a method of anaerobically curing a (meth)acrylate composition comprising the steps of:

providing a (meth)acrylate composition comprising:-

(a) a (meth)acrylate component;

(b) a cure inducing component; and

(c) a toughening agent comprising a combination of a styrene butadiene block copolymer and methacrylate functionalised polybutadiene wherein the methacrylate functionalised polybutadiene is present in an amount of from 8 to 16 wt% based on the total weight of the composition, and wherein the styrene butadiene is present in an amount of from 14 to 18 wt% based on the total weight of the composition, and wherein the weight ratio of the methacrylate functionalised polybutadiene to the styrene butadiene block copolymer is about 2:3; and exposing the (meth)acrylate composition to an anaerobic environment for a time sufficient to cure the composition.

[0037] Furthermore, the present invention also provides a process for preparing a reaction product from a curable composition as set out in the claims.

[0038] The present disclosure provides a process for preparing a reaction product from a curable composition, comprising the steps of:

applying an activator composition to desired substrate surface;

applying to that surface a composition comprising:

(a) a (meth)acrylate component;

(b) a cure inducing component; and

(c) a toughening agent comprising a combination of a styrene butadiene block copolymer and methacrylate functionalised polybutadiene wherein the methacrylate functionalised polybutadiene is present in an amount of from 8 to 16 wt% based on the total weight of the composition, and wherein the styrene butadiene is present in an amount of from 14 to 18 wt% based on the total weight of the composition, and wherein the weight ratio of the methacrylate functionalised polybutadiene to the styrene butadiene block copolymer is about 2:3;

mating a second surface to that substrate surface to form an assembly; and

exposing the (meth)acrylate composition to an anaerobic environment for a time sufficient to cure the composition.

Brief Description of the Drawings

[0039] Embodiments of the invention will be described, by way of example only, with reference to the accompanying drawings:

[0040] Figure 1: Evaluation of the tensile strength performance on various substrates of (meth)acrylate compositions with and without rubber toughening agent. The rubber toughening agent is a combination of a styrene butadiene block copolymer and methacrylate functionalised polybutadiene.

[0041] Figure 2: Evaluation of the tensile strength performance of (meth)acrylate compositions comprising a rubber toughening agent comprising a combination of a styrene butadiene block copolymer and methacrylate functionalised polybutadiene versus (meth)acrylate compositions comprising varying levels of styrene butadiene block copolymer on various passive substrates.

[0042] Figure 3: Evaluation of the tensile strength performance of (meth)acrylate compositions comprising a rubber toughening agent comprising a combination of a styrene butadiene block copolymer and methacrylate functionalised polybutadiene versus (meth)acrylate compositions comprising varying levels of methacrylate functionalised polybutadiene on various passive substrates.

[0043] Figure 4: Evaluation of the tensile strength performance of (meth)acrylate compositions comprising a rubber toughening agent comprising a combination of a styrene butadiene block copolymer and methacrylate functionalised polybutadiene on various substrates wherein the ratio of the styrene butadiene block copolymer and the methacrylate functionalised polybutadiene is varied by weight.

[0044] Figure 5: Evaluation of the tensile strength performance on various substrates of (meth)acrylate compositions with propoxylated bisphenol A fumarate polyester toughening agent, (meth)acrylate compositions comprising a combination of a styrene butadiene block copolymer and methacrylate functionalised polybutadiene, and (meth)acrylate compositions without a toughening agent.

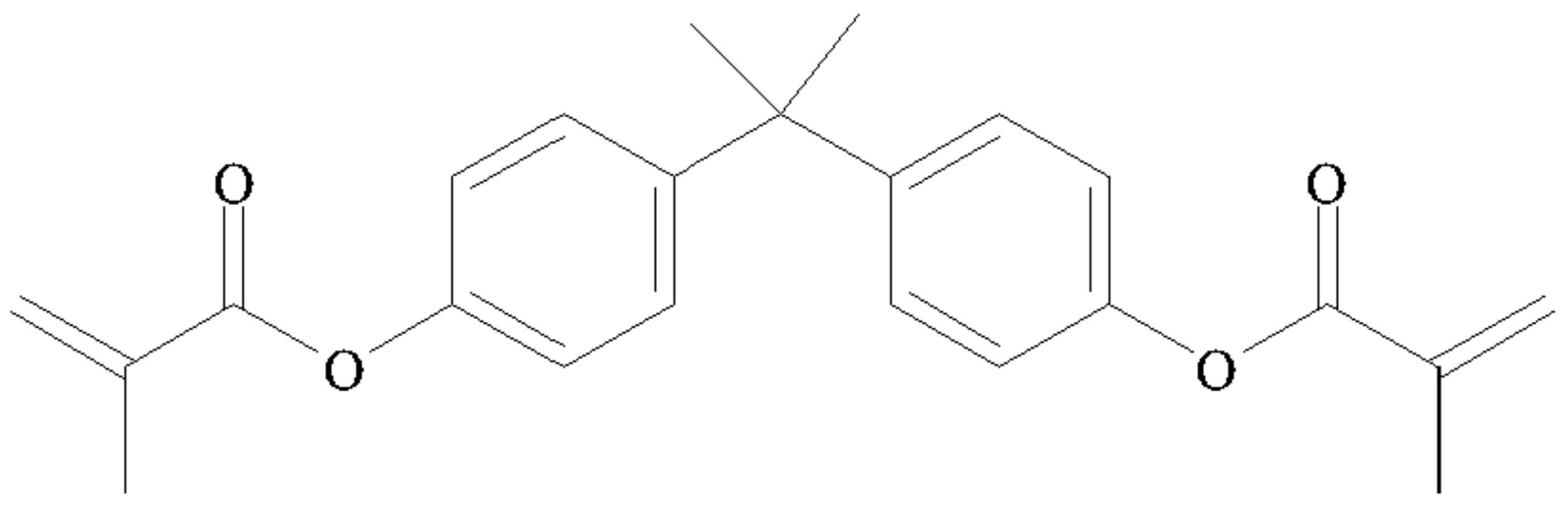
[0045] Figure 6: Evaluation of the tensile strength performance on various substrates of (meth)acrylate compositions with and without the application of an activator.

Detailed Description

[0046] The (meth)acrylate component may be a (meth)acrylate monomer having the formula: $H_2C{=}CGCO_2R^8$, where G may be hydrogen, halogen or alkyl groups having from 1 to about 4 carbon atoms, and R^8 may be selected from alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkaryl, aralkyl or aryl groups having from 1 to about 16 carbon atoms, any of which may be optionally substituted or interrupted as the case may be with silane, silicon, oxygen, halogen, carbonyl, hydroxyl, ester, carboxylic acid, urea, urethane, polyurethane, carbonate, amine, amide, sulfur, sulfonate, and sulfone.

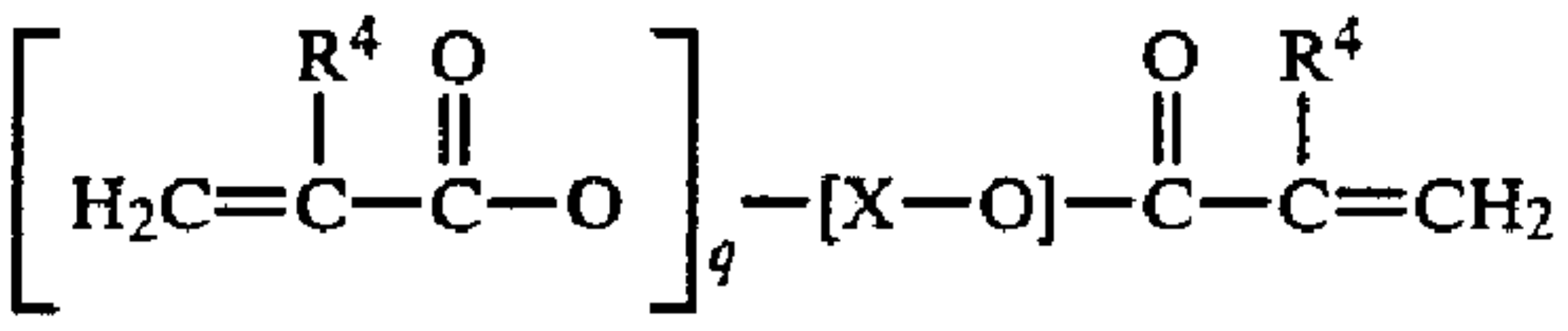
[0047] Additional (meth)acrylate monomers suitable for use herein include polyfunctional (meth)acrylate monomers, such as, but not limited to, di-or tri-functional (meth)acrylates like polyethylene glycol di(meth)acrylates, tetrahydrofuran (meth)acrylates and di(meth)acrylates, hydroxypropyl (meth)acrylate (“HPMA”), hexanediol di(meth)acrylate, trimethylol propane tri(meth)acrylate (“TMPTMA”), diethylene glycol dimethacrylate, triethylene glycol dimethacrylate (“TRIEGMA”), tetraethylene glycol dimethacrylate, dipropylene glycol dimethacrylate, di-(pentamethylene glycol) dimethacrylate, tetraethylene diglycol diacrylate, diglycerol tetramethacrylate, tetramethylene dimethacrylate, ethylene dimethacrylate, neopentyl glycol diacrylate, trimethylol propane triacrylate and bisphenol-A mono and di(meth)acrylates, such as ethoxylated bisphenol-A (meth)acrylate ("EBIPMA"), and bisphenol-F mono and di(meth)acrylates, such as ethoxylated bisphenol-F (meth)acrylate.

[0048] For example the anaerobically curable component may include Bisphenol A dimethacrylate:



[0049] Still other (meth)acrylate monomers that may be used herein include silicone (meth)acrylate moieties ("SiMA"), such as those taught by and claimed in U.S. Patent No. 5,605,999 (Chu), the disclosure of which is hereby expressly incorporated herein by reference.

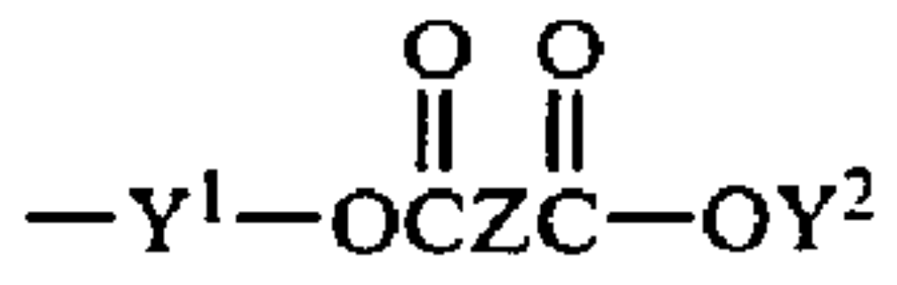
[0050] Other suitable monomers include polyacrylate esters represented by the formula



$$\left[H_2C=\overset{R^4}{\underset{}{C}}-\overset{O}{\overset{\|}{C}}-O\right]_q-[X-O]-\overset{O}{\overset{\|}{C}}-\overset{R^4}{C}=CH_2$$

where R^4 is a radical selected from hydrogen, halogen or alkyl of from 1 to about 4 carbon atoms; q is an integer equal to at least 1, and suitably equal to from 1 to about 4; and X is an organic radical containing at least two carbon atoms and having a total bonding capacity of q plus 1. With regard to the upper limit for the number of carbon atoms in X, workable monomers exist at essentially any value. As a practical matter, however, a general upper limit is about 50 carbon atoms, such as desirably about 30, and desirably about 20.

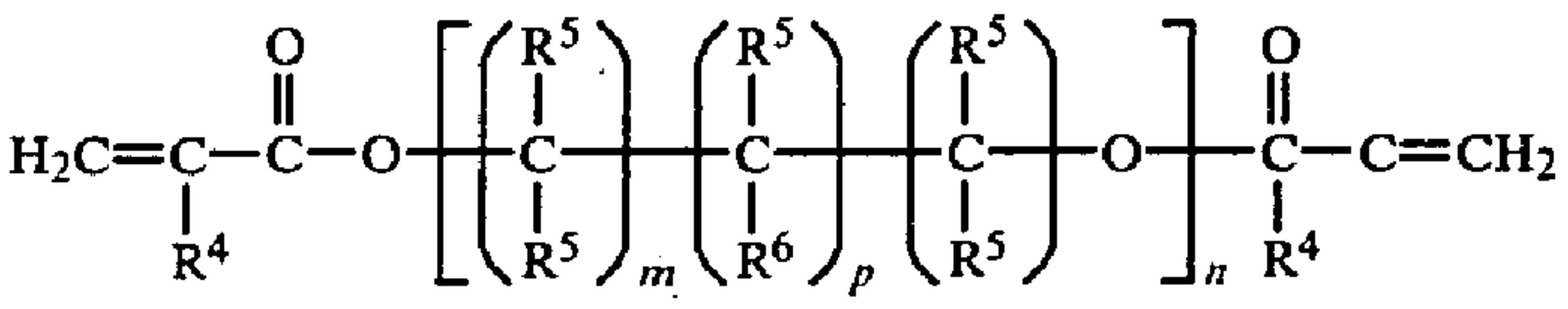
[0051] For example, X can be an organic radical of the formula:



$$-Y^1-O\overset{O}{\overset{\|}{C}}Z\overset{O}{\overset{\|}{C}}-OY^2$$

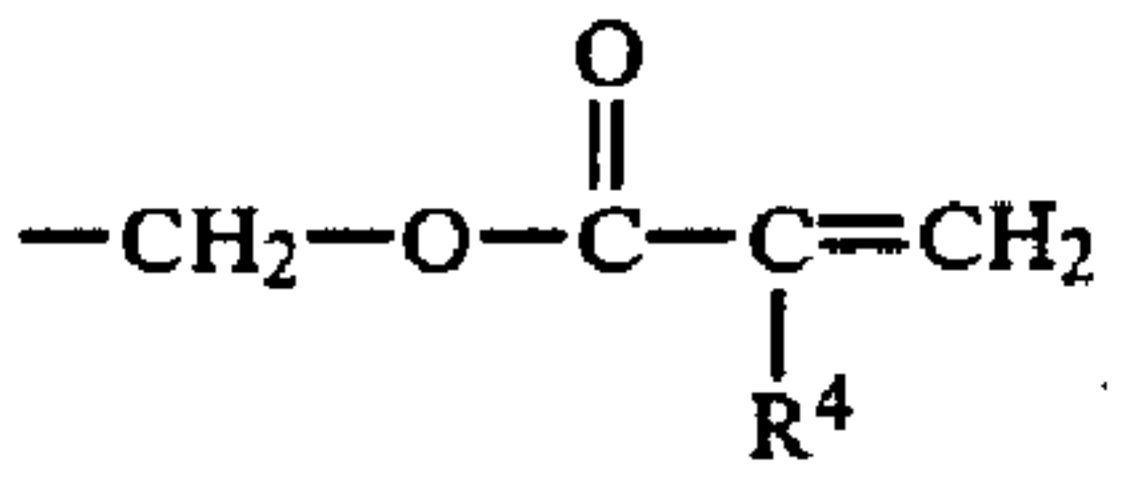
where each of Y^1 and Y^2 is an organic radical, such as a hydrocarbon group, containing at least 2 carbon atoms, and desirably from 2 to about 10 carbon atoms, and Z is an organic radical, suitably a hydrocarbon group, containing at least 1 carbon atom, and suitably from 2 to about 10 carbon atoms. Other classes of useful monomers are the reaction products of di- or tri-alkylolamines (e.g., ethanolamines or propanolamines) with acrylic acids, such as are disclosed in French Pat. No. 1,581,361.

[0052] Oligomers with (meth)acrylate functionality may also be used. Examples of useful (meth)acrylate-functionalized oligomers include those having the following general formula:



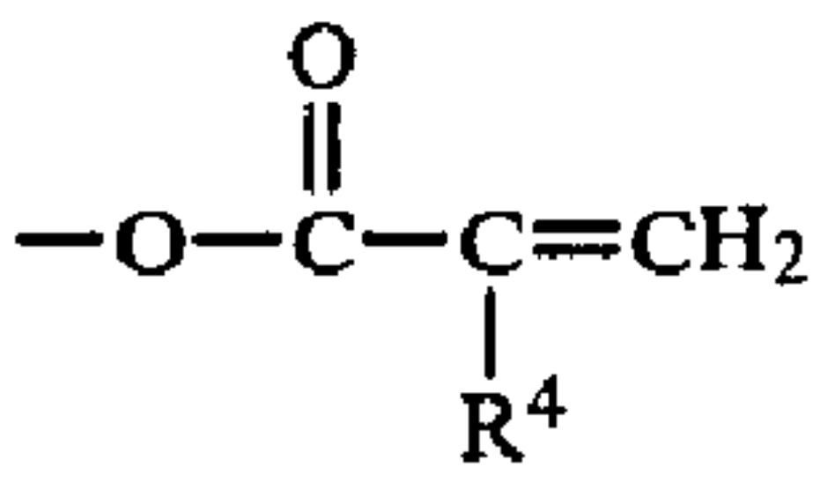
$$H_2C=\underset{R^4}{C}-\overset{O}{\overset{\|}{C}}-O-\left[\left(\underset{R^5}{\overset{R^5}{C}}\right)_m\left(\underset{R^6}{\overset{R^5}{C}}\right)_p\left(\underset{R^5}{\overset{R^5}{C}}\right)-O\right]_n-\overset{O}{\overset{\|}{C}}-\underset{R^4}{C}=CH_2$$

where R^5 represents a radical selected from hydrogen, alkyl of from 1 to about 4 carbon atoms, hydroxy alkyl of from 1 to about 4 carbon atoms, or



$$-CH_2-O-\overset{O}{\overset{\|}{C}}-\underset{R^4}{C}=CH_2$$

where R^4 is a radical selected from hydrogen, halogen, or alkyl of from 1 to about 4 carbon atoms; R^6 is a radical selected from hydrogen, hydroxyl, or



$$-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{R^4}{|}}{C}=CH_2$$

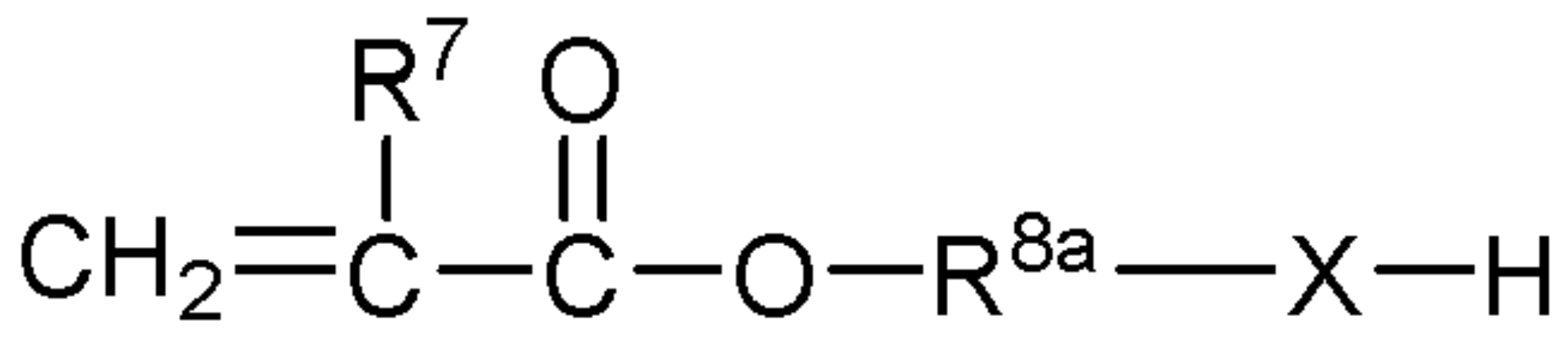
m is an integer equal to at least 1, e.g., from 1 to about 15 or higher, and desirably from 1 to about 8; n is an integer equal to at least 1, e.g., 1 to about 40 or more, and desirably between about 2 and about 10; and p is 0 or 1.

[0053] Typical examples of acrylic ester oligomers corresponding to the above general formula include di-, tri- and tetraethyleneglycol dimethacrylate; di(pentamethyleneglycol)dimethacrylate; tetraethyleneglycol diacrylate; tetraethyleneglycol di(chloroacrylate); diglycerol diacrylate; diglycerol tetramethacrylate; butyleneglycol dimethacrylate; neopentylglycol diacrylate; and trimethylolpropane triacrylate.

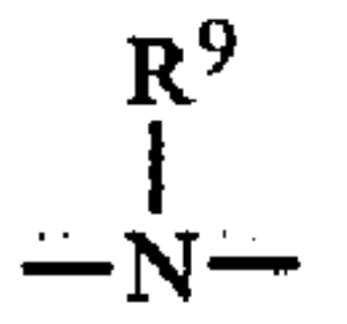
[0054] While di- and other polyacrylate esters, and particularly the polyacrylate esters described in the preceding paragraphs, can be desirable, monofunctional acrylate esters (esters containing one acrylate group) also may be used. When dealing with monofunctional acrylate esters, it is highly preferable to use an ester which has a relatively polar alcoholic moiety. Such materials are less volatile than low molecular weight alkyl esters and, more important, the polar group tends to provide intermolecular attraction during and after cure, thus producing more desirable cure properties, as well as a more durable sealant or adhesive. Most suitably, the polar group is selected from labile hydrogen, heterocyclic ring, hydroxy, amino, cyano, and halo polar groups. Typical examples of compounds within this category are cyclohexylmethacrylate, tetrahydrofurfuryl methacrylate, hydroxyethyl acrylate, hydroxypropyl methacrylate, t-butylaminoethyl methacrylate, cyanoethylacrylate, and chloroethyl methacrylate.

[0055] Another useful class of materials are the reaction product of (meth)acrylate-functionalized, hydroxyl- or amino-containing materials and polyisocyanate in suitable proportions so as to convert all of the isocyanate groups to urethane or ureido groups, respectively.

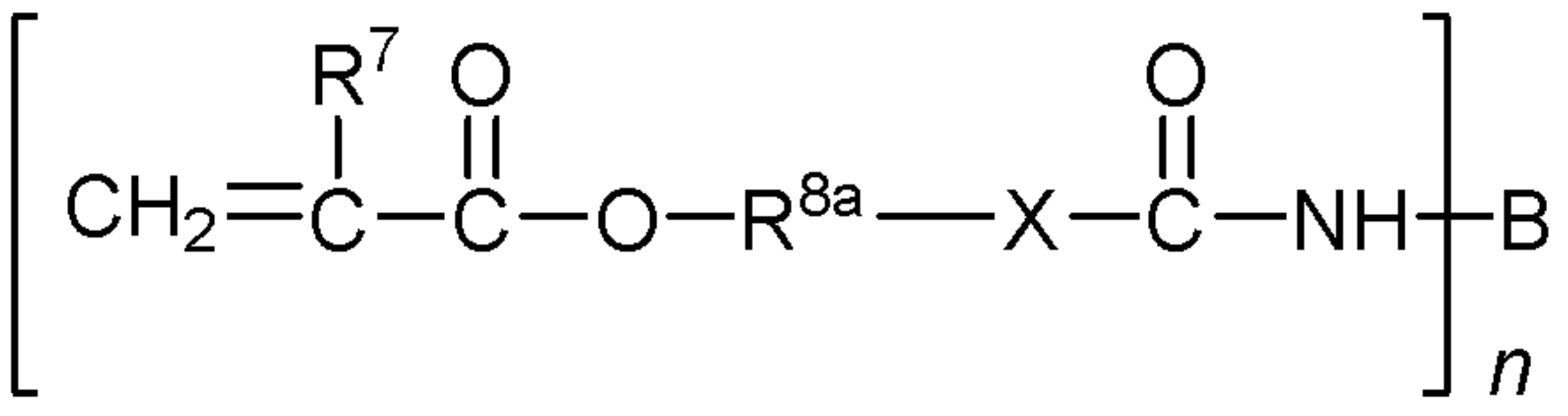
[0056] The so-formed (meth)acrylate urethane or urea esters may contain hydroxy or amino functional groups on the non-acrylate portion thereof. (Meth)acrylate esters suitable for use have the formula:



$$CH_2=\overset{\overset{R^7}{|}}{C}-\overset{\overset{O}{\|}}{C}-O-R^{8a}-X-H$$

where X is selected from --O-- and  $-\overset{\displaystyle R^9 \atop |}{N}-$,
where R^9 is selected from hydrogen or lower alkyl of 1 through 7 carbon atoms; R^7 is selected from hydrogen, halogen (such as chlorine) or alkyl (such as methyl and ethyl radicals); and R^{8a} is a divalent organic radical selected from alkylene of 1 through 8 carbon atoms, phenylene and naphthylene.

[0057] These groups upon proper reaction with a polyisocyanate, yield a monomer of the following general formula:



$$\left[CH_2{=}\overset{\displaystyle R^7 \atop |}{C}-\overset{\displaystyle O \atop \|}{C}-O-R^{8a}-X-\overset{\displaystyle O \atop \|}{C}-NH \right]_n B$$

where n is an integer from 2 to about 6; B is a polyvalent organic radical selected from alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, alkaryl and heterocyclic radicals both substituted and unsubstituted, and combinations thereof; and R^7, R^{8a} and X have the meanings given above.

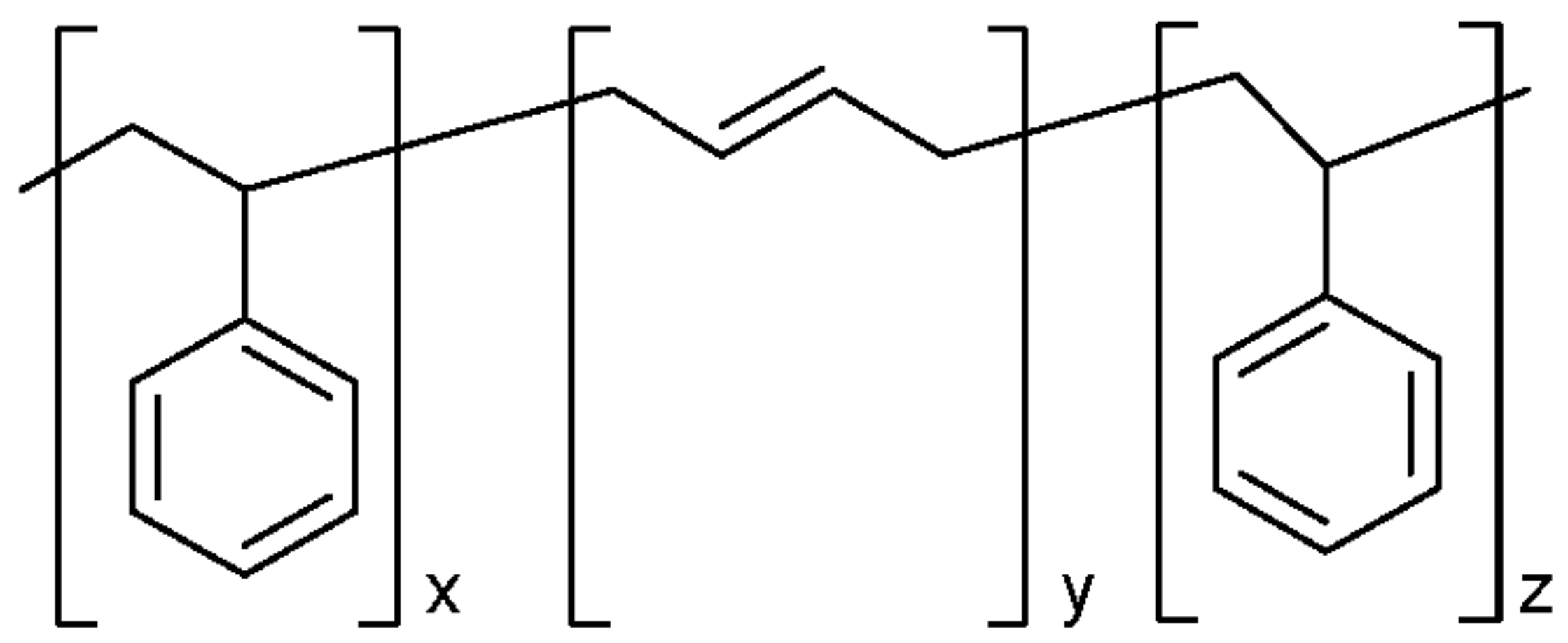
[0058] Depending on the nature of B, these (meth)acrylate esters with urea or urethane linkages may have molecular weights placing them in the oligomer class (such as 1,000 up to 5,000) or in the polymer class (such as about greater than 5,000).

[0059] Of course, combinations of these (meth)acrylate monomers may also be used.

[0060] The (meth)acrylate component should comprise from 50 to 70 percent by weight of the composition, such as 55 to 57 percent by weight, based on the total weight of the composition.

[0061] The styrene butadiene block copolymer may be a linear block copolymer based on styrene and butadiene. The skilled person will appreciate that the styrene butadiene block copolymer is also known as polystyrene-block-polybutadiene-block-polystyrene. Polystyrene may account for 35 percent by weight to 45 percent by weight of the copolymer, optionally the copolymer may contain about 40 percent by weight.

[0062] For example the styrene butadiene block copolymer may be of the formula:



or

$$[CH_2CH(C_6H_5)]_x\,(CH_2CH{=}CHCH_2)_y\,[CH_2CH(C_6H_5)]_x$$

where x, y and z are integers.

[0063] The methacrylate functionalised polybutadiene may be methacrylate (vinyl) terminated butadiene ("VTB") polymer and/or butadiene acrylonitrile ("VTBNX") polymer. Suitable methacrylate functionalised polybutadiene polymers are available under the trade name Hypro®, for example Hypro® 2000X168LC which is a methacrylate (vinyl) terminated polybutadiene, or Hypro® 1300X33LCVTBNX which is a butadiene-acrylonitrile polymer, or Hypro® 1300X43LC VTBNX which is also a butadiene-acrylonitrile polymer.

[0064] The methacrylate functionalised polybutadiene may have a number average molecular weight of from 3,000 to 5,500. The methacrylate functionalised polybutadiene may be methacrylate (vinyl) terminated polybutadiene having a number average molecular weight of 4,200 to 4,800, for example the number average molecular weight may be about 4,450. The methacrylate functionalised polybutadiene may be butadiene-acrylonitrile polymer having a number average molecular weight of 3,500 to 4,000, for example the number average molecular weight may be 3,700 or 3,900. Advantageously, compositions of the invention comprising methacrylate (vinyl) terminated polybutadiene and/or butadiene acrylonitrile ("VTBNX") polymer proved particularly effective at bonding a wide variety of substrates, particularly bonding passive substrates to metallic substrates.

[0065] The inventive compositions may also comprise a transition metal. The transition metal may be present in the form of a salt. The transition metal may be any transition metal selected from Groups 3 to 12 of the Periodic Table of Elements and combinations thereof. For example a salt of any transition metal selected from Groups 3 to 12 of the Periodic Table of Elements, and combinations of those salts, may be used. In all cases however it will be appreciated that the transition metal is redox active. Being redox active allows it to participate in the activation of (anaerobic cure of) the anaerobic composition.

[0066] The transition metal may be titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, silver, vanadium, molybdenum, ruthenium, and combinations thereof.

[0067] Desirably the transition metal may be copper, iron, vanadium, cobalt and chromium, and combinations thereof.

[0068] Desirably the transition metal is provided in the form of a salt. Suitable salts include the following salts and any combination thereof.

[0069] Titanium salts include: titanium(IV) bromide; titanium carbonitride powder, Ti2CN; titanium(II) chloride; titanium(III) chloride; titanium(IV) chloride; titanium(III) chloride-aluminum chloride; titanium(III) fluoride; titanium(IV) fluoride; titanium(IV) iodide; titanium(IV) oxysulfate solution.

[0070] Chromium salts include: chromium(II) chloride; chromium(III) bromide; chromium(III) chloride; chromium(III) chloride tetrahydrofuran complex; chromium(III) fluoride; chromium(III) nitrate; chromium(III) perchlorate; chromium(III) phosphate; chromium(III) sulfate; chromyl chloride; CrO_2; potassium chromium(III) oxalate.

[0071] Manganese salts include: manganese(II) bromide; manganese(II) carbonate; manganese(II) chloride; manganese(II) cyclohexanebutyrate; manganese(II) fluoride; manganese(III) fluoride; manganese(II) formate; manganese(II) iodide; manganese(II) molybdate; manganese(II) nitrate; manganese(II) perchlorate; and manganese(II) sulfate.

[0072] Iron salts include: ammonium iron(II) sulfate; iron(II) bromide; iron(III) bromide; iron(II) chloride; iron(III) chloride; iron(III) citrate; iron(II) fluoride; iron(III) fluoride; iron(II) iodide; iron(II) molybdate; iron(III) nitrate; iron(II) oxalate; iron(III) oxalate; iron(II) perchlorate; iron(III) phosphate; iron(III) pyrophosphate; iron(II) sulfate; iron(III) sulfate; iron(II) tetrafluoroborate; and potassium hexacyanoferrate(II).

[0073] Cobalt salts include: cobalt (II) naphthenate; Ammonium cobalt(II) sulfate; cobalt(II) benzoylacetonate; cobalt(II) bromide; cobalt(II) carbonate; cobalt(II) chloride; cobalt(II) cyanide; cobalt(II) fluoride; cobalt(III) fluoride; cobalt(II) hydroxide; cobalt(II) iodide; cobalt(II) nitrate; cobalt(II) oxalate; cobalt(II) perchlorate; cobalt(II) phosphate; cobalt(II) sulfate; cobalt(II) tetrafluoroborate; cobalt(II) thiocyanate; cobalt(II) thiocyanate; trans-dichlorobis(ethylenediamine)cobalt(III) chloride; Hexaamminecobalt(III) chloride; and pentaamminechlorocobalt(III) chloride.

[0074] Nickel salts include: ammonium nickel(II) sulfate; bis(ethylenediamine)nickel(II) chloride; nickel(II) acetate; nickel(II) bromide; nickel(II) bromide ethylene glycol dimethyl ether complex; nickel(II) bromide 2-methoxyethyl ether complex; nickel carbonate, nickel(II) carbonate hydroxide; nickel (II) chloride; nickel(II) cyclohexanebutyrate; nickel (II) fluoride; nickel (II) hexafluorosilicate; nickel(II) hydroxide; nickel(II) iodide; nickel (II) nitrate; nickel(II) oxalate; nickel(II) perchlorate; nickel(II) sulfamate; nickel(II) sulfate; potassium nickel(IV) paraperiodate; and potassium tetracyanonickelate (II).

[0075] Copper salts include: copper acetate, copper hexanoate, copper-2-ethylhexanoate copper carbonate; copper (II) acetylacetonate; copper(I) bromide; copper(II) bromide; copper(I) bromide dimethyl sulfide complex; copper(I) chloride; copper(II) chloride; copper(I) cyanide; copper(II) cyclohexanebutyrate; copper(II) fluoride; copper(II) formate; copper(II) D-gluconate; copper(II) hydroxide; copper(II) hydroxide phosphate; copper(I) iodide; copper(II) molybdate; copper(II) nitrate; copper(II) perchlorate; copper(II) pyrophosphate; copper(II) selenite; copper(II) sulfate; copper(II) tartrate; copper(II) tetrafluoroborate; copper(I) thiocyanate; tetraamminecopper(II) sulfate.

[0076] Zinc salts include: zinc bromide; zinc chloride; zinc citrate; zinc cyanide; zinc fluoride; zinc hexafluorosilicate; zinc iodide; zinc methacrylate; zinc molybdate; zinc nitrate; zinc oxalate; zinc perchlorate; zinc phosphate; zinc selenite; zinc sulfate; zinc tetrafluoroborate; zinc p-toluenesulfonate.

[0077] Silver salts include: silver bromate; silver carbonate; silver chlorate; silver chloride; silver chromate; silver citrate; silver cyanate; silver cyanide; silver cyclohexanebutyrate; silver(I) fluoride; silver(II) fluoride; silver heptafluorobutyrate; silver hexafluoroantimonate; silver hexafluoroarsenate(V); silver hexafluorophosphate; silver(I) hydrogenfluoride; silver iodide; silver lactate; silver metavanadate; silver molybdate; silver nitrate; silver nitrite; silver pentafluoropropionate; silver perchlorate; silver(I) perrhenate; silver phosphate; silver(I) sulfadiazine; silver sulfate; silver tetrafluoroborate; silver thiocyanate; silver p-toluenesulfonate.

[0078] Vanadium salts include: vanadium (III) acetylacetonate; vanadium(II) chloride; vanadium(III) chloride; vanadium(IV) chloride; vanadium(III) chloride tetrahydrofuran complex; vanadium(V) oxychloride; vanadium(V) oxyfluoride.

[0079] Molybdenum salts include: Molybdenum (III) chloride; Molybdenum (V) chloride; Molybdenum (VI) dichloride dioxide.

[0080] Ruthenium salts include: chloropentaammineruthenium (II) chloride; hexaammineruthenium (II) chloride; hexaammineruthenium (III) chloride; pentaamminechlororuthenium (III) chloride; ruthenium (III) chloride; ruthenium iodide; ruthenium(III) nitrosyl chloride; ruthenium (III) nitrosyl nitrate.

[0081] The transition metal salt may be selected from cobalt (II) naphthenate; copper carbonate; copper (II) acetylacetonate; silver nitrate; vanadium (III) acetylacetonate and combinations thereof.

[0082] The inventive compositions may also include other conventional components, such as free radical initiators, free radical accelerators, inhibitors of free radical generation, as well as metal catalysts, such as iron and copper.

[0083] A number of well-known initiators of free radical polymerization may be incorporated into the inventive compositions including, without limitation, hydroperoxides, such as cumene hydroperoxide ("CHP"), para-menthane hydroperoxide, t-butyl hydroperoxide ("TBH") and t-butyl perbenzoate. Other peroxides include benzoyl peroxide, dibenzoyl peroxide, 1,3-bis(t-butylperoxyisopropyl)benzene, diacetyl peroxide, butyl 4,4-bis(t-butylperoxy)valerate, p-chlorobenzoyl peroxide, t-butyl cumyl peroxide, t-butyl perbenzoate, di-t-butyl peroxide, dicumyl peroxide, 2,5-dimethyl-2,5-di-t-butylperoxyhexane, 2,5-dimethyl-2,5-di-t-butyl-peroxyhex-3-yne, 4-methyl-2,2-di-t-butylperoxypentane and combinations thereof.

[0084] Such peroxide compounds are typically employed in the present invention in the range of from 0.1 to 10 percent by weight, based on the total weight of the composition, with 1 to 5 percent by weight being desirable.

[0085] If desired the initiator component may be encapsulated. For example the initiator component may be an encapsulated peroxide, for example encapsulated benzoyl peroxide.

[0086] Free radical accelerators may optionally be included in the compositions of the invention: suitable accelerators include 1-acetyl-2-phenylhydrazine ("APH"), Dimethyl-para-Toluidine ("DMpT"), Diethyl-para-Toluidine ("DEpT") with Dimethyl-ortho-Toluidine ("DMoT"), succinylphenylhydrazine, tetrahydroquinoline, p-toluenesulphonylhydrazine, and dihydroxyethyl-para-toluidine and combinations thereof.

[0087] Suitably, the free radical accelerator may be present in an amount of from 0.1 to 1.0 percent by weight, based on the total weight of the composition, with 0.5 to 0.8 percent by weight being desirable.

[0088] Inhibitors of free radical generation may optionally be included in the compositions of the invention: suitable inhibitors include benzoquinone, naphthoquinone, phenothiazine and hydroquinone and combinations thereof. Suitably, the inhibitors of free radical generation may be present in an amount of from 0.01 to 0.5 percent by weight, based on the total weight of the composition, with 0.1 to 0.3 percent by weight being desirable.

[0089] Metal chelators may optionally be included in the compositions of the invention; suitable chelators include tetrasodium salt of ethylene diamine tetra-acetic acid ("EDTA") or etidronic acid and combinations thereof. Suitably, the metal chelators may be present in an amount of from 0.5 to 2.0 percent by weight, based on the total weight of the composition, with 0.8 to 1.0 percent by weight being desirable.

[0090] The compositions of the invention may optionally include a carboxylate component. The carboxylate component is a component comprising a carboxylic acid group or an ester group. Without being bound by theory, the carboxylate component may act as an accelerator and an adhesion promoter. Suitable carboxylate groups include methacrylic acid, acrylic acid, hydroxyethyl methacrylate ("HEMA") succinate ("HEMA succinate"), hydroxyethyl methacrylate maleate ("HEMA maleate"), hydroxyethyl methacrylate phosphate ("HEMA phosphate"), or maleic acid and combinations thereof.

[0091] Suitably, the carboxylate component may be methacrylic acid and is present in an amount of from 6 to 12 percent by weight, based on the total weight of the composition, with 9.0 to 11.0 percent by weight being desirable.

[0092] Compositions used in the present invention may further comprise thickeners and/or fillers.

[0093] As mentioned above, it will be appreciated that the composition used in the invention can include non-reactive species including resins. Such components do not participate in an anaerobic cure reaction. They are unreactive. Such components may however become part of the cure product having been incorporated therein during the curing of other components. Examples of such non-reactive species include: fumed silica, polyethylene, PTFE, mica, polyamide wax, titanium dioxide, barium sulphate.

[0094] The present invention also provides methods of bonding using the anaerobic adhesive compositions, as well as the reaction products of the compositions.

[0095] The anaerobically curable compositions for use in the present invention may be prepared using conventional methods which are well known to those persons of skill in the art. For instance, the components of the composition may be mixed together in any convenient order consistent with the roles and functions the components are to perform in the compositions. Conventional mixing techniques using known apparatus may be employed.

[0096] Conventional stabilizers and inhibitors (such as phenols including hydroquinone and quinones) may be employed to control and prevent premature peroxide decomposition and polymerization of the composition of the present invention.

[0097] Conventional anaerobic cure-inducing compositions to induce and accelerate anaerobic cure may be included. For example compositions of the present invention may include one or more of saccharin, toluidines, such as N,N-diethyl-p-toluidine ("DE-p-T") and N,N-dimethyl-o-toluidine ("DM-o-T"), and acetyl phenylhydrazine ("APH").

[0098] Compositions of the present invention may further comprise thickeners and/or fillers.

[0099] The composition advantageously provides enhanced physical properties when cured in the presence of passive and active substrates.

[00100] All percentages by weight are based on the total weight of the composition unless otherwise indicated.

Examples

[00101] The components of a representative composition according to the invention are listed in Table 1:

Table 1	
Material	**Amt/%wt**
Methyl methacrylate (MMA)	50 - 70
Methacrylate functionalised polybutadiene	8 - 16
Styrene butadiene block copolymer	14 - 18
Free radical inhibitor (e.g. Naphthoquinone 5wt% in polyethylene glycol methacrylate (PEGMA))	0.01 - 0.3
Metal chelator (EDTA 3.5 wt% in propylene glycol (PEG))	0.5 - 2.0
Methacrylic acid	6.0 - 12.0
1-acetyl-2-phenylhydrazine	0.5 - 1.0
Saccharin	1.0 - 2.0
Cumene hydroperoxide	1.0 - 2.0

[00102] The composition of Table 1 may optionally be used with an activator composition to bond a first substrate to a second substrate. A representative activator composition is provided in Table 2:

Table 2	
Material	**Amt/%wt**
heptane	53 – 55
isopropyl alcohol	14 – 17
dihidropyridine	20 – 40
Cupric (II) acetylacetonate	0.001 - 0.02

[00103] The anaerobic composition is prepared by mixing the materials in Table 1 at room temperature (MMA is volatile at elevated temperatures).

[00104] A suitable activator can be prepared by mixing the materials in Table 2 at room temperature. Alternatively, a suitable commercially available activator may be used. For example, LOCTITE® 7387™ Depend® Activator is a suitable activator.

[00105] Tensile strength was assessed for various substrates using various compositions within the ranges set forth in Table 1. The following methodology was employed unless otherwise indicated.

[00106] An activator is applied to one side of a first passive adherend (metal or plastic lapshear) by either a brush or using a pipette and the entrained solvent is allowed to evaporate. The anaerobically curable composition of the invention or a comparative anaerobically curable composition is applied as a coating to a second lapshear adherend (for example a metallic substrate) and an assembly is prepared by clamping the first lapshear to the second lapshear with the activator and the specified anaerobically curable composition sandwiched between said first and second adherends. The clamped assembly is allowed to cure for a period of 24 hours, and the tensile break force is determined on an Instron, according to ASTM D1002-05.

[00107] Example 1

Material	Composition/Amt (%wt)	
	A	B
Methyl methacrylate (MMA)	56.73	62.97
Methacrylate functionalised polybutadiene (HYPRO® 2000X168LC)	11.12	0
Styrene butadiene block copolymer (KRATON® D1155E)	16.69	0
Naphthoquinone 5wt% in PEGMA	0.21	0.20
EDTA 3.5wt% in PEG	0.93	0.99
Methacrylic acid	10.00	0
Acrylic acid	0	4.16
1-acetyl-2-phenylhydrazine	0.77	0.75
Saccharin	1.70	1.00
Propoxylated bisphenol A fumarate polyester (FILCO® 663 P)	0	28.93
Cumene hydroperoxide	1.85	1.00

[00108] The methacrylate functionalised polybutadiene employed in Example 1 is methacrylate (vinyl) terminated butadiene (VTB) polymer having a number average molecular weight of about 4,450. Such a VTB polymer is available from Emerald Performance Materials® under the tradename Hypro® 2000X168LC.

[00109] A suitable styrene butadiene block copolymer is available from Kraton Performance Polymers under the trade name Kraton® D1155 E polymer. Kraton® D1155 E is a clear, linear block copolymer based on styrene and butadiene with bound styrene of 40% mass.

[00110] A suitable source of propoxylated bisphenol A fumarate polyester is FILCO® 663 P, other sources include those available under the tradenames ATLAC® 382 and DION® 382E.

[00111] Figures 1 to 6 show the tensile strengths observed for various compositions on the various substrates. The substrates shown are abbreviated as follows: Perspex (poly methyl methacrylate; “PX”); mild steel (“MS); stainless steel (“SS”); aluminium (“Al”); grit blasted mild steel (“GBMS”); polyvinyl chloride (“PVC”); poly carbonate (“PC”); nylon 6’6 (“Ny”); and acrylonitrile butadiene styrene (“ABS”).

[00112] Figure 1 shows the tensile strength performance of composition A on various passive substrates. The presence of styrene butadiene block copolymer and methacrylate functionalised polybutadiene, (specifically, methacrylate (vinyl) terminated butadiene polymer) resulted in a significant increase in tensile strength performance.

[00113] Example 2 (Comparative): The tensile strength performance of methyl methacrylate (MMA) compositions comprising varying levels of styrene butadiene block copolymer on lapshear substrates was assessed. Compositions comprising 10wt% and 20wt% styrene butadiene block copolymer were prepared as outlined below.

Material	Composition/Amt (%wt)	
	C	D
Methyl Methacrylate	74.60	64.60
Styrene Butadiene Block Copolymer (Kraton® D1155E)	10.00	20.00
Naphthoquinone 5wt% in PEGMA	0.20	0.20
EDTA 3.5wt% in PEG	0.90	0.90
Methacrylic Acid	10.00	10.00
1-Acetyl-2-Phenylhydrazine	0.80	0.80
Saccharin	1.70	1.70
Cumene Hydroperoxide	1.90	1.90

[00114] Figure 2 shows the tensile strength performance of composition A versus compositions C and D on various passive substrates. While the inclusion of styrene butadiene block copolymer improved tensile strength performance for several substrates, the combination of styrene butadiene block copolymer and methacrylate functionalised polybutadiene resulted in enhanced tensile strength performance.

[00115] Example 3 (Comparative): The tensile strength performance of MMA compositions comprising varying levels of methacrylate functionalised polybutadiene on lapshear substrates was assessed. Compositions comprising 10wt% and 20wt% methacrylate functionalised polybutadiene were prepared as outlined below.

Material	Composition/Amt (%wt)	
	E	F
Methyl Methacrylate	74.54	64.54
Methacrylate functionalised polybutadiene (HYPRO® 2000X168LC)	10.00	20.00
Naphthoquinone 5wt% in PEGMA	0.21	0.21
EDTA 3.5wt% in PEG	0.93	0.93
Methacrylic Acid	10.00	10.00
1-Acetyl-2-Phenylhydrazine	0.77	0.77
Saccharin	1.70	1.70
Cumene Hydroperoxide	1.85	1.85

[00116] Figure 3 shows the tensile strength performance of composition A versus compositions E and F on various passive substrates. While the inclusion of methacrylate functionalised polybutadiene improved tensile strength performance for several substrates, the combination of styrene butadiene block copolymer and methacrylate functionalised polybutadiene resulted in enhanced tensile strength performance for certain substrates.

[00117] Example 4: Comparison of lapshear strength with variations in rubber content.

Material	**Composition/Amt (%wt)**		
	G	**H**	**I**
Methyl methacrylate (MMA)	72.04	56.73	46.90
Methacrylate functionalised polybutadiene (HYPRO® 2000X168LC)	5.00	11.12	27.00
Styrene butadiene block copolymer (KRATON® D1155E)	7.50	16.69	18.00
Naphthoquinone 5wt% in PEGMA	0.21	0.21	0.20
EDTA 3.5wt% in PEG	0.93	0.93	0.99
Methacrylic acid	10.00	10.00	4.16
1-acetyl-2-phenylhydrazine	0.77	0.77	0.75
Saccharin	1.70	1.70	1.00
Cumene hydroperoxide	1.85	1.85	1.00

[00118] In Example 4, the ratio of methacrylate functionalised polybutadiene to styrene butadiene block copolymer was varied. Composition H wherein the ratio of methacrylate functionalised polybutadiene to styrene butadiene block copolymer is approximately 11:17 proved to be optimal. Accordingly, compositions wherein the ratio of methacrylate functionalised polybutadiene to styrene butadiene block copolymer is about 2:3 proved particularly advantageous. The tensile strength performance of compositions G, H and I on lapshear substrates was assessed (see Figure 4).

[00119] Example 5: Performance of MMA compositions with and without propoxylated bisphenol A fumarate polyester.

Material	**Composition/Amt (wt%)**	
	J	**K**
Methyl methacrylate (MMA)	84.50	55.60
Methacrylate functionalised polybutadiene	-	-
Styrene butadiene block copolymer	-	-
Naphthoquinone 5wt% in PEGMA	0.20	0.20
EDTA 3.5wt% in PEG	0.90	0.90
Methacrylic acid	10.0	10.00
1-acetyl-2-phenylhydrazine	0.80	0.80
Saccharin	1.70	1.70
Propoxylated bisphenol A fumarate polyester (FILCO® 663 P)	-	28.90
Cumene hydroperoxide	1.90	1.90

[00120] Figure 5 shows the tensile strength performances of composition A and composition K versus that of composition J on various substrates. Composition A which comprises styrene butadiene block copolymer and methacrylate functionalised polybutadiene resulted in enhanced tensile strength performance in comparison to composition J. Composition K which comprises propoxylated bisphenol A fumarate polyester also resulted in enhanced tensile strength performance when compared to composition J which does not comprise a toughening agent.

[00121] Figure 6 shows the tensile strength performance of composition A with and without the use of an activator.

[00122] The words “comprises/comprising” and the words “having/including” when used herein with reference to the present invention are used to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

Clean Amended Claims

1. An anaerobically curable composition comprising:

(a) at least one (meth)acrylate component;

(b) an anaerobic cure inducing component; and

(c) a toughening agent comprising a combination of a styrene butadiene block copolymer and methacrylate functionalised polybutadiene, wherein the methacrylate functionalised polybutadiene is present in an amount of from 8 to 16 wt% based on the total weight of the composition, and wherein the styrene butadiene is present in an amount of from 14 to 18 wt% based on the total weight of the composition, and wherein the weight ratio of the methacrylate functionalised polybutadiene to the styrene butadiene block copolymer is about 2:3.

2. An anaerobically curable composition according to claim 1, wherein the methacrylate component is a (meth)acrylate monomer having the formula: $H_2C=CGCO2R^1$, wherein G may be hydrogen, halogen or alkyl groups having from 1 to 4 carbon atoms, and R^1 may be selected from alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkaryl, aralkyl or aryl groups having from 1 to 16 carbon atoms, any of which may be optionally substituted or interrupted as the case may be with silane, silicon, oxygen, halogen, carbonyl, hydroxyl, ester, carboxylic acid, urea, urethane, polyurethane, carbonate, amine, amide, sulfur, sulfonate, and sulfone.

3. An anaerobically curable composition according to any preceding claim, wherein the toughening agent is a combination of a styrene butadiene block copolymer and methacrylate functionalised polybutadiene, and wherein the methacrylate functionalised polybutadiene is selected from the group consisting of methacrylate (vinyl) terminated polybutadiene and butadiene-acrylonitrile polymer.

4. An anaerobically curable composition according to claim 3, wherein the methacrylate functionalised polybutadiene is methacrylate (vinyl) terminated polybutadiene.

5. An anaerobically curable composition according to claim 3, wherein the methacrylate functionalised polybutadiene is butadiene-acrylonitrile polymer.

6. An anaerobically curable composition according to any one of claims 3 to 5, wherein the methacrylate functionalised polybutadiene has a number average molecular weight of from 3,000 to 5,500.

7. An anaerobically curable composition according to claim 6, wherein the methacrylate functionalised polybutadiene has a number average molecular weight of about 4,500.

8. An anaerobically curable composition according to claim 6, wherein the methacrylate functionalised polybutadiene has a number average molecular weight of from 3500 to 4,000.

9. An anaerobically curable composition according to any preceding claim, further comprising a transition metal.

10. An anaerobically curable composition according to claim 9, wherein the transition metal is selected from copper, iron, vanadium, cobalt, chromium, silver and manganese, or combinations thereof.

11. An anaerobically curable composition according to claim 10, wherein the transition metal is in salt form and is selected from the group consisting of: cobalt (II) naphthenate, copper carbonate, copper (II) acetylacetonate, silver nitrate, vanadium nitrate, vanadium (III) acetylacetonate and combinations thereof.

12. Use of an anaerobically curable composition according to any preceding claim, for bonding a first substrate to a second substrate.

13. Use of an anaerobically curable composition according to claim 12, wherein the first substrate is a passive substrate.

14. Use of an anaerobically curable composition according to claim 13, wherein the passive substrate is a plastic.

15. Use of an anaerobically curable composition according to claim 14, wherein the plastic substrate is selected from: acrylonitrile butadiene styrene, polycarbonate, polycarbonate/acrylonitrile butadiene styrene, polyarylamides, polyamides, acrylic plastic, polyvinyl chloride, nylon 6’6, and polymethyl methacrylate.

16. Use of an anaerobically curable composition according to any one of claims 12 to 15, wherein the second substrate is metallic.

17. Use of an anaerobically curable composition according to claim 16, wherein the second substrate is selected from the group consisting of steel, including mild steel and stainless steel, brass including clock brass, bronze, or zinc, aluminium, iron, copper, beryllium, cobalt, manganese, nickel, cadmium, gold, silver or alloys thereof.

18. A method of bonding together two substrates comprising the steps of:

applying a (meth)acrylate composition according to any one of claims 1 to 11, to at least one of the substrates and mating together the substrates for a time sufficient to permit an adhesive bond to form from the (meth)acrylate composition between the mated substrates.

19. An assembly comprising two substrates bonded together by the cure product of composition according to any one of claims 1 to 11.

20. A method of anaerobically curing a (meth)acrylate composition comprising the steps of:

providing a (meth)acrylate composition comprising:-

(a) a (meth)acrylate component;

(b) a cure inducing component; and

(c) a toughening agent comprising a combination of a styrene butadiene block copolymer and methacrylate functionalised polybutadiene, wherein the methacrylate functionalised polybutadiene is present in an amount of from 8 to 16 wt% based on the total weight of the composition, and wherein the styrene butadiene is present in an amount of from 14 to 18 wt% based on the total weight of the composition, and wherein the weight ratio of the methacrylate functionalised polybutadiene to the styrene butadiene block copolymer is about 2:3; and

exposing the (meth)acrylate composition to an anaerobic environment for a time sufficient to cure the composition.

21. A process for preparing a reaction product from a curable composition, comprising the steps of:

applying an activator composition to a desired substrate surface;

applying to that surface a composition comprising:

(a) a (meth)acrylate component;

(b) a cure inducing component; and

(c) a toughening agent comprising a combination of a styrene butadiene block copolymer and methacrylate functionalised polybutadiene, wherein the methacrylate functionalised polybutadiene is present in an amount of from 8 to 16 wt% based on the total weight of the composition, and wherein the styrene butadiene is present in an amount of from 14 to 18 wt% based on the total weight of the composition, and wherein the weight ratio of the methacrylate functionalised polybutadiene to the styrene butadiene block copolymer is about 2:3;

mating a second surface to that substrate surface to form an assembly; and

exposing the (meth)acrylate composition to an anaerobic environment for a time sufficient to cure the composition.