(54) Title: A NEW COATING COMPOSITION FOR PROPPANT AND THE METHOD OF MAKING THE SAME

(57) Abstract: A coated proppant comprising a proppant particulate substrate and a coating layer on the substrate. The coating layer is formed from a composition comprising a resin, a curing agent, an adhesion promoter, and a toughening agent.
A NEW COATING COMPOSITION FOR PROPPANT AND THE METHOD OF MAKING THE SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to proppant particulates coated with a toughened epoxy resin composition. The coated particulates exhibit enhanced toughness and can be used as a proppant in hydraulic fracturing of subterranean formations. The present invention also relates to coated proppant particulates with reduced dust formation during the handling and the transportation of the same.

2. Discussion of Background Information

To stimulate subterranean formations to enhance oil and gas production, fluid is pumped from the surface into an oil or gas bearing sub-surface at a rate and pressure sufficient, e.g. about 5000-7000 psi, to cause a fracture of the subterranean formations. This process is commonly referred to as hydraulic fracturing. In hydraulic fracturing process, proppant particulates are blended into fluids and injected into the formation to fill the underground fracture to maintain the fracture in the open or fractured condition. The proppants create a permeable pathway through which oil and gas can flow into the oil bore.

To prepare proppant particulates for hydraulic fracturing process, epoxy resin coatings have been used to coat proppant particulates. There are a number of patents teaching the use of epoxy coatings for proppants. Some of the patents describing the epoxy coatings are U.S. Patent No. 3,854,533, U.S. Patent No. 3,867,986, U.S. Patent No. 4,829,100, U.S. Patent No. 4,869,960, and U.S. Patent No. 5,422,183. However, the epoxy coatings on the proppants, under the pressure of about 5000-7000 psi, will disintegrate and become brittle. The fracture of the coated surface exposes the particulate proppants, such as silica sand which pulverizes at pressures of greater than 5000 psi. When pulverized, both the epoxy coating fines and the silica fines plug the permeable path thus reducing the conductivity of the pack placed between the opened subsurface fracture. The fines are generally caused by a closure stress of greater than 5000 psi within the
fractured zone and also when the proppants are passed through the pumping and mixing equipment used to introduce the proppants into the subterranean formation.


Therefore, this is a need to have an improved epoxy resin for coating the proppant particulates to minimize the coating fracture and brittle failures under high closure stress such as greater than 5000 psi.

Recently, there have been several studies related to increasing the fracture resistance or toughness of epoxy resins by adding to the epoxy resin various block copolymers as toughening agent. Much of the work is focused on the use of amphiphilic diblock copolymers having an epoxy miscible block and an epoxy immiscible block. In those studies, the epoxy miscible block is poly(ethylene oxide) (“PEO”) and the immiscible block is a saturated polymeric hydrocarbon. For example, Journal of Polymer Science, Part B: Polymer Physics, 2001, 39(23), 2996-3010 discloses that the use of a poly(ethylene oxide)-b-poly(ethylene-alt-propylene) (“PEO-PEP”) diblock copolymer provides micellar structures in cured epoxy systems; and that block copolymers self-assembled into vesicles and spherical micelles can significantly increase the fracture resistance of model bisphenol A epoxies cured with a tetrafunctional aromatic amine curing agent. Journal of The American Chemical Society, 1997, 119(11), 2749-2750 describes epoxy systems with self-
assembled microstructures brought about using amphiphilic PEO-PEP and poly(ethylene oxide)-b-poly(ethyl ethylene) ("PEO-PEE") diblock copolymers. These block copolymer containing-systems illustrate characteristics of self-assembly. Although effective at providing templated epoxies with appealing property sets, the known block copolymer materials are too expensive to be used in some applications.

Other block copolymers incorporating an epoxy-reactive functionality in one block have been used as modifiers for epoxy resins to achieve nanostructured epoxy thermosets. For example, Macromolecules, 2000, 33(26) 9522-9534 describes the use of poly(epoxyisoprene)-b-polybutadiene ("Blxn") and poly(methylacrylate-co-glycidyl methacrylate)-b-polysoprene ("MG-1") diblock copolymers that are amphiphilic in nature and are designed in such a way that one of the blocks can react into the epoxy matrix when the resin is cured. Journal of Applied Polymer Science, 1994, 54, 815 describes epoxy systems having submicron scale dispersions of poly(caprolactone)-b-poly(dimethylsiloxane)-b-poly(caprolactone) triblock copolymers.

Other self-assembled amphiphilic block copolymers for modifying thermalizing epoxy resins to form nanostructured epoxy thermosets are known. For example, Macromolecules 2000, 33, 5235-5244 and Macromolecules, 2002, 35, 3133-3144, describe the addition of a poly(ethylene oxide)-b-poly(propylene oxide) ("PEO-PPO") diblock and a poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) ("PEO-PPO-PEO") triblock to an epoxy cured with methylene diaminol, where the average size of the dispersed phase in the diblock-containing blends is of the order of 10-30 nm. A polyether block copolymer such as a PEO-PPO-PEO triblock is also known to be used with an epoxy resin as disclosed in JP H9-324110.

While some of the previously known diblock and triblock copolymers mentioned above are useful for improving the toughness of epoxy resins, none of them was used in proppant applications in hydraulic fracturing.
SUMMARY OF THE INVENTION

The present invention provides a coated proppant particulate which comprises a proppant particulate substrate and a coating layer thereon. The coating layer is formed from a composition comprising a resin, a curing agent, an adhesion promoter, and a toughening agent.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is an electron micrograph illustrating resin coated sand with dust on the sand when the coating does not contain any toughening agent.

Figure 2 is an electron micrograph illustrating resin coated sand without dust on the sand when the coating contains toughening agent.

Figure 3 is a bar chart illustrating the comparison of Fracture Toughness and corresponding Tg of various Examples prepared.

Figure 4 is a bar chart illustrating a Fracture Toughness comparison of some Examples at room temperature (about 25°C) and at 125°C.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

In the following detailed description, the specific embodiments of the present invention are described in connection with its preferred embodiments. However, to the extent that the following description is specific to a particular embodiment or a particular use of the present techniques, it is intended to be illustrative only and merely provides a concise description of the exemplary embodiments. Accordingly, the invention is not limited to the specific embodiments described below, but rather; the invention includes all alternatives, modifications, and equivalents falling within the true scope of the appended claims.

As used herein, unless otherwise stated, all percentages (%) are by weight based on the total weight of the composition.
The present invention provides a way to improve toughness while still maintaining other physical properties primarily glass transition temperature ($T_g$) of epoxy and other thermosetting coatings on proppant particulates. Thermosetting coatings like epoxy, phenolic, and others while providing good chemical resistance and modulus, are known to be brittle when subjected to deformation. Epoxy and phenolic resins are an important class of thermoset polymers that are extensively used in applications ranging from coatings to adhesives to composites. The crosslinked nature of these polymers provides them with many useful properties, especially a combination of thermal and chemical resistance and excellent adhesion. The properties of these thermoset coatings are influenced by the resin and the resin backbone, curing agent, and the crosslink density of the final coating. The crosslinked nature of the coatings, however, typically renders them relatively brittle. As a result, enhanced toughness is required for many applications.

The Glass Transition Temperature ($T_g$) also plays an important role on the final properties of the thermosetting coatings. When $T_g$ is high, the thermoset coatings will tend to be more brittle. Most of the fully cured phenolic coatings have $T_g$ of greater than 120°C and as high as 200°C. The $T_g$ of typical epoxy coatings may depend upon the type of curing agent used with the epoxy resins. For example, the aliphatic amine curing agents like D.E.H. 20®, also from The Dow Chemical Company, gives a $T_g$ of an epoxy resin such as D.E.R. 383® of The Dow Chemical Company of about 120°C. Cycloaliphatic amines and aromatic amines give a $T_g$ of epoxy resins such as D.E.R. 383® between 120°C and 180°C.

The fracture toughness of these thermosetting resins is improved by the addition of small amounts of block copolymers to the resin. The resin can then be mixed with curing agent, applied and cured on the proppant particulates.

It is noted that in preparing proppant particulates coated with resins without the toughening agent, a large amount of dust is generated as shown in Figure 1. Dusting can be severe during proppants coating process and during shipment of proppants. Dusting is probably caused by the collision of the proppant particulates during the coating and transportation process. It is believed that the dust so formed comprises of the coating polymer formed as a result of the coating breaking up because of the brittle nature of the
coating when toughening agent is not present in the coating. However, when toughening agent is used in the coating composition, the dusting is significantly reduced or disappears as shown in Figure 2.

The present invention provides such a coated proppant, having a toughening agent in coating, which comprises of a proppant particulate substrate and a coating layer on the substrate. The coating layer is formed from a coating composition which comprises a resin, a curing agent, an adhesion promoter, and a toughening agent.

The particulate substrate of the present invention may be one or more of sand, silica particles, ceramic particles, metallic particles, synthetic organic particles and mixture thereof. The sizes of these particulate substrates are usually from about 20 to about 200 mesh.

In the coating composition of the present invention, the resin may be an epoxy resin or a phenolic resin or a mixture thereof. Once cured, the coating will contain a cross-linked thermoset resin. In one embodiment, the epoxy resin is a diglycidyl-ether of Bisphenol A epoxy resin, diglycidyl-ether of Bisphenol F epoxy resin, or epoxy novolac resin. In another embodiment, the epoxy resin is a diglycidyl ether of cycloaliphatic epoxy resin.

In the coating composition, the curing agent may be one or more of a) an aliphatic or modified aliphatic amine, b) aromatic amine, c) a cycloaliphatic or modified cycloaliphatic amine, d) an anhydride, e) Lewis acid like boron trifluoride or f) a hexamethylenetetramine compound.

In the coating composition, the toughening agent may be any one of the commercially available toughening agent. There are a number of commercial toughening agents available such as carboxyl-terminated copolymer of butadiene and acrylonitrile liquid rubber and other functionalize liquid rubbers. Some core-shell rubber can also be added to the epoxy resin as toughening agents. For example, CTBN® from Novean and KANE ACE® MX-117 from Kaneka Corporation may be used as toughening agents in the present application on proppants. In preferred embodiments, a block amphiphilic block copolymer is used. The amphiphilic block copolymer contains at least one epoxy resin
miscible block segment and at least one epoxy resin immiscible block segment. The immiscible block segment may comprise at least one polyether structure provided that the polyether structure of the immiscible block segment contains at least one or more alkylene oxide monomer units having at least four carbon atoms.

In one preferred embodiment of the present invention, XU 19110 epoxy resin from The Dow Chemical Company is used. The XU 19110 is a toughened liquid epoxy resin and contains a standard Bisphenol-A epoxy resin blended with a toughening agent. This product is a blend of about 95 wt% standard Bisphenol-A epoxy resins and about 5 wt.% of toughening agent such as amphiphilic block copolymer. The EEW value of XU 19110 is between 192-202 measured with ASTM D-1652.

The coating composition may contain from about 1 to about 20 wt. %, preferably from about 1 to about 10 wt. %, and more preferably from about 1 to about 5 wt. % of toughening agent as a distinct phase from the composition. The distinct phase is referred to as a second phase.

The coating composition of the present invention may further comprise an adhesion promoter such as organo-silanes (example Z-6011® from Dow Corning). The coating composition may comprise from about 0.05 to about 2 wt. % and most preferably from about 0.1 to about 0.5 wt. % of one or more adhesion promoters.

The coating composition of the present invention may further comprise a surfactant such as 3M™ Novec™ Fluorosurfactant FC-4430. In preferred embodiments, the surfactant may be one or more of anionic or nonionic surfactants at less than about 1 wt.% of the composition.

The present invention provides some unique properties of a coated proppant particulate suitable for application in subsurface fracture environment. For example, the coating layer of the coated proppant particulate has a glass transition temperature above about 120°C and fracture toughness (K_{1c}) from about 0.6 to about 2.5 MPa.m^{1/2}.
The coating composition of the present invention is usually cured at a temperature between about 50 to about 300°C, preferably at a temperature between about 75 to about 275 °C, and more preferably at a temperature between about 100 to about 250 °C.

In one preferred embodiment, the coating composition comprises about 60 to about 90 wt. % of an epoxy resin, about 10 to about 25 wt.% of a curing agent, and about 1 to about 20 wt. % of a block copolymer.

Without the need for further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following specific examples are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

**General Procedure for Preparing Clear Castings**

Several clear casting plaques are prepared for testing as substrates of different coating compositions. Same or at least similar testing results are expected if a particulate substrate is used since the testing is directed to the toughness of the coating and a plaque substrate is easier to handle during the testing. A homogenized monomer mixture containing a resin and curing agent is first prepared. The mixture is then heated and poured into 8 oz. (225 grams) glass, capped, and placed in an IEC Centra-8 centrifuge (International Equipment Co.) and degassed at 1500 rpm for 3 minutes. The degassed liquid is then poured into the pre-heated mold and cured. A 6" x 6" x 1/8" (15 cm x 15 cm x 0.3 cm) plaque is cast for each sample.

**General Procedure for Preparing Coating Compositions**

Seven (7) different coating compositions are prepared using the following proportions. Compositions of Examples 2, 4, 6 and 7 include a toughening agent. Compositions of Examples 1, 3, 5 do not include a toughening agent and are prepared for comparison purposes.
### Example 1

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>D.E.R.* 331 epoxy resin</td>
<td>88.3</td>
</tr>
<tr>
<td>D.E.H.* 26 amine hardener</td>
<td>11.7</td>
</tr>
</tbody>
</table>

### Example 2

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>D.E.R. 331 epoxy resin</td>
<td>84.2</td>
</tr>
<tr>
<td>D.E.H. 26 amine hardener</td>
<td>11.4</td>
</tr>
<tr>
<td>KANE ACE** MX-117 Toughening Agent</td>
<td>4.4</td>
</tr>
</tbody>
</table>

### Example 3

<table>
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<tr>
<th>Raw Materials</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>D.E.R. 324 epoxy resin</td>
<td>90</td>
</tr>
<tr>
<td>D.E.H. 24 amine hardener</td>
<td>10</td>
</tr>
</tbody>
</table>

### Example 4

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>XU 19110 epoxy resin(^1)</td>
<td>88.5</td>
</tr>
<tr>
<td>D.E.H. 26 amine hardener</td>
<td>11.1</td>
</tr>
</tbody>
</table>

### Example 5

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>Weight %</th>
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</thead>
<tbody>
<tr>
<td>D.E.R. 383</td>
<td>81</td>
</tr>
<tr>
<td>Ancamine® 2450 amine hardener</td>
<td>19</td>
</tr>
</tbody>
</table>

### Example 6

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>D.E.R. 383 epoxy resin</td>
<td>77.9</td>
</tr>
<tr>
<td>Ancamine 2450 amine hardener</td>
<td>18</td>
</tr>
<tr>
<td>KANE ACE** MX-117 Toughening Agent</td>
<td>4.1</td>
</tr>
</tbody>
</table>

### Example 7

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>XU 19110 epoxy resin(^1)</td>
<td>81.1</td>
</tr>
<tr>
<td>Ancamine 2450 amine hardener</td>
<td>18.9</td>
</tr>
</tbody>
</table>

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* Trademark of Dow Chemical Company  
© Trademark of Air Products  
** Trademark of Kaneka Corporation  
\(^1\) XU 19110 epoxy resin contains 5% amphibolic block copolymer

Note: Examples 1, 3, 5 are comparative Examples and are not Examples of the Present Invention.
Test Procedures

Glass Transition Temperature

“Tg or Glass Transition Temperature” means the temperature at which a thermosetting polymer changes from being a glassy solid to a rubbery solid (modulus changing from 1-3 GPa to around 1-5 MPa). In typical crosslinked polymers (i.e. thermosets), Tg is the temperature range (depending on molecular weight distribution) over which the modulus of the cured material drops by roughly 2-3 orders of magnitude. Tg is measured using a Dynamic Mechanical Thermal Analyse (DMTA) method. The results of DMTA of plaques with various coating compositions are obtained in torsion mode using a TA Instruments ARES rheometer. A frequency of 1 radian per second is used for the test and each test spans a temperature range of 25 to 250 °C. Rectangular bars are first cut on a band saw and then brought to its final dimensions using a fine-tooth burr on a vertical TensilKut router. Data related to storage and loss modulus, tan delta and torque are recorded for analysis.

Tensile Testing

Tensile Strength is the stress carried by a body prior to rupture or break. Typically this stress is calculated by dividing the measured load by the undeformed cross sectional area carrying the load. Quasi-static tensile tests are run on Type I dog-bone specimens in accordance with ASTM D-638. The specimens are cut into rectangular strips on a circular wet saw and then brought to dog-bone geometry using a TensilKut router. In an attempt to minimize scatter in the data caused by defects, the edges are wet-sanded using a series of graded grit sand papers 360, 600, 800 and finally 1200 grit. Samples are then gripped using sandpaper as tabs on an Instron electro-mechanical test frame leaving a gage section of 2 inch and tested at a prescribed displacement rate of 0.2 inches/minute. An extensiometer is used to measure strain. Load, stroke and strain signals are recorded using a computer controlled data acquisition system. All tests are performed at standard room temperature conditions.
Fracture Toughness ($K_{IC}$)

Fracture Toughness (or $K_{IC}$) is a measure of the material's resistance under stress to the propagation of an incipient flaw. Casting specimens are tested for Mode I fracture toughness using the compact tension specimen geometry in accordance with ASTM D-5045. Samples are cut to dimension by Hydrocut Company, Angleton, Texas, on their water jet-cutter. Water jet cutting is used because the material is brittle and cracked during conventional mechanical cutting methods. This technique also results in almost no residual stresses in the specimen, a feature that tends to exist while using conventional machining operations. A starter crack is very carefully introduced using a blade that is gently tapped into the chevron notch in the specimen at room temperature (about 25 °C). Specimens in which the crack is either too long across the width of the specimen or twisted to any one side are not tested. Specimens are loaded on a servo-hydraulic Instron test frame by means of a clamp and dowel pin and loaded at a constant displacement rate. Load and stroke data are recorded during the test using the computer controlled data acquisition system. Around 5-8 specimens are tested for each resin casting.

Test Results

All data is graphically shown in Figure 3 and Figure 4 and summarized in Tables 1 and 2 below.

Fracture Toughness and Glass Transition Temperature for the various examples are shown in Table 1. Examples 2 and 4 contain toughening agents and the fracture data clearly showing improved toughness for these systems (higher $K_{IC}$) compared to that without the toughening agent (e.g. Example 1).

The epoxy resin of Examples 5, 6, and 7 are high Tg systems and all cured with a cycloaliphatic amine. Example 5 does not have any toughening agent in the formulation and Examples 6 and 7 contain toughening agent. The $K_{IC}$ data clearly shows improved toughness for Examples 6 and 7 (higher $K_{IC}$) over that of Example 5.
Example 3 is the one with the lowest Tg and has a high fracture toughness even without the presence of any toughening agent. It is relatively easy to achieve high fracture toughness at lower values of Tg below 100°C. The challenge for the present invention is to have high fracture toughness at Tg value of greater than 100°C or even better at greater than 150°C. The lower Tg material of less than 100°C even though are tougher will fail catastrophically at the applications temperature of 125°C and above.

Table 1: Room temperature fracture toughness and Tg

<table>
<thead>
<tr>
<th>Coatings System</th>
<th>$K_{1C}$ (MPa.m$^{1/2}$)</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 1</td>
<td>0.82</td>
<td>133</td>
</tr>
<tr>
<td>Example 2</td>
<td>0.964</td>
<td>133</td>
</tr>
<tr>
<td>Example 3</td>
<td>0.81</td>
<td>88</td>
</tr>
<tr>
<td>Example 4</td>
<td>1.038</td>
<td>135</td>
</tr>
<tr>
<td>Example 5</td>
<td>0.524</td>
<td>191</td>
</tr>
<tr>
<td>Example 6</td>
<td>0.754</td>
<td>185</td>
</tr>
<tr>
<td>Example 7</td>
<td>0.796</td>
<td>185</td>
</tr>
</tbody>
</table>

Note: Examples 1, 3, 5 are comparative Examples and are not Examples of the Present Invention.

Table 2: Tensile Testing at Room Temperature (about 25 °C) and at 125°C

<table>
<thead>
<tr>
<th></th>
<th>Tensile Modulus (ksi)</th>
<th>Tensile Strength Break/Yield (ksi)</th>
<th>Tensile Elongation at Break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Room Temperature</td>
<td>125°C</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>Example 1</td>
<td>358.24</td>
<td>203.15</td>
<td>11.6</td>
</tr>
<tr>
<td>Example 2</td>
<td>342.6</td>
<td>191.12</td>
<td>10.45</td>
</tr>
<tr>
<td>Example 3</td>
<td>358.1</td>
<td>258.6</td>
<td>8.94</td>
</tr>
</tbody>
</table>

Note: Examples 1, and 3 are comparative Examples and are not Examples of the Present Invention.
The tensile testing data from Table 2 indicates that there is no negative effect of the toughening agent on tensile modulus, tensile strength, and tensile elongation at break. Both Example 1 (without toughening agent) and Example 2 (with toughening agent) have similar tensile properties at room temperature (about 25 °C) and at 125°C.

While the present invention may be susceptible to various modifications and alternative forms, the exemplary embodiments discussed above have been shown by way of example. However, it should again be understood that the invention is not intended to be limited to the particular embodiments disclosed herein. Indeed, the present techniques of the invention are to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the following appended claims.
WHAT IS CLAIMED IS:

1. A coated proppant comprising a proppant particulate substrate and a coating layer on the proppant particulate substrate; wherein the coating layer is formed from a composition comprising a resin, a curing agent, an adhesion promoter, and a toughening agent.

2. The coated proppant according to claim 1, wherein the particulate substrate comprises one or more of sand, silica particles, ceramic particles, metallic particles, and synthetic organic particles.

3. The coated proppant according to claim 1, wherein the coating layer comprises a cross-linked thermoset resin.

4. The coated proppant according to claim 3, wherein the resin is an epoxy resin.

5. The coated proppant according to claim 4, wherein the epoxy resin is a diglycidyl-ether of Bisphenol A epoxy resin.

6. The coated proppant according to claim 4, wherein the epoxy resin is a diglycidyl-ether of Bisphenol F epoxy resin or an epoxy novolac resin.

7. The coated proppant according to claim 4, wherein the epoxy resin is diglycidyl ether of cycloaliphatic epoxy resin.

8. The coated proppant according to claim 3, wherein the resin is a phenolic resin.

9. The coated proppant according to claim 1, wherein the curing agent is one or more of a) an aliphatic or modified aliphatic amine, b) aromatic amine, c) a cycloaliphatic or modified cyclophatic amine, d) an anhydride, e) Lewis acid, or f) a hexamethylenetetramine compound.

10. The coated proppant according to claim 1, wherein the toughening agent is a block copolymer.
11. The coated proppant according to claim 10 comprising an amphiphilic block copolymer having at least one epoxy resin miscible block segment and at least one epoxy resin immiscible block segment; wherein the immiscible block segment comprises at least one polyether structure at least one or more alkylene oxide monomer units with at least four carbon atoms.

12. The coated proppant according to claim 1, wherein the composition comprises about 1 to about 20 wt. % of a toughening agent.

13. The coated proppant according to claim 11 wherein the composition comprises about 1 to about 10 wt. % of a toughening agent.

14. The coated proppant according to claim 12, wherein the composition comprises about 1 to about 5 wt. % of a second phase toughening agent.

15. The coated proppant according to claim 1, where in the coating layer has a glass transition temperature above about 100 °C and a fracture toughness (K_{IC}) value of about 0.6 to about 1.2 M. Pa.m^{1/2}.

16. The coated proppant according to claim 1, wherein the composition is cured at a temperature between about 50 to about 300 °C.

17. The coated proppant according to claim 16, wherein the composition is cured at a temperature between about 75 to about 275 °C.

18. The coated proppant according to claim 17, wherein the composition is cured at a temperature between about 100 to about 250 °C.

19. The coated proppant according to claim 1, wherein the composition comprises about 60 to about 90 wt. % of an epoxy resin, about 10 to about 25 wt.% of a curing agent, and about 1 to about 20 wt. % of a block copolymer.

20. The coated proppant according to claim 1, wherein the composition further comprises a surfactant.
21. The coated proppant according to claim 20, wherein the surfactant is one or more of anionic or nonionic surfactants.

22. The coated proppant according to claim 20, wherein the composition comprises about 0 to about 1 wt. % of surfactant.
FIG. 4

Fracture Toughness K1c

- Example 1: Tg = 133°C
- Example 4: Tg = 135°C
- Example 5: Tg = 191°C
- Example 7: Tg = 185°C

K1c RT
K1c 125°C