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NANOPARTICLES AS STRENGTHENING AGENTS IN POLYMER SYSTEMS

By

NAUREEN SHAHID

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE
DOCTOR OF PHILOSOPHY

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Abstract

Nanoparticles as Strengthening Agents in Polymer Systems

by

Naureen Shahid

Carboxylate-substituted alumina nanoparticles are produced solvent free using mechanical shear. The general nature of this method has been demonstrated for L-lysine-, stearate, and $p$-hydroxybenzoate-derived materials. The reaction rate and particle size is controlled by a combination of temperature and shear rate. The nanoparticles are spectroscopically equivalent to those reported from aqueous syntheses, however, the average particle size can be decreased and the particle size distribution narrowed depending on the reaction conditions.

Lysine and $p$-hydroxybenzoato alumoxanes have been introduced in carbon fiber reinforced epoxide resin composites. Different preparation conditions have been studied to obtain composite with enhanced performances that are ideal for the motor sports and aerospace industries.

A new composite material has been fabricated utilizing surface-modified carboxylate alumoxane nanoparticles and the biodegradable polymer poly(propylene fumarate)/poly(propylene fumarate)-diacrylate (PPF/PPF-DA). For this study, composites were prepared using various functional groups including: a surfactant alumoxane to enhance nanoparticle dispersion into the polymer; an activated-alumoxane to enhance nanoparticle interaction with the polymer matrix; a mixed alumoxane containing both activated and surfactant groups. Nanocomposites prepared with all types of alumoxane, as well as blank polymer resin and unmodified boehmite, underwent mechanical testing and were characterized by SEM and microprobe analysis. A nanocomposite composed of mixed alumoxane nanoparticles dispersed in PPF/PPF-DA exhibited increased flexural
modulus compared to polymer resin alone, and a significant enhancement over both the activated and surfacted alumoxanes.

Boric acid is used as the cross-linking agent in oil well drilling industry even though the efficacy of the borate ion, [B(OH)₄]⁻, as a cross-linking agent is poor. The reaction product of boric acid and the polysaccharide guaran (the major component of guar gum) has been investigated by ¹¹B NMR spectroscopy. By comparison with the ¹¹B NMR of boric acid and phenyl boronic acid complexes of 1,2-diols [HOCH₂CH₂OH, cis-C₆H₁₀(OH)₂, trans-C₆H₁₀(OH)₂, o-C₆H₄(OH)₂], 1,3-diols (neol-H₂), monosaccharides (L-fucose, mannose and galactose) and disaccharides (celloboiße and sucrose) it is found that the guaran polymer is cross-linked via a borate complex of two 1,2-diols both forming chelate 5-membered ring cycles, this contrasts with previous proposals. Based upon steric constraints it has been shown that there is preferential cross-linking occurs in the guaran polymer via the 3,4-diols of the galactose side chain. The ΔH and ΔS for complexation of boric acid to cis- and trans-1,2-cyclohexanediol have been determined, from the temperature dependence of the appropriate equilibrium constants, and used in conjunction with ab initio calculations on model compounds, to understand prior conflicting proposals for guaran-boric acid interactions. ¹¹B NMR derived pH dependent equilibrium constants and ab initio calculations have been used to understand the reasons for the inefficiency of boric acid to cross-link guaran (almost 2 borate ions per 3 monosaccharide repeat unit are required for a viscous gel suitable as a fracturing fluid): the most reactive sites on the component saccharides (mannose and galactose) are precluded from reaction by the nature of the guar structure; the comparable acidity (pKₐ) of the remaining guaran alcohol substituents and the water solvent, results in a competition between cross-linking and borate formation; a significant fraction of the boric acid is ineffective in cross-linking guar due to the modest equilibrium (Kₑq). In contrast to prior work, the study presents evidence for the reaction of alcohols with boric
acid, rather than the borate anion. Based up the results obtained for phenyl boronic acid alternative cross-linking agents are proposed.
“Nothing in life is to be feared. It is only to be understood.”

- Marie Curie
Acknowledgements

First, I would like to thank my advisor, Professor Andrew R. Barron, for his guidance, encouragement and support. He provided a stimulating research environment, and suggested many interesting projects, and I thank him for this wonderful opportunity. I would like to thank Professors Wilson and Mikos for kindly agreeing to be on my thesis committee. I would like to thank Dr. Larry Alemany for his patient help with NMR experiments and Professor Barrera for allowing me access to his laboratory. I enjoyed collaborating with Mr. Ricardo Villate of the Alltech Group and Ms. Kathy Chung of NASA and I would like to thank both of them. The members of the Barron Lab created a great research environment and made graduate school enjoyable, and I would like to thank them all. Amit Mistry and Adam Horch were wonderful colleagues. I thank Jane McNeel for her helpful advice and encouragement. Anirban Mandal, Rajarshi Bandyopadhyay and Sitaram Iyer helped me in countless ways. Finally, I would like to thank my husband Sanjeeb Dash for his tireless support throughout my Ph.D.
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<tr>
<td>A-A</td>
<td>acetic-alumoxane</td>
</tr>
<tr>
<td>alumina</td>
<td>Al₂O₃ in any phase</td>
</tr>
<tr>
<td>alumoxane</td>
<td>An oligomeric or polymeric material consisting of an Al-O backbone and containing various pendant groups</td>
</tr>
<tr>
<td>amorphous</td>
<td>Lacking in crystallinity</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>avg.</td>
<td>average</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom, 10⁻¹⁰ m</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett, and Teller method</td>
</tr>
<tr>
<td>bioactive</td>
<td>A material having an interfacial response that results in tissue bonding. The prerequisite for this interfacial response of the tissue is that the bioactive material is not corrosion resistant in the body. It must be resorbent; it must be soluble but only very slowly</td>
</tr>
<tr>
<td>bioengineering</td>
<td>The application of engineering principals to the solution of problems</td>
</tr>
<tr>
<td>biomaterial</td>
<td>Living or processed tissues or materials used to reproduce the function of living tissue in conjugation with them</td>
</tr>
<tr>
<td>bleeder cloth</td>
<td>Usually a felt-like, non-woven material used in vacuum molding that soaks up excess resin during cure. Also allows removal of air during application of vacuum</td>
</tr>
<tr>
<td>bioengineering</td>
<td>The application of engineering principals to the solution of problems</td>
</tr>
<tr>
<td>biomaterial</td>
<td>Living or processed tissues or materials used to reproduce the function of living tissue in conjugation with them</td>
</tr>
<tr>
<td>boehmite</td>
<td>γ-alumina, AlO(OH), a naturally occurring material</td>
</tr>
</tbody>
</table>
°C  degree centigrade
ccp  cubic close-packed
cm  centimeter, $10^{-2}$ m
ceramic  A class of inorganic, non-metallic material which is subjected to
temperatures in excess of 500 °C for the purposes of manufacture
or use
composite  A material created by combining a fiber reinforcement with a resin
matrix
composite resin  A functionalized carboxylate-alumoxane incorporated into a
commercially available epoxy and hardener system
contact angle  The interior angle formed between the edge of a solvent “bubble”
and the surface on which it rests. Angles are measured either
advancing or receding; low numbers reflect hydrophilic surfaces
(“wetting”) while high numbers represent hydrophobic surfaces
(“non-wetting”)
cross-linking agent  A compound with reactive functional groups that can ring open an
epoxy resin
cure point  The point at which an epoxide cross-linking reaction reaches
completion
curing temperature  The temperature at which a resin impregnated reinforcement is
intended to be cured
curing time  The period of time that a molded component is required to be
cured prior to removal from the mould
δ  delta, chemical shift (NMR)
DTA  differential thermal analysis
DER 332  diglycidyl ether of bisphenol-A
d  doublet (NMR)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta, \delta$</td>
<td>change, or difference</td>
</tr>
<tr>
<td>epoxy resin</td>
<td>A polyether resin most commonly formed by the reaction of bisphenol-A and epichlorohydrin</td>
</tr>
<tr>
<td>Eq.</td>
<td>equation</td>
</tr>
<tr>
<td>FID</td>
<td>free induction decay</td>
</tr>
<tr>
<td>fatigue</td>
<td>Failure fracture that occurs as a result of cyclic or repetitive loading of a device</td>
</tr>
<tr>
<td>fabric</td>
<td>A material made by intertwining yarns, fibers or filaments into a flat flexible sheet</td>
</tr>
<tr>
<td>femur</td>
<td>The bone of the upper leg or the thigh</td>
</tr>
<tr>
<td>flexural strength</td>
<td>The resistance of a fiber or material to bending forces; the ultimate strength of a material at the point of failure when subjected to bending forces</td>
</tr>
<tr>
<td>g</td>
<td>grams</td>
</tr>
<tr>
<td>GPa</td>
<td>giga-pascals, $10^9$ Pa</td>
</tr>
<tr>
<td>guar gum</td>
<td>It is a mannogalactan gum extracted from the seeds of <em>Cyanmopsis tetragonoloba</em>, an annual legume plant. The term “guar” is thought to be derived from the Sanskrit word go or gov, meaning “cow”</td>
</tr>
<tr>
<td>hardener</td>
<td>A compound containing both a cross-linking agent and a base catalyst</td>
</tr>
<tr>
<td>hardness</td>
<td>A measure of scratch resistance</td>
</tr>
<tr>
<td>hcp</td>
<td>hexagonal close-packed</td>
</tr>
<tr>
<td>hybrid resin</td>
<td>A functionalized carboxylate-alumoxane cross-linked with an epoxy resin (no additional hardener is used)</td>
</tr>
<tr>
<td>Hz</td>
<td>hertz</td>
</tr>
<tr>
<td>implant</td>
<td>Any medical device, made from one or more biomaterials, intentionally placed within the body, either totally or partially</td>
</tr>
</tbody>
</table>
buried beneath an epithelial surface, where it is intended to remain for a significant period

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>impregnate</td>
<td>Wet out the reinforcement fabric with resin</td>
</tr>
<tr>
<td>IR</td>
<td>infrared spectroscopy</td>
</tr>
<tr>
<td>kHz</td>
<td>kilohertz, $10^3$ Hz</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>lambda, wavelength</td>
</tr>
<tr>
<td>L</td>
<td>liters</td>
</tr>
<tr>
<td>L-A</td>
<td>Lysine-alumoxane</td>
</tr>
<tr>
<td>L-H</td>
<td>Lysine acid</td>
</tr>
<tr>
<td>m</td>
<td>meta</td>
</tr>
<tr>
<td>m</td>
<td>meters, medium, multiplet</td>
</tr>
<tr>
<td>$\mu$m</td>
<td>micro-meters, $10^{-6}$ m</td>
</tr>
<tr>
<td>$\mu$s</td>
<td>micro-seconds, $10^{-6}$ s</td>
</tr>
<tr>
<td>min</td>
<td>minutes</td>
</tr>
<tr>
<td>mL</td>
<td>milliliters, $10^{-3}$ L</td>
</tr>
<tr>
<td>mm</td>
<td>millimeters, $10^{-3}$ m</td>
</tr>
<tr>
<td>modulus</td>
<td>A physical property of materials, it is a constant relating stress to strain and is a measure of elasticity</td>
</tr>
<tr>
<td>mol</td>
<td>mole</td>
</tr>
<tr>
<td>Mp</td>
<td>melting point</td>
</tr>
<tr>
<td>MPa</td>
<td>mega-pascals, $10^6$ Pa</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectroscopy</td>
</tr>
<tr>
<td>mwt, $M_w$</td>
<td>molecular weight</td>
</tr>
<tr>
<td>nm</td>
<td>nanometers, $10^{-9}$ m</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>$o$</td>
<td>ortho</td>
</tr>
<tr>
<td>$p$</td>
<td>para</td>
</tr>
</tbody>
</table>
\( p\text{-HB-alumoxane} \)  \textit{para}-hydroxybenzoate-alumoxane

\( \text{ppm} \) parts per million

\( \text{Pa} \) pascals

\( \text{Ph} \) phenyl, \(-\text{C}_6\text{H}_5\)

\( \text{PMMA} \) polymethyl methacrylate

\( \text{pot life} \) The period of time, also known as its ‘working life’, that a quality of catalyst resin remains in a workable liquid form before it gels

\( \text{pressure molding} \) A form of molding requiring the used of matched male and female moulds, which are pressed together to apply pressure to a laminate during cure

\( \text{R} \) alkyl group

\( \text{reinforcement} \) A fiber, or assemblage of fibers embedded into and bonded by a cured plastic resin matrix, which greatly enhance the mechanical properties of the matrix

\( \text{release agent} \) A chemical that is applied to the surface of a mold prior to laminating to prevent the resin in the laminate from bonding to the mold

\( \text{s} \) second, singlet (NMR), sharp (IR)

\( \text{SEI} \) secondary electron image

\( \text{SEM} \) scanning electron microscopy

\( \text{sintering} \) General term for densification of a powder compact or solid by heating to produce crystallinity

\( \text{specific stiffness} \) Stiffness relative to density

\( \text{strength} \) A measurement of tensile, torsional, or other strains

\( \text{surface area} \) The area, per unit weight of a granular or powdered or formed porous solid, of all external plus internal surfaces that are accessible to a penetrating gas
<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>t</td>
<td>triplet (NMR)</td>
</tr>
<tr>
<td>tensile strength</td>
<td>The maximum load a cross-sectional area can bear prior to failure</td>
</tr>
<tr>
<td>thread count</td>
<td>The number of threads per distance across or along a woven fabric</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>vitallium alloy</td>
<td>An alloy or 60% cobalt, 20% chromium, 5% molybdenum, and traces of other substances</td>
</tr>
<tr>
<td>wet out</td>
<td>The process of ensuring that a fabric is fully impregnated with resin</td>
</tr>
<tr>
<td>wt:wt</td>
<td>ratio of parts by weight</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
Introduction

Carboxylate Alumoxanes

Aluminum is the most abundant metal in the earth's crust (8.3 wt%). It is a major constituent of minerals such as feldspars, micas, spinels, and garnets. Aluminum derives its name from alum, the commonly used name for K[Al(SO₄)₂].12(H₂O). Even though alum was known since ancient times, aluminum chemistry research began when the element was isolated in the late eighteenth century by the Danish scientist H. C. Ørsted. Metallic aluminum was first isolated by the reduction of aluminum trichloride with potassium or sodium. A commercially viable method for obtaining aluminum metal, by the electrolysis of alumina dissolved in cryolite, was independently discovered in 1886 by Hall in the U.S. and by Heroult in France (the Hall-Heroult process).

Cryolite, a natural ore found in Greenland, is no longer widely used in commercial production. Instead, aluminum is mined as bauxite (typically Al₂O₃.2H₂O), which contains Fe₂O₃, SiO₂, and other impurities. Today aluminum is primarily isolated by the Bayer process; named for Les Baux de Provence in southern France, where geologist Pierre Berthier first discovered it in 1821. Treatment of bauxite with sodium hydroxide solution results in the formation of sodium aluminate and sodium silicate, while the iron remains behind as a solid. When CO₂ is blown through the resulting solution, the sodium silicate stays in solution while the aluminum silicate reacts and is precipitated out as aluminum hydroxide. The hydroxide is filtered, washed, and heated to form pure alumina, Al₂O₃. Metallic aluminum is obtained by electrolysis of pure Al₂O₃ dissolved in Na₃AlF₆ at a temperature between 940 and 980 °C in a carbon lined steel cell acting as the cathode with carbon anodes. As a general rule, four tons of bauxite is required to produce two tons of alumina, which, in turn, provide one ton of aluminum metal. The primary commercial considerations for aluminum production are therefore, the availability of bauxite and inexpensive electric power. The world production (1988)
exceeded 17 million tons per annum, the leading producers being the USA (23%), China (21%) the former Soviet Union (14%), Canada (9%), Australia (7%), and Brazil, Norway and Czechoslovakia (5% each).\(^1\)

In addition to their use in aluminum metal production, aluminum oxides and hydroxides are of great commercial importance themselves, because they have excellent physical and chemical properties and can be prepared by relatively low cost raw materials.\(^1,4\) The annual production is over 30 million tons, and is used as abrasives, refractories, catalysts, catalyst supports, ion exchangers, and in a diverse range of advanced, technical and fine ceramic materials.\(^3\) The main structural types of aluminum oxides and hydroxides are corundum (\(\alpha\)-Al\(_2\)O\(_3\)), diaspore [\(\alpha\)-AlO(OH)], bayerite [\(\alpha\)-Al(OH)\(_3\)], boehmite [\(\gamma\)-AlO(OH)], and gibbsite [\(\gamma\)-Al(OH)\(_3\)].\(^1,4,5\) In addition, numerous transitional phases and structural modifications have been characterized during partial dehydration.\(^4,5,6\)

The many crystalline forms of aluminum oxides and hydroxides are linked by complex structural relationships. For example, the mineral bauxite has the formula Al\(_x\)(OH)\(_{3-2x}\) (0 < x < 1) and is a mixture of \(\alpha\)-Al\(_2\)O\(_3\), \(\gamma\)-Al(OH)\(_3\), and \(\gamma\)-AlO(OH).\(^1\) Diaspore, \(\alpha\)-AlO(OH), is a polymorph of boehmite, has an ideal structure comprising a hexagonal close-packed (hcp) array of oxygen atoms with continuous chains of edge-shared octahedra stacked in layers and further interconnected by hydrogen bonds, with aluminum atoms in certain octahedrally coordinated sites.\(^4\) The structure of boehmite differs from diapore in that it is not close-packed overall, but within each layer of AlO\(_6\) octahedra the oxygen atoms are arranged in cubic close-packing (ccp). The structure of boehmite is shown in Figure I.1.

Alumina based ceramics are typically produced through the “sol-gel” method. In this process, a water dispersion of an aluminum oxide (the “sol”) is initially formed; the solvent is slowly evaporated to leave a gel that is then dried, and finally fired to yield the ceramic body. This is a “bottom-up” synthetic approach as it consists of reacting small
**Figure I.1.** The topographic structure of boehmite, $\gamma$-AlO(OH), showing the continuous chains of edge-shared octahedra stacked in layers and the interconnecting hydrogen bonding (double lines).

Inorganic molecules to form larger oligomeric and polymeric materials (Eq. I.1).

$$\text{Al(OR)}_3 + \text{H}_2\text{O}/\text{H}^+ \rightarrow \text{Al-gel} \xrightarrow{\Delta} \text{Al}_2\text{O}_3$$  \hspace{1cm} (I.1)

These sol-gel intermediates that are formed during the process of aluminum hydrolysis are known as alumoxanes. They were first reported in 1958 by Andrianov, and were proposed to consist of linear (I) or cyclic (II) chains (i.e., analogous to that of polysiloxanes). Research by the Barron group has since redefined the structural view of alumoxanes, revealing that they are not truly polymeric but three-dimensional cage compounds. In addition it has been shown that the hydrolytically stable siloxy-alumoxanes \([\text{Al(O)(OH)}_x(\text{OSiR}_3)_{1-x}]_n\), consist of an aluminum-oxygen core structure (III) analogous to that found in boehmite \([\text{Al(O)(OH)}]_n\), with a siloxide substituted periphery.

The result of this discovery led to research to find out whether instead of the traditional “bottom-up” approach used to synthesize alumoxanes from low molecular
weight precursors, a top down approach to these compounds in a “one pot” synthesis using readily available material could be accomplished.$^{14}$

Previous work in the Barron research group at Rice University had established that the “organic” unit itself in the siloxy-alumoxanes contained aluminum, i.e., IV.$^{12}$ In order to similarly prepare an alumoxane with a siloxide substituted periphery, the anionic moiety [Al(OH)$_2$(OSiR$_3$)$_2$]$^-$ would be required as a bridging group; adding this unit clearly present a significant synthetic challenge. The carboxylate anion, [RCO$_2$]$^-$, is an isoelectronic and isostructural analog of the organic periphery found in the previously reported siloxy-alumoxanes, (IV and V).

Following this rationale, a "top-down" approach was developed based upon the reaction of boehmite, [Al(O)(OH)$_n$], with carboxylic acids (Eq. 1.2).$^{14}$ This reaction resulted in the formation of carboxylate-alumoxane nanoparticles, [Al(O)$_n$(OH)$_y$(O$_2$CR)$_2$]$_n$ (V).
\[
[\text{Al(O)OH}]_n \xrightarrow{\text{HO}_2\text{CR}} [\text{Al(O)}_x\text{(OH)}_y\text{(O}_2\text{CR})_z]_n
\] (I.2)

A wide range of carboxylate alumoxanes have been prepared using a range of acids, including, methoxyethoxyethoxyacetic acid \([\text{HO}_2\text{CCH}_2(\text{OCH}_2\text{CH}_2)_2\text{OCH}_3, \text{MEEA-H}],\) methoxyethoxyacetic acid \([\text{HO}_2\text{CCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3, \text{MEA-H}],\) methoxyacetic acid \([\text{HO}_2\text{CCH}_2\text{OCH}_3, \text{MA-H}],\) acetic acid \([\text{HO}_2\text{CCH}_3, \text{A-H}],\) gluconic acid \([\text{HO}_2(\text{CHOH})_4\text{CH}_2\text{OH, glu-H}],\) \(\text{para-hydroxybenzoic acid [HO}_2\text{CC}_6\text{H}_4\text{OH, p-HB-H}],\) and lysine \([\text{HO}_2\text{CCH}(\text{NH}_2)(\text{CH}_2)_4\text{NH}_2, \text{L-H}].\)\(^{14,15,16,17}\) For simplicity the alumoxanes will be referred to by the acronym of the acid, i.e., \(\text{A-alumoxane rather than acetate-alumoxane.}\)

Pseudoboehmite and the appropriate carboxylic acid were reacted in water to yield the respective carboxylate-alumoxane, see Figure I.2.\(^{15}\) The carboxylate-alumoxanes prepared in aqueous solution are spectroscopically similar to their analogs prepared in xylene: the solution \(^{27}\text{Al NMR spectra indicates that aluminum is in an octahedral AIO}_6\) coordination environment and the IR spectra is consistent with a bridging mode of coordination of the carboxylate to the boehmite-like core.

The Barron researchers also found that the solubilities of these carboxylate-alumoxanes depend on the identity of the carboxylic acid. Solution particle size measurements were performed in water on some carboxylate-alumoxanes by photon correlation spectroscopy (PCS), shown in Figure I.3.\(^{15}\) The particle size number average follows the order MEEA-alumoxane (67 nm) > MEA-alumoxane (50 nm) > A-alumoxane (28 nm), consistent with their formation via the cleavage of the significantly larger boehmite starting material (30 - 100 \(\mu\text{m})).\(^{15}\)

The particle size distribution follows the same order. Gel permeation chromatography (GPC) measurements in \(\text{HOC(H)(CF}_3)_2\) for the samples of MEEA-,
Figure 1.2. Pictorial representation of the reaction with boehmite and carboxylic acids to form carboxylate-alumoxanes. The shaded triangles represent a side view of the aluminum-oxygen fused octahedra, while the carboxylate groups are represented by a semicircle with bar.

MEA-, and MA-alumoxane, are consistent with the PCS data. The pH dependence of each of the previously mentioned alumoxanes has been determined and shows that particle size increases with increasing pH. In all cases, the particle size increases linearly to up a pH of 6 after which point the size increase become exponential. Based upon the spectroscopic characterization the carboxylate-alumoxanes are best considered to be nano-particles of aluminum oxide hydroxide (or boehmite) that are capped with carboxylate residues.

Despite the ease of synthesis of the alumoxanes, it was found that when prepared in organic solutions produce a large amount of undesirable organic solvent as waste. When water was used as the solvent this could be mitigated, however, the reaction
Figure 1.3. A plot of particle size distribution, determined by photon correlation spectroscopy (PCS), of the MEEA-, MEA-, and A-alumoxanes in water.\textsuperscript{15}

The product has to be washed many times with Et$_2$O to get a clean batch of alumoxane. Also all the alumoxanes produced by the solution methods require a long reaction time to get the desired partial sizes. Particle size was found to be controlled by the solution pH, allowing for post processing control.\textsuperscript{18} Additional work showed that the size of the alumoxane particle is important in determining the porosity of a ceramic formed from those particles.\textsuperscript{19} It would be desirable to develop a low waste method to uniformly small particles. As a result, reactions have been designed so that the desired alumoxanes are prepared in the solid state using minimum time and getting smaller particles at lower reaction time. These results are described in Chapter 1.

Prior research in the Barron group demonstrated that alumoxanes containing chemically functional substituents (i.e., those containing a substituent that allows further
reaction) could be used as a component in polymeric resin systems.\textsuperscript{16,17,20} These studies were limited to simple two or three part epoxide systems, in which the alumoxane replaced all or some of the hardener usually mixed with an epoxy resin. For aerospace and automotive composites the use of fiber reinforcement is very important. Chapter 2 describes the effect of introducing chemically functionalized alumoxanes in carbon fiber reinforced epoxide resin composites. Although prior work was limited to epoxides, the range of potential use of polymers is extensive.\textsuperscript{21} Chapter 3 describes the application of carboxylate alumoxanes as a nanoscale reinforcement of the biodegradable polymer poly(propylene fumarate)/poly(propylene fumarate)-diacrylate (PPF/PPF-DA).

The function of the alumoxanes in both the epoxide and PPF/PPF-DA composites is to cross-link the polymer. The effect of cross-linking is to increase composite strength and also potentially limit diffusion through the composite. A commercially significant cross-linking reaction is that of the guaran polymer in guar gum for down hole applications in the oil and gas industry.\textsuperscript{22} Boric acid is used for the cross-linking reaction in a manner similar to that of the alumoxanes as described in Chapters 2 and 3. The efficacy of the borate ion, [B(OH)\textsubscript{4}]\textsuperscript{-}, as a cross-linking agent is poor, despite its commercial usage. Chapter 4 details our investigation of the reasons why boric acid is not ideal.

Reference


7 The term alumoxane is commonly used to describe a species containing an oxo (O2-) bridge binding (at least) two aluminum atoms, i.e., Al-O-Al.


9 S. Pasynkiewicz, Polyhedron, 1990, 9, 429.


Chapter 1

Solvent free synthesis of carboxylate-alumoxane nanoparticles using mechanical shear

Introduction

Particles with a diameter of less than 1 micrometer can be found in daily use in a broad range of applications: for example, silicon dioxide (SiO$_2$) is used in cosmetics and toothpastes; titanium dioxide (TiO$_2$) is a component of sunscreen lotions and also constitutes the pigments in paints. The new and promising effects generated by nanoparticles, however, increase significantly when the particle diameter is reduced below 0.1 micrometers (100 nm). The transition from microparticles to nano particles can lead to a number of changes in physical properties. Two of the major factors in this are the increase in the ratio of the surface-area-to-volume, and the size of the particle moving in to the realm where quantum effect predominates.

Nanoparticles have been used for a very long time. Probably the earliest use was glazes for early dynasty Chinese porcelain. A Roman cup, called the Lycurgus cup,$^1$ used nanosized gold clusters to create different colors depending whether it was illuminated from the front or the back. The increase in the surface-area-to-volume ratio, as the particle gets smaller, leads to an increasing dominance of the behavior of the atoms on the surface of a particle over that of those in the interior of the particle. This affects both the properties of the particle in isolation and its interaction with other materials. The large surface area of nano particles results in a lot of interactions between the intermixed materials in nanocomposites, leading to special properties such as increased strength and increased chemical/heat resistance.$^2$

Ceramic nanoparticles are already commercially available from a number of companies worldwide. Typical materials include oxides of aluminum, zinc, copper, and cerium, with applications in personal care, sunscreens, abrasion-resistant coatings,
environmental catalysts, antimicrobial products, and a variety of polishing applications. The majority of commercial ceramic nanoparticles are produced using plasma-based processes in which specialized reactors are used to flash chemical precursors at extreme temperatures. While scalable and allowing for control over particle size, these processes are energy-intensive and require significant specialized equipment. Although less common in commercial production, sol-gel style processes have been demonstrated to yield nanoparticle ceramics with good size uniformity. Of particular note is the formation of highly controllable silica nanospheres. As with plasma processing, sol-gel synthesis involves a “bottom-up” approach in which a molecular precursor is converted to an oxide. However, whereas plasma formed nanoparticles are ‘pure’ ceramic, those formed from sol-gel often contain organic surface functional groups to provide stabilization or a particular required chemical property. In 1992, the Barron researchers outlined a solvent-based “top-down” approach to the formation of chemically functionalized alumina nanoparticles. This method involved the reaction of boehmite with carboxylic acids resulting in the formation of carboxylate-substituted alumina nanoparticles or ‘carboxylate-alumoxanes’, shown in Figure I.2. Initially, the syntheses were performed in xylene, but in an effort to develop a more environmentally benign process it was switched to an aqueous system. However, the synthesis was still a batch process, and since the key driver of a nanoparticle’s cost and performance is the viability of its manufacturing process, the synthesize carboxylate-alumoxanes in a solvent free, and potentially continuous, process has been developed.

**Results and Discussion**

Mechanical shear has previously been shown to allow for the exfoliation of clays in polymer matrices. Since the reaction of boehmite with carboxylic acids may be classed as a reactive exfoliation process (Figure 1.1), shear-based reactions have been
investigated over here. In particular for alumoxanes derived from solid carboxylic acids, e.g., lysine-alumoxane.\textsuperscript{8,9}

**Figure 1.1.** Typical torque/time plot for the shear mixing of L-lysine and boehmite at a reaction temperature of 80 °C and a mixing rate of 60 rpm.

The reaction time was calculated, from the torque versus time plot (e.g., Figure 1.1), to be the time at which the torque shows a sharp reduction. Multiple reaction runs showed a maximum variation of 6 min. in reaction time between samples. Samples were studied as prepared or extracted into water to allow for the removal of any unreacted boehmite. Such solutions were dried in vacuum or precipitated with ethanol. The resulting white solid was air-dried and characterized by thermogravimetric analysis (TGA), IR spectroscopy and molecular weight measurements.

As may be seen from Figure 1.2a the time for the reaction between the carboxylic acid and boehmite at a constant mixing rate reduces dramatically between 70 and 80 °C, with a smaller further decrease at 130 °C. A reaction time of \textit{ca.} 40 min. at 100 °C should be compared to reactions times in excess of 8 h. in aqueous solution at the same
temperature.\textsuperscript{6,7} The average particle sizes of the alumoxanes produced at and above 80 °C (1 – 2 nm) are significantly smaller than those observed for solution based synthesis (ca. 25 nm).\textsuperscript{8} Furthermore, the particle size distribution in all cases is narrower than observed for solution synthesis. For example, samples produced at 110 °C with a mixing rate of 80 rpm have a particle size and distribution of 1.5±1 nm. All samples with particle sizes of 2 nm or less have similar distributions. This is in contrast to the solution method where lysine-alumoxane has been prepared with a particle size and distribution of 25±13 nm. Obviously samples with large particle sizes have correspondingly large distributions, e.g., samples produced at 60 °C with a mixing rate of 60 rpm have a particle size and distribution of 1800 ±600 nm.

An example of the effect of rotation speed (and hence shear rate) is observed in Figure 1.2b. At any particular temperature the particle size decreases. While particle size appears to be less dependent on mixing speed than temperature, the reaction times may be further decreased by increased rotation speeds.

The relative organic content (as measured by ceramic yield) is a function of the particle size. The ceramic yield for samples made in solution as compared to those made by shear mixing is as follows: L-lysine-alumoxane (18% versus 23%), p-hydroxybenzoate-alumoxane (23% versus 35%), and stearate-alumoxane (8% versus 28%). It has been previously observed that the reaction rates and particle size correlate in part with the pK_a of the acid,\textsuperscript{4,6} however in the present case the melting point of the acid is also a factor.

**Conclusions**

We have shown that for carboxylate-alumoxane nanoparticle synthesis, shear mixing dramatically reduces reaction times under comparable temperatures when compared to solution methods. Furthermore, lower temperatures than usually employed may be used providing potential additional energy savings. It should be noted that the rapid reactions is not only due to concentration affects. The present study shows
Figure 1.2. Plots of average particle size (●, nm) and reaction time (□, min.) as a function of (a) reaction temperature (°C) at constant mixing rate (60 rpm), and (b) mixing rate (rpm) at constant reaction temperature (110 °C).

significant reductions in reaction time (along with much smaller particle sizes) in comparison to the synthesis of a range of carboxylate-alumoxanes in neat carboxylic acid, where only large particles are formed even after extended reaction times (> 12 h.).³ The
smaller sizes resulting from shear synthesis allows for better dispersion of the nanoparticles, which is especially important in polymer composite applications.\textsuperscript{6}

**Experimental Section**

Samples of L-lysine (97%, Aldrich) were mixed with boehmite (Vista Chemical Company) in a Haake Rheomixer 600 miniaturized internal mixer, fitted with roller style blades and internal heating elements, at temperatures ranging from 60 - 130 °C and roller rates of 60 - 110 rpm. The temperature range was chosen to bracket the reaction temperatures ordinarily employed for carboxylate-alumoxane synthesis.\textsuperscript{5,6,8} The heaters and the roller rotors were allowed to reach the desired temperature and rpm, respectively, prior to the addition the boehmite to the carboxylic acid. Each experiment was allowed to run for 120 min.

The miniaturized internal mixer (MIM) consists of three independent sections, each heated and controlled by its own heater and temperature controller. The mixing chamber is shaped like a figure eight, with rotor in each chamber. The mixing rotors revolve in opposite directions and at different controlled speed, to achieve shear action. MIM’s have two characteristic geometric features; they have a narrow a gap between the rotor wings and the mixer wall and a large space between the rotors. The mixture is sheared repeatedly through the narrow gap and recycled to the core of the mixture between the rotors. The rotors themselves have helical projection that performs additional axial mixing by moving the mixture around the rotor and towards the center. Extensive mixing takes place exclusively in the core of the mixture while dispersion occurs in the vicinity of the narrow gap under the rotor wing, in which high shear stresses are created exposing the agglomerates to hydrodynamic forces that will tend to break up the agglomerates.

Using a standard set of conditions samples of stearate-alumoxane and p-hydroxybenzoate-alumoxane were prepared under conditions analogous to those of L-
lysine-alumoxane. The relative rates of reaction for these acids, as compared to L-lysine (23 min) under identical conditions (110 °C, 90 RPM), are as follows: p-hydroxybenzoate-alumoxane (125 min.) and stearate-alumoxane (238 min.).

IR spectra of all the carboxylate-alumoxanes, prepared above, contain bands at 1596 - 1586 and 1473 - 1466 cm⁻¹, consistent with the bridging mode of coordination of the carboxylate to the boehmite core we have previously described.¹⁰ TGA measurements showed ceramic yields appropriate to the measured particle size,⁹ when compared to samples prepared in aqueous solution.

Particle size measurements were obtained on a Coulter N4 Plus Particle Size Analyzer at an angle of 90° and a concentration of 1.0 g.L⁻¹. The water used for dispersing the alumoxanes was distilled and filtered (using a 0.2 μm filter) prior to use.

References


(a) R. Wagener and T. J. G. Reisinger, *Polymer*, 2003, 44, 7513


(a) Y. Koide and A. R. Barron, *Organometallics*, 1995, 14, 4026
Chapter 2
Chemically Functionalized Alumina Nanoparticle Effect on Carbon Fiber/Epoxy Composites

Introduction

Fibrous materials are known to have some of the best mechanical properties of all available structural materials; yet they have less ability to cope on their own with bending and compression loads. However, it is possible to take full advantage of the outstanding strength and stiffness that becomes available by embedding fibers in a matrix such as cured resin. A fiber reinforced plastic (FRP) composite material is a mass of reinforcing fibers combined with a plastic ‘resin’ matrix that binds and holds them. The properties of the resulting material depend on the properties of the fiber, the properties of the resin and the manner in which the two are combined. The physical processes involved in FRP molding are not particularly complex even though the chemical ones are. FRP’s have been widely adopted in the motorsports and aerospace industries for various reasons, primarily because of their performance and the ease in which low volume parts can be manufactured.

Carbon fibers were originally produced and used commercially in the late 19th century by Sir Joseph Swan and Thomas Edison, to provide the filament material in the first electric light bulbs. Finally, in 1963, structurally useful carbon fibers were produced at the Royal Aircraft Establishment at Farnborough in the United Kingdom. At that time carbon fiber was an extremely expensive materials and it use could only be financially supported by an aerospace program research budget. Today, raw carbon fibers are widely produced by controlled thermal treatment of polyacrylonitrile (PAN) precursor fibers and as a result the application of carbon fibers has moved into the automotive and sports industries. Cellulose and fibers produced from coal tar pitch are also used as precursors. The precursor fibers are heated to ‘carbonize’ away non-carbonaceous matter. This is
followed by the graphitization of the fibers at the temperatures in the range 2,600 - 3,000 °C. This process, and the deliberate prevention of shrinkage, arranges the carbon atoms into an ordered, graphitic crystalline structure along the length of the filaments. It is this aligned structure that gives the fibers their useful mechanical properties, namely high strength and stiffness. Carbon fibers have the highest specific stiffness of any currently commercially available fiber in addition to having high tensile and compressive strength, and good resistance to corrosion and fatigue.

Whereas non-woven fabrics are made up of randomly oriented fibers, in woven fabrics the fibers are aligned in specific orientations (Figure 2.1). A wide range of styles and weights of woven reinforcing fabrics is available just by the flexibility of weave styles and thread count. Woven fabrics need less resin to wet them out fully and this produces a high fiber volume fraction (i.e., a high fiber:resin ratio). The function of the resin system is to combine with and bond to the reinforcing fibers so that loads may be supported by the latter and transmitted through the material from fiber to fiber. It also stabilizes the fiber against buckling under compressive loads and protects them from mechanical and environmental damage. Thermoset resins, such as epoxy resins, start off as liquids but are turned irreversibly into solids by the application of heat or chemical reaction.

Epoxy resins are easily extruded and/or molded, have moderate strength, and low hardness.⁴ Common resin systems usually consist of two parts, a resin and a hardener, which are mixed and cured at elevated temperatures (50 – 100 °C).⁵ A schematic representation of the formation of a two-part epoxy resin is shown in Figure 2.2a. The resin component is commonly a low molecular weight bi-functional oxirane (i.e., epoxide-ring containing molecule), while the hardener⁶ contains both the cross-linking agent and the catalyst.⁷ The materials used most often for reaction with the oxirane ring are primary and secondary amines and hydroxyl groups.⁸ Modifiers include flexibilizers
e.g., long chain aliphatic di-epoxides) and cross-link density improvers (e.g., multi functional novolac resins).\textsuperscript{9,10,11}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{carbon_fiber_fabric.jpg}
\caption{Photograph of a typical carbon fiber fabric showing twill weave.}
\end{figure}

In general, unfilled thermoset polymers tend to be harder and more brittle than thermoplastic polymers. Thus, it is common practice to add multiple phases (i.e., fillers, modifiers, etc.) to thermosetting polymers to improve their physical properties (e.g., Figure 2.2b). In addition, the incorporation of fillers into the polymer matrices also strengthens and stiffens the material allowing for use in an expanded range of structural applications.\textsuperscript{9}

Inorganic ceramic fillers impart a number of desirable mechanical and barrier properties to the polymer. These properties include improved tensile strength, stiffness, abrasion resistance, dimensional stability and barriers to gases, solvents and water vapor. As a second phase, the inorganic fillers can also affect other polymer properties such as shelf life, cure exotherms, shrinkage, thermal and electrical conductivity, machinability, hardness, compressive, flexural, and impact strength. The extent to which the fillers modify polymer properties is closely associated with the size, shape and dispersion uniformity of the filler as well as the degree of interaction between the inorganic filler and the organic matrix. Therefore, an ideal performance is achieved with inorganic fillers
consisting of small particles that are uniformly dispersed throughout the polymer and interact strongly with the organic matrix.\textsuperscript{12,13,14} Unmodified nanoparticles often aggregate, losing their nanoscale size and corresponding properties,\textsuperscript{15} thus some form of surface modification is required to provide miscibility.

\textbf{Figure 2.2.} Schematic representation of a typical epoxy resin (green) and hardener (blue) system (upper left), with a typical filler (upper right), in comparison with (lower) an epoxy-alumoxane (purple) system.\textsuperscript{16}
Until recently, the particle sizes of fillers used to improve polymeric properties have been on the micron length scale or larger.\textsuperscript{12,14} These dense fillers provide crack initiation points within the polymer matrix. Nanometer-sized particles have higher surface areas and, at the same weight, have higher volume loadings than do larger particles. In addition, smaller particles produce smaller stress concentrations in the composite material. Unfortunately, most common fillers are inorganic oxides that are hydrophilic whereas most polymers are hydrophobic. This leads to segregation of the two phases and agglomeration of the powders yielding to a decrease in the overall performance of the polymer composite. The performance of the polymer-filler composite is strongly dependent on the strength of the interaction between polymer and filler, independent of size. The weakest to strongest interactions between the polymer and the inorganic filler are van der Waals and dipole-dipole interactions, followed by hydrogen bonding, and then finally, covalent bonding. The polymer-filler covalent bonding interactions are on the order of 30 to 100 times greater than those that can be obtained by hydrogen bonding.\textsuperscript{17} Covalent bonding of the particles to the polymer lattice allows better load-transfer of mechanical loads to the particles and also promotes toughening of the polymer composite.\textsuperscript{18,19} Covalent attachment of the particles to the polymer matrices can also promote toughening of the polymer composite since numerous bonds must be broken before cracks can propagate through the polymer. It is therefore desirable to identify small size (i.e., nanometer scale) chemically functionalized inorganic fillers that can readily be incorporated into polymer matrices through covalent bonds.

It has previously been reported that chemically functionalized alumina nanoparticles (carboxylate-alumoxanes) may be used as the inorganic component of a new class of inorganic-organic hybrid materials.\textsuperscript{12} The peripheral organic hydroxides and amines of these carboxylate-alumoxanes either react directly with epoxide resins to form a hybrid material, or in the presence of an organic resin and hardener system to form a composite material. The properties and cure times of the alumoxane hybrid and
composite materials are distinct from both the pure resins and from a physical blend of the resins with traditional ceramic fillers. A significant increase in thermal stability and tensile strength is observed for both the hybrid and composite resin systems. In addition to epoxy resins, it has been reported that the functionalized carboxylate-alumoxane nanoparticles impart desirable performance enhancement to biodegradable poly(propylene fumarate)/poly(propylene fumarate)-diacrylate polymers for bone tissue engineering applications.²⁰

With the enhancement of resin properties observed, there has been interest in investigating the effects of the alumoxane nanoparticles on the properties of a FRP composite. In addition, initial results had shown that the addition of the alumoxanes made a significant improvement of the densification of resins. These studies are reported below.

**Results and Discussion**

SEM images of composite samples were collected of both surface and cross section. Surfaces were generally featureless and consistent with prior studies.¹² Cross sectional images and their associated EDS elemental maps were used to determine the uniformity and distribution of the alumoxanes.

Figure 2.3a shows the SEM image for a Lysine-alumoxane (L-alumoxane) containing composite prepared by Method 1. The associated Al-elemental map (Figure 2.3b) is consistent with a uniform distribution of the L-alumoxane nanoparticles within the resin as well as within the fiber tows. However, the surface of the panel does show some aggregation of the L-alumoxane. Samples prepared by Methods 2 and 3 (where the L-alumoxane is “painted” on the surface of the fibers) show similar distribution of aluminum suggesting that the L-alumoxane is miscible in the resin-hardener and dissolves readily to produce a uniform composition. The presence of voids, as shown in Figure 2.3a, may be obviated by the use of vacuum bag processing.
By contrast with the results obtained with L-alumoxane the use of para-hydroxybenzoate-alumoxane (p-HB-alumoxane) does not result in full infiltration of fibers when mixed with the resin/hardener (i.e., Method 1). Not only do the SEM and associated Al-elemental map (Figure 2.4a and b, respectively) show resin rich areas, but distinct aggregates of aluminum (associated with p-HB-alumoxane) may be seen, with sizes up to 150 μm. Based upon this data and prior results with epoxy resins\textsuperscript{12} and other polymers\textsuperscript{20} it can be concluded that p-HB-alumoxane is not miscible with the resin/hardener. If p-HB-alumoxane is to be used, alternative process methods must be used.

Figure 2.3. SEM (a) and associated aluminum elemental map (b) of a L-alumoxane/epoxy panel made by Method 1, see Experimental Section.

Instead of mixing the p-HB-alumoxane with the resin/hardener, the carbon fibers were dipped into an acetone solution of p-HB-alumoxane. Prior studies have shown that this will create a uniform coating of the nanoparticles on the fiber surface.\textsuperscript{21} Panels
Figure 2.4. SEM (a) and associated aluminum (b) elemental maps of a p-HB-alumoxane/epoxy panel made by method 1, see Experimental.

prepared by Method 2 (see Experimental) shows better distribution of aluminum throughout the resin and fiber tows (Figure 2.5a and b) than those prepared by Method 1. Some clumping of p-HB-alumoxane occurs in resin rich regions. It is significant, however, that the intra-tow dispersion is improved by pre-coating the fibers. In an effort to improve miscibility the fibers are dipped in the acetone solution of p-HB-alumoxane and used without drying (Method 3, see Experimental). As can be seen from Figure 2.6b the use of Method 3 results in a highly uniform dispersion of p-HB-alumoxane through the fiber tows and any resin rich areas. Furthermore, there are no aggregates of the alumoxane >20 μm. Unfortunately, significant cracking is observed if fiber is wet prior to the addition of resin/hardener. The panels are “crispy” in feel and exhibit significant voids presumably due to the evaporation of the acetone (Figure 2.6a). It can be concluded that the use of Method 2 provides the best combination of uniform composition and limited voids. Further improvements are obtained by vacuum bagging the samples, and this process (Method 4) was employed for further characterization.
Figure 2.5. SEM (a) and associated aluminum (b) elemental maps of a \( p \)-HB-alumoxane/epoxy panel made by Method 2, see Experimental.

Figure 2.6. SEM (a) and associated aluminum (b) elemental maps of a \( p \)-HB-alumoxane/epoxy panel made by Method 3, see Experimental.

In order to study the uniformity of the alumoxane and its effects on the density of the final composite, samples were studied by c-scan in transmission mode (see
Experimental). Samples with L-Alumoxane and p-HB-alumoxane, as well as a blank containing no alumoxane were prepared by Method 4. As may be seen from Figure 2.7a, the sample with no alumoxane shows a low, non-uniform, density, while those with the alumoxanes appear to have significant improvements in uniformity (Figure 2.7b and c). Most importantly, the L-alumoxane sample shows much higher density than the p-HB-alumoxane containing samples. This trend is confirmed by measurements on the transmission of oxygen through the sample. The L-alumoxane containing composite shows only 25% transmission of oxygen, while the p-HB-alumoxane containing sample has a higher transmission (60%) consistent with the lower density (Figure 2.7b versus 7c). In contrast, the base resin composite shows 80% transmission of oxygen. Thus, irrespective of any alteration in strength, the addition of chemically functionalized alumoxane nanoparticles provides a novel route to increasing density and decreasing permeability of resin composites.

The chemical stability of nanoparticle-resin composites has been investigated, in particular with regard to stability to acids. Acid removal of oxide particles from resin composites has been used as a route to membrane structures, however in these systems the oxide particles are not covalently bound to the resin. A resin panel (in the absence of fiber) was prepared using 3% L-alumoxane by weight. Three 1” x 1” samples were cut out from the center of the panel. Each panel was dipped in either concentrated in HCl or HF for 24 hours and then washed thoroughly with water. The SEM images and the aluminum distribution images are shown in Figure 2.8. The aluminum distribution images show that the samples exposed to concentrated acid solutions have equivalent amounts of aluminum to the untreated sample. Additionally, no significant change in the physical properties was observed. Thus, despite the solubility of the carboxylate-alumoxanes in acid solution, it is clear that the nanoparticles are not attacked by acid once they are covalently bonded into the resin. This is in contrast to resin samples with
Figure 2.7. Transmission mode c-scan images of (a) a base fiber/resin composite, (b) a composite containing p-HB-alumoxane, and (c) a composite containing L-alumoxane.
boehmite filler, where the mineral is removed by acid etching.

Mechanical testing was limited to tensile and flexural tests since these parameters are very sensitive to the identity and concentration of the alumoxane. When compared to the base composite (no alumoxane), the L-alumoxane reinforced composite panels shows a significant increase in the tensile modulus, shown in Figure 2.9a. At very low loadings $\leq 0.7$ wt% there is an increase in modulus of approximately 100%. Up to this level the tensile strength shows no effect (Figure 2.10a). With higher loadings the modulus and strength show a rapid decrease until at high alumoxane concentration (>25%), the modulus reaches a value less than half of the base composite (Figure 2.9a). The strength of the panels is similarly decreased (Figure 2.10b). In contrast to the L-alumoxane reinforced composites, the use of $p$-HB-alumoxane results in a drastic decrease in tensile modulus (Figure 2.9b), although the strength is within experimental error unaffected until $>5\%$ loading (Figure 2.10b).

With regard to the flexural properties of the panels, both alumoxanes have a deleterious effect on the flexural modulus at the loadings studied (Figure 2.11). However, while the L-alumoxane reinforced panels show rapid decrease in strengths with alumoxane loading, the $p$-HB-alumoxane composites appear less susceptible at low concentrations (Figure 2.12).

Conclusions

The best results for the mechanical improvement of epoxy resins were for moderately high alumoxane contents. In contrast, a recent study of biodegradable ester composites shows that ca. 5% alumoxane provides optimum performance enhancement. This study indicates that even where the alumoxane is miscible with the resin (i.e., L-alumoxane), high loadings results in a marked decrease in performance. Based upon the prior results that suggest high alumoxane content results in an increase in the brittle nature of a resin, it can be proposed that the decreased strength is due to weak inter-phase
Figure 2.8. SEM (a, c, and e) with associated aluminum (b, d, and f) elemental maps of a L-alumoxane/epoxy panel (a and b) after immersing in concentrated HCl (c and d) or HF (e and f) for 24 hours.
Figure 2.9. Plot of tensile modulus as a function of alumoxane concentration for composite panels made with (a) L-alumoxane and (b) p-HB-alumoxane.
Figure 2.10. Plot of tensile strength as a function of alumoxane concentration for composite panels made with (a) L-alumoxane and (b) p-HB-alumoxane.
Figure 2.11. Plot of flexural modulus as a function of alumoxane concentration for composite panels made with (a) L-alumoxane and (b) p-HB-alumoxane.
Figure 2.12. Plot of flexural strength as a function of alumoxane concentration for composite panels made with (a) L-alumoxane and (b) p-HB-alumoxane.
bonding (i.e., between the resin and fiber). The poor miscibility of the \( p \)-HB-alumoxane in the epoxy resins compounds these problems.

The following conclusions have been arrived at based on the current results. First, based upon the results obtained with \(<5\%\) loadings of \( L \)-alumoxane, it is apparent that loadings must be significantly lower than heretofore studied, in order to provide enhanced performance. Barrera and co-workers at Rice University have found a similar trend with carbon nanotube composites.\(^{23,24}\) Second improved miscibility would possibly allow for better distribution. At present the best results were obtained when the alumoxanes were applied to the fibers, the region of resin adjacent to the fiber will be rich in alumoxane nanoparticles and hence be more brittle than the remainder of the resin matrix. Despite issues with obtaining uniform compositions, it has been have shown over here that highly uniform density composites may be prepared with high aluminum content. These show significantly reduced permeability of oxygen.

**Experimental Section**

Lysine-alumoxane (\( L \)-alumoxane) and \( para \)-hydroxybenzoate-alumoxane (\( p \)-HB-alumoxane), shown in Figure 2.13, were chosen due to the presence of reactive primary amine and hydroxide groups, respectively. Earlier it has been shown that these substituents react with the resins.\(^{12}\) The alumoxanes were prepared by previously reported methods.\(^{25,26}\) The resin used was HTR 212 epoxy resin Resin Services, Inc. Resin Services 874 (curing time 5 minutes) and 302 (curing time 12 - 24 hours) were used as curing agents. The carbon fabric used was IM7-GP-6K-5HS. External mold release F-57NC was obtained from Axel Plastic Research Lab, Inc.

**Laminate preparation techniques.** Uniform composite samples were prepared each using five 6 x 6 pieces of Carbon Fabric IM7-GP-6K-5HS. Four methods were used to prepare composite samples. The resin:fiber ratio was between 0.92 and 1.05 for all
Figure 2.13. Schematic representations of chemically functionalized alumoxanes: (a) lysine-alumoxane and (b) para-hydroxybenzoate alumoxane.

samples. In method 1, two 7" x 7" stainless steel plates were covered with aluminum foil. The foils were coated with a mold release agent on one side of the plate. The mold release agent was allowed to dry. The resin, hardener and alumoxane were mixed together using a mechanical stirrer. This mixture was brushed on to both sides of the carbon fabric. The fabrics were stacked between the two plates. The plates were clamped together and then placed in an oven that was preheated to 150 °C for 2 and 12 hours, depending on the hardener. In method 2, the fabrics were dipped in a saturated solution of alumoxane and dried. The amount of alumoxane on the fabric was determined by subtracting the weight of the dried coated fabric from the uncoated fabric. Two 7 x 7 stainless steel plates were covered with aluminum foil. The foils were coated with a mold release agent on one side of the plate. The mold release agent was allowed to dry. Resin and hardener were mixed together and brushed on to the carbon fabric. The fabrics were stacked between the two plates. The plates were clamped together and then placed in an
oven that was preheated to 150 °C for 2 and 12 hours, depending on the hardener. Method 3 is a variation of method 2, but the fabrics once dipped in a saturated solution of alumoxane were not dried. The resin and hardener are dissolved in acetone and brushed on to the carbon fabric. The fabrics were placed between two stainless steel plates and cured at 150 °C for 2 and 12 hours, depending on the hardener. For method 4 samples were prepared in an identical manner to method 2, but the fabrics were cured for 12 hours at room temperature in a vacuum bag and then placed at 150 °C for 12 hours. All samples used for mechanical testing were prepared by method 4. (Appendix A).

**Characterization methods.** SEM studies were performed on a Phillips XL-30 ESEM. Samples were mounted onto an aluminum specimen mount (Electron Microscopy Sciences). Before imaging, insulating samples were sputter coated (Plasma Sciences CRC 100) with a thin layer of gold to prevent charging. Energy dispersive spectroscopy (EDS) was collected using a Sun computer based Cameca SX50 electron microprobe equipped with a PGT. All the instrument controls (analytical calibration and calculation, digital imaging and image processing) were performed on a Sun Ultra Spark 1 computer with Solaris 2.5.1 operating system and Cameca SXRayN50 software. The computer calculates results for WDS analysis using the PAP method. The imaging modes used for this set of experiments includes secondary electron emission for topography and morphology and X-ray emission for element distribution. All mechanical testing was performed as per ASTM standards by OCM Test Laboratories (Anaheim, CA) using ASTM-D-638-02a (tensile) and ASTM-D-790-03 (flexural) with specimens conditions of 73 °F and 38% relative humidity. All samples underwent lateral failure at the top of the sample at the center of the load bar during flexural testing. In regard to tensile measurements high modulus samples failed at the bottom or top of the gauge area, while lower modulus samples failed in the middle. Failure occurred at an angle or by edge delamination. The c-scan was conducted on Ultrasonic C-scan Imaging System, Ultrapac
II. Physical Acoustic Corp. in transmission mode, using Plexiglas with the same thickness as the specimen as the standard for ultrasonic transmission calibration.

References


2 http://www.fibersource.com/f-tutor/history.htm


6 In general, the term hardener and curing agent are used interchangeably. Both materials are composed of a catalyst and cross-linker (or cross-linking agent).

7 Although the application of temperature may be sufficient to cause cross-linking between an epoxy and the active functional groups in the hardener, catalysts such as basic tertiary amines are used to initiate the cross-linking reaction.


Chapter 3
Use of Alumina Based Nanoparticles for Strengthening Biodegradable Scaffold Polymers for Bone Replacement

Introduction

Biomaterial is defined as any substance other than a drug or combination of substances synthetic or natural in origin, which can be used for any period of time, as a whole or as a part of a system that treats, augments, or replaces any tissue, organ or function of the body.\(^1\) Theoretically, any material can be a biomaterial as long as it serves the stated medical and surgical purposes. The history of biomaterials dates back to antiquity where man made attempts to correct deformities. However, such surgical procedures were limited to body surfaces. In 600 BC, Hindu surgeon Sushruta Samhita performed the earliest recorded operation for restoration of missing parts by repairing an injured nose with a patch of living flesh taken off the region of the cheek. This technique later traveled to the West and in 1430 was perfected in Sicily by using skin flap taken from the arm and as such is now referred to as the “Italian method” of nose reconstruction.\(^2\)

The use of surgical implants is also not new. The Romans, Chinese and Aztecs used gold in dentistry more than 2000 years ago.\(^3\) The earliest written record of the use of metal in surgical procedures is from 1565. In this era, bronze or copper were the main materials utilized. The implants used were successful but they resulted in copper ion poisoning effect in the body. No other suitable materials for implantation other than copper and bronze were known until the mid-nineteenth century.\(^4\) In 1891, Gluck in Germany designed an ivory ball and socket joint that was fixed by nickel-plated screws.\(^5\) In 1902, gold was used in capsule form interposing between the articular heads of the
implant. This experiment was a success and led to further study on chemically inert and stable materials.

Despite early efforts, metal and tissue transplantations were not largely successful mainly due to infection after implantation. Success rates increased after Lister developed aseptic surgical techniques in the 1860s. The first metal prosthesis made of Vitallium alloy was produced in 1938. This prosthesis was used until 1960 when doctors realized the harmful effects of metal contact corroding.

Skeletal defects can occur as a result of congenital abnormalities, cancer treatments and traumatic injuries. Approximately 1 million fractures requiring hospitalization occur each year in the US, more than half of which affect the load-bearing bones of the lower extremities. Current treatments for severe bone injuries replace a non-union defect with a permanent biomaterial. The functions of an implant falls into four different categories: load bearing or transmissions; the control of fluid flow in order to stimulate normal physiological function or situation; passive space filling either for cosmetic reasons or functional reasons; generation of electrical stimuli and transmission of light and sound. Metallic biomaterials and non-degradable polymeric bone cements can easily support the load of the body, however, materials of high mechanical strength absorb the mechanical stimulation required for bone re-growth and thereby inhibit growth of natural bone. This stress shielding effect ultimately results in bone resorption around the implant. Metals and non-degradable polymers must serve as either permanent implants that induce bone resorption, or require a second invasive surgery for implant removal. There is a significant need for an injectable, in-situ crosslinkable, biodegradable, biocompatible, and mechanically strong biomaterial for use in bone tissue engineering applications.

Since the late 1960’s, scientists have been trying to design bioactive bone cement. In 1972, Boutin, in France, started to study ceramics such as alumina and zirconia, which do not have biological drawbacks and are considered permanent. Boutin
introduced the alumina ceramic cup combined with an alumina femoral head. He was concerned about tissue reactions to both metal and plastic debris and was therefore intrigued by the reputation of alumina ceramic as a highly wear-resistant bearing surface for extreme conditions. The ceramic did not react with the body. But the cement did not anchor to the tissue and thus led to implants loosening very quickly and resulted in clinical failure including fracture of the implant or the bone adjacent to the implant. This was improved when Hench$^{15}$ and Jarcho$^{16}$ developed biologically active or bioactive materials such as bioglass and hydroxyapatite.

Currently, the general idea is to replace the trauma area with bone cement, cells and growth factors in a biodegradable polymer scaffold. This cement should solidify instantly and be able to take the load originally taken by the “trauma” bone. The stromal osteoblasts cells in combination with suitable growth factors poly(alpha-hydroxy ester)$^{17,18}$ will make new bone that is imbedded within the polymer scaffold. This scaffold should disintegrate as new bone grows obviating the need for a second operation for “implant” removal. This process is shown schematically in Figure 3.1.

The primary challenge towards this goal is mimicking the unique mechanical properties of bone tissue with a degradable, synthetic material. Human cortical bone has a compressive modulus of 17-20 GPa and a compressive strength of 106-133 Mpa.$^{19}$ Reported values of flexural modulus and flexural strength of bone are 15.5 GPa and 180 MPa, respectively.$^{20}$ These unique tissue properties are partially derived from the nanoscale interactions between inorganic and organic components of bone. Hydroxyapatite nanocrystals provide compressive strength to bone, while bundles of collagen fibers impart tensile strength to bone.$^{21}$ Henceforth, a degradable biomaterial composed of inorganic and organic components with mechanical properties in the range of natural bone tissue may be suitable for load-bearing bone tissue engineering applications.
Figure 3.1. Schematic representation of the replacement of a trauma area with bone cement, cells and growth factors in a biodegradable polymer scaffold.

Poly(propylene fumarate) (PPF) is a material being investigated in the Mikos laboratory at Rice University which has favorable mechanical and degradation properties. PPF is a linear, unsaturated polyester capable of cross-linking with poly(propylene fumarate)-diacrylate (PPF-DA) to form a degradable polymeric network (Figure 3.2).\textsuperscript{22} PPF/PPF-DA networks degrade via hydrolyzed ester groups into mostly fumaric acid and propylene glycol, both of which are biocompatible. The Mikos research group has also shown that mechanical properties (e.g., compressive modulus) are better for photo initiation versus chemical initiation.\textsuperscript{23}

In a study of the mechanical properties of PPF/PPF-DA over 52 weeks of degradation \textit{in-vitro}, these network formulations showed an initial increase in compressive properties followed by a faster decrease as they degraded.\textsuperscript{24} In addition, degradation and compressive properties of PPF/PPF-DA can be adjusted through
variations in composition, synthesis conditions, and crosslinking method. However, it would be desirable for a scaffold to exhibit a similar mechanical strength as the bone it is temporarily replacing. In this regard, the PPF/PPF-DA scaffolds show a flexural modulus of 3,000 MPa, which is higher than cancellous (porous) bone (200 MPa), but significantly weaker than cortical (compact) bone (>17,000 MPa). The unique tissue properties are partially derived from the nanoscale interactions between inorganic and organic components of bone.\textsuperscript{19,20}

\begin{figure}
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\includegraphics[width=\textwidth]{figure3.2.png}
\caption{Formation of PPF/PPF-DA biodegradable polymeric network.}
\end{figure}

Nano-sized inorganic fillers can add tensile strength, stiffness, abrasion resistance, and stability to polymer networks. The extent to which the fillers modify polymer properties is closely associated with the size, shape and dispersion uniformity of the filler as well as the degree of interaction between the inorganic filler and the organic matrix. Therefore, an ideal performance is achieved with inorganic fillers consisting of small
particles that are uniformly dispersed throughout the polymer and interact strongly with the organic matrix.\textsuperscript{25} A major limitation to the use of ceramic nanomaterials in polymer composites is the problems of the dispersion of a hydrophilic nanoparticles in a hydrophobic polymer. Unmodified nanoparticles often aggregate, losing their nanoscale size and corresponding properties,\textsuperscript{26} thus some form of surface modification is required to provide miscibility.

The performance of the polymer-filler composite is strongly dependent on the strength of the interaction between polymer and filler, independent of size. The weakest to strongest interactions between the polymer and the inorganic filler are van der Waals and dipole-dipole interactions, followed by hydrogen bonding, and then finally, covalent bonding. The polymer-filler covalent bonding interactions are on the order of 30 to 100 times greater than those that can be obtained by hydrogen bonding\textsuperscript{27}. Covalent bonding of the particles to the polymer lattice allows better load-transfer of mechanical loads to the particles and also promotes toughening of the polymer composite.\textsuperscript{28} It is therefore desirable to identify small size (i.e., nanometer scale) chemically functionalized inorganic fillers that can readily be incorporated into polymer matrices through covalent bonds. It has been demonstrated that chemically functionalized alumina nanoparticles (carboxylate-alumoxanes) may be used as the inorganic component of a new class of inorganic-organic composite material for which a significant increase in thermal stability and tensile strength is observed.\textsuperscript{29} This work was originally aimed at epoxide resins.

This study was designed to determine the effects of incorporating functionalized alumoxane nanoparticles into the biopolymer PPF/PPF-DA. Specifically, three general types of functionalized alumoxanes were examined: activated alumoxanes with reactive double bonds for enhanced polymer interaction; surfactant-modified alumoxanes with an organophilic carbon chain;\textsuperscript{30} and dual-modified alumoxanes with both activating and surfactant groups (either within the same substituent or as a mixed ligand system). This chapter describes the effect of surface modifications of alumoxane nanoparticles on
dispersion within PPF/PPF-DA, the effect of each surface modification of nanoparticles have on the mechanical properties of the composite material, and the effect of the loading concentration of each type of functionalized alumoxane nanoparticle on mechanical reinforcement.

**Results and Discussion**

The objective of this study was to examine the effect of functionalized alumoxane nanoparticle incorporation into PPF/PPF-DA polymer networks. The functional groups investigated in this study had different effects on nanoparticle dispersion within polymer matrices, which thereby affected the mechanical properties of composite materials. Initially two types of carboxylate-alumoxane were prepared for comprehensive studies: diacryloyl lysine alumoxane ("activated") and stearic acid alumoxane ("surfactant") (Figure 3.3a, and b, respectively). The goal was to determine was to determine the effects of a substituent (acryloyl) that would react with the PPF/PPF-DA to become covalently incorporated into the polymer chain and compare the results with an alumoxane that would be miscible, but inert with regard to reaction with the PPF or PPF-DA. Subsequently, a Ca-doped diacryloyl lysine alumoxane ("Ca-activated") was prepared to determine the effects of dopants within the alumoxane structure. In addition a "mixed" alumoxane with both diacryloyl lysine and stearic acid substituents was synthesized.

The base alumoxane nanoparticles were characterized by IR spectroscopy, TG/DTA and particle size measurements, and were shown to be equivalent to previously reported materials.31 IR spectroscopy was used to verify the appropriate functionalization of alumoxane nanoparticles. The presence of bands at 1596 - 1586 and 1473 - 1466 cm⁻¹ are consistent with a bridging mode of coordination of the carboxylate to the boehmite core,32 and are within the ranges observed previously for carboxylate- alumoxanes.33,34 The FTIR-ATR spectra of undecanoic amino acid alumoxane and its acryloyl derivative (Figure 3.4) show the presence of an amide peak (1580 cm⁻¹) due to the acryloylation
Figure 3.3. Chemical structures of modified alumoxanes: (a) diacryloyl lysine alumoxane (activated), (b) stearic acid alumoxanes (surfactant-modified), and (c) acryloyl undecanoic amino acid alumoxanes (dual-modified).
modification. Similar FTIR-ATR spectral changes were observed between the lysine and diacryloyl lysine alumoxanes.

Figure 3.4. FTIR-ATR spectra of (1) boehmite, (2) acryloyl undecanoic amino acid alumoxanes, and (3) undecanoic amino acid alumoxane (without acrylate group). Formation of the alumoxane modification is shown by amino acid-associated peaks in the undecanoic amino acid alumoxane spectrum (3) that are not present in the boehmite spectrum (1). Successful acrylation of the modified alumoxane is shown by the evolution of an amide peak at 1580 cm\(^{-1}\) in the acryloyl undecanoic amino acid alumoxane spectrum (2).

The solid state \(^{13}\text{C}\) CPMAS NMR spectra for lysine-alumoxane and the diacryloyl lysine alumoxane derivative show the addition of peaks due to the acryloyl moieties. The surface area of the “surfacted” stearate-alumoxane (6.432 m\(^2\text{g}^{-1}\)) was significantly higher than the lysine or diacryloyl lysine alumoxanes (0.729 m\(^2\text{g}^{-1}\)). This difference is commensurate with the larger particle sizes observed for lysine-alumoxane versus stearate-alumoxane.\(^{35}\)
Flexural moduli of the four modifications of alumoxanes are shown at four loading concentrations with polymer resin alone in Figure 3.5a. The flexural modulus of PPF/PPF-DA alone was 1559 ±114 MPa. Composites prepared using unmodified boehmite showed no significant difference in flexural modulus compared to polymer resin at all loading concentrations (p < 0.05). Nanocomposite samples activated with diacryloyl lysine showed significant increases in flexural modulus compared to polymer alone at 2.5 wt. % and 5 wt. % loading (Figure 3.5a). Surfactant-modified alumoxane/polymer composites (stearic acid functionalization) showed significant increases in flexural modulus at all loading concentrations, with a maximum modulus of 2471 ±125 MPa at 2.5 wt. % loading. The mixed alumoxane containing both state and diacryloyl lysine ligands shows an enhancement over either of the alumoxanes with a maximum modulus of 3300 ±269 MPa at 2.5 wt. % loading. The greatest improvement in flexural modulus was observed with the hybrid, acryloyl undecanoic amino acid alumoxane/polymer composite. With a loading of 1 wt. %, the hybrid nanocomposite exhibited a flexural modulus of 5410 ± 457 MPa, which is more than a three-fold increase compared to PPF/PPF-DA polymer alone or unmodified boehmite composite. This material group also showed significant increases compared to unmodified boehmite samples at all other loading concentrations.

Flexural fracture strength showed little variation between material groups, however, a noticeable trend was observed with respect to loading concentration (Figure 3.5b). Increased loading concentration generally led to decreased fracture strength within each material group. Significant decreases in flexural fracture strength compared to blank polymer were observed only at higher loading concentrations for unmodified, activated and surfactant-modified alumoxanes. No significant difference was observed for hybrid alumoxane nanocomposites.
Figure 3.5. Flexural modulus (a) and flexural fracture strength (b) of the different nanocomposites tested as a function of nanoparticle loading weight percentage. Error bars represent mean ± standard deviation for n = 5. The symbol "*" indicates a statistically significant difference compared to the pure polymer resin (p < 0.05).
Figure 3.6. Compressive modulus (a) and compressive fracture strength (b) of the different nanocomposites tested as a function of nanoparticle loading weight percentage. Error bars represent mean ± standard deviation for n = 5. The symbol "*" indicates a statistically significant difference compared to the pure polymer resin (p < 0.05).
Compressive moduli and fracture strength varied very little with differing material groups and loading concentrations (Figures 3.6). Unmodified boehmite/polymer composites showed a significantly lower modulus and fracture strength only at 5% loading. No significant differences were observed for modified alumoxanes compared to polymer alone.

Unmodified boehmite particles impart little, if any, mechanical reinforcement to PPF/PPF-DA polymer in flexion (Figures 3.5), likely due to aggregate formation within the polymer matrix (Figure 3.7a). Applied loads are concentrated at these large aggregates, which are several microns in diameter, and provide sites for crack propagation. Further evidence of this weakening of mechanical properties is seen at the 5% loading of unmodified boehmite into polymer, which demonstrated a significant decrease in compressive modulus and compressive fracture strength compared to blank polymer resin.

ESEM images of unmodified boehmite particles in the polymer show large aggregated clusters that are several micrometers in diameter (Figure 3.7a). Diacryloyl lysine-alumoxane nanoparticles (activated) were dispersed better in the polymer matrix, but still aggregated into submicron-sized clusters (Figure 3.7b). Alumoxane nanoparticles modified with stearic acid (surfactant-modified) achieved the best dispersion compared to other modifications, as demonstrated by the ESEM image of a smooth fracture surface (Figure 3.7c). Aggregates of stearate-alumoxane particles in the polymer composite were estimated to be no more than 50 nm in diameter based on these images. Similarly, the acryloyl undecanoic amino acid alumoxanes (hybrid) also demonstrated a fine dispersion of particles with clusters approximately 100 nm in diameter (Figure 3.7d).

Diacrtyloyl lysine-alumoxane/polymer composites showed slight improved dispersion in polymer matrices as seen by ESEM (Figure 3.7b) and EDX (Figure 3.8), though they still existed in micron-sized clusters which may serve as sites of crack
Figure 3.7. ESEM images of flexural fracture planes of nanocomposite samples (1 wt. % loading): (a) Unmodified boehmite crystals in polymer; (b) diacryloyl lysine alumoxanes in polymer (activated); (c) stearic acid alumoxanes in polymer (surfactant-modified); (d) acryloyl undecanoic amino acid alumoxanes (dual-modified).

Diacryloyl lysine-alumoxane/polymer composites showed slight improved dispersion in polymer matrices as seen by ESEM (Figure 3.7b) and EDX (Figure 3.8), though they still existed in micron-sized clusters which may serve as sites of crack propagation. Increased flexural moduli observed at loadings greater than 1% may be attributed to the two double bonds on the alumoxane functionality available for crosslinking with the polymer matrix (Figure 3.5a). However, interactions between
nanoparticles and polymer are hindered by aggregate formation, thus demonstrating only a modest improvement in modulus over polymer alone.

**Figure 3.8.** Aluminum elemental maps (EDX) of a diacyryloyl lysine alumoxane (activated alumoxane) composite showing the aggregation of alumoxane particles.

The enhanced dispersion of the surfactant and hybrid alumoxanes as compared to the diacyryloyl lysine-alumoxane (activated) is also confirmed by the aluminum EDX maps of the composites. As may be seen from Figure 3.8 there is significant agglomeration of diacyryloyl lysine-alumoxane particles within the polymer matrix. Based upon Figure 3.8, the aggregation of the diacyryloyl lysine-alumoxane particles in the polymer composite is in the range of 1 - 10 μm, significantly larger than for the stearate-alumoxane. The equivalent EDX images of the stearate-alumoxane (surfactant derived) shows no particles larger than 50 nm.

The rational for the application of an activated alumoxane is to provide covalent bonding to the polymer matrix, and thus allow better load-transfer of mechanical loads in the composite.28 It was previously shown that for epoxy systems, the presence of functional groups on the alumoxane significantly enhances the structural strengths of polymer composites as compared to alumoxane that simply serve the function as inert fillers.29 Therefore it is surprising that the stearate-alumoxane (where no covalent
interaction with the polymer is possible) shows a considerable increase in the composite strength as compared to the “activated” alumoxane (in which covalent cross-linking is possible). A consideration of the SEM and EDX images for the stearate-alumoxane/polymer composites suggest that the enhanced performance of the hydrophobic stearic acid derived nanoparticles is due to the uniform dispersion of an inert filler within the hydrophobic polymer matrix. Well-dispersed nanoparticles in small cluster sizes reinforce the polymer matrix by immobilizing polymer chains, resulting in modulus increases.

The greatest mechanical reinforcement was achieved by alumoxanes dually modified with a long carbon chain allowing dispersion of the alumoxane and reactive double bonds available for covalent bonding to the polymer. Thus, the combination of both stearate and diacryloyl lysine substituents shows improved dispersion and a 50% improvement ion flexural strength. However, the hybrid alumoxane containing diacryloyl undecanoic amino acid substituents (Figure 3.3c) offers a far superior approach to the mixed ligand alumoxane.  

A 1% loading of diacryloyl undecanoic amino acid modified alumoxane nanoparticles improved flexural modulus by a factor of almost 3.5 over polymer alone to 5410 ±457 MPa. Hybrid alumoxanes in ESEM showed a much better dispersion than activated alumoxanes, explained by the hydrophobic long carbon chain in the functionality. While dispersion was not quite as good as the surfactant-modified alumoxanes, mechanical reinforcement was significantly improved due to the reactive double bond in the functional group available for crosslinking with the polymer matrix. Thus, alumoxane nanoparticles modified for enhanced dispersion in a hydrophobic matrix and activated for covalent interaction with the polymer backbone provided the most significant increases in mechanical properties over polymer resin alone.

It has previously been reported that doped alumoxanes may be prepared by metal exchange reaction between the alumoxane and an acetylacetone complex (Figure 3.9).
There is interest in the potential effects of metal dopants on the strength of the polymer composites especially that of calcium. Calcium, a natural component of bone, is of particular interest as it may enhance assimilation into natural bone tissue in a clinical application. Although ionic species may be problematic for implant materials, free calcium ions are not expected to be released from the alumoxane nanoparticles in the composite. As may be seen from Figure 3.10 the presence of calcium dopant (approximately 10 wt %) does not have a significant effect on the properties of the composite.

\[ \text{Figure 3.9. Schematic representation of the reaction of carboxylate-alumoxane with M(acac)_3.} \]

In general, the ideal reinforcing filler for polymers is a stable nanomaterial that easily disperses into polymer and covalently binds to the matrix.\(^ {29} \) For bone engineering applications, nano-sized hydroxyapatite particles have been incorporated into polymer matrices as they are similar to the inorganic components of bone. Liu et al. incorporated nano-apatite crystals into poly(ethylene glycol)/poly(butylene terephthalate) (PEG/PBT) polymer and observed increases in tensile modulus of nanocomposites.\(^ {37} \) However, these
Figure 3.10. Flexural modulus (a) and flexural fracture strength (b) of the different nanocomposites tested.

Increases were associated with decreases in tensile strength and elongation at break. Modified silicate clays have also been incorporated into a variety of polymers for purposes of increasing mechanical properties of the base resin.\textsuperscript{38}
Conclusions

This study demonstrated that chemically functionalized alumina nanoparticles (carboxylate-alumoxanes) may be used as the inorganic component of a new class of inorganic-organic hybrid material for which a significant increase in thermal stability and tensile strength is observed. A biodegradable, biocompatible polymer was mechanically reinforced by a ceramic nanoparticle chemically modified to achieve both dispersion and interaction within the polymer matrix. The importance of both dispersion and reactivity are highlighted by the results of this study. Hybrid alumoxane nanoparticle with both a long carbon chain (surfactant) and a reactive double bond (activated) within the same substituent has been developed. Dispersed in PPF/PPF-DA this hybrid materials shows over a three-fold increase in flexural modulus over polymer resin alone. This significant increase has not been observed elsewhere in the literature for a biodegradable, hard-tissue biomaterial.

Experimental Section

Materials. Research grade pseudo-boehmite (100%) was provided by Sasol North America, Inc (Houston, TX). 11-Undecanoic acid, acryloyl chloride, diethyl fumarate, fumaric acid, hydroquinone, L-lysine, stearic acid, and NMe3 were purchased from Sigma-Aldrich (St. Louis, MO) and used as received. Ca(acac)2·(H2O)x was purchased from Strem Chemicals and used as received (Newburyport, MA). Hydrochloric acid, propylene glycol, propylene oxide, pyridine, sodium hydroxide, sodium sulfate, zinc chloride, and all other organic solvents were purchased from Fischer-Acros (Fair Lawn, NJ). Bis-(2,4,6-trimethylbenzoyl) phenylphosphine oxide (BAPO) was provided by Ciba Specialty Chemicals (Tarrytown, NY). PPF and PPF-DA were synthesized using previously described methods.23
Nanoparticle synthesis and characterization. Three types of carboxylate-alumoxane were prepared for comprehensive studies: diacryloyl lysine alumoxane ("activated"), stearic acid alumoxane ("surfactant"), and acryloyl undecanoic amino acid alumoxane ("hybrid") (Figures 3.3a, b, and c, respectively). Two additional alumoxane were prepared for comparison with specific alumoxanes. These were a "mixed" alumoxane with both diacryloyl lysine and stearic acid substituents, and a Ca-doped diacryloyl lysine alumoxane ("Ca-activated"). In each case the base alumoxanes were prepared using two methods. The first method was a modification of previously published methods, while the second method (described below) was aimed at removal of any carboxylic acid impurities. No significant difference was observed for the two methods.

Lysine-alumoxane was prepared by previously published methods (surface area = 6.432 m²g⁻¹) or by combining boehmite mineral with an excess of lysine in a large volume of 1 N HCl with stirring at 115 °C. The reactor vessel was covered in foil to prevent exposure to light and kept open through a reflux condenser to prevent evaporation. After reacting for a minimum of 12 hours, reactor solution was diluted 1:1 with 1 N HCl. Nanoparticles were then brought to their isoelectric point by dropwise addition of a solution of supersaturated NaOH. Precipitated particles were centrifuged, redissolved in acid, and re-precipitated twice more to remove unreacted amino acids. Reactive acrylate groups were added to the amino termini of the lysine substituents by Schotten-Baumann acylation. Lysine-alumoxane (from either synthesis) dissolved in double-distilled water were mixed with an equal volume of hexanes and chilled to 10 °C in a large three-neck reaction flask with stirring. An excess of acryloyl chloride was gradually added to the reaction mixture. The interphase reaction was carefully monitored and concentrated NaOH solution was periodically added to maintain a slightly basic pH. The reaction mixture was then removed, brought to an acidic pH, and centrifuged. Particles were washed with water, chilled, and washed with acetone three times in the absence of light. Particles were then dissolved in CH₂Cl₂ and acetone was removed by
rotary evaporation. Functionalization of alumoxane nanoparticles was verified by Fourier transform infrared-attenuated reflectance spectroscopy (FTIR-ATR).

Stearic acid alumoxanes (surfactant modification) may be prepared by a method similar to that described for the activated-alumoxane. As an alternative, a mixture of stearic acid (173 g) and boehmite (3.0 g) was refluxed in toluene (150 mL). The mixture was refluxed for four days to yield a clear viscous solution that solidified to an immobile gel upon cooling to room temperature. All volatiles were removed under vacuum. The resulting solid was washed with Et₂O resulting in a white powder. Surface area = 0.729 m²g⁻¹.

The hybrid alumoxane was prepared by reaction of boehmite with 11-amino undecanoic acid followed by the Schotten-Baumann acylation as described above. The mixed-alumoxane was prepared by the reaction of L-lysine (20 g) and stearic acid (20 g) with boehmite (20 g) in refluxing toluene (500 mL). The product was slowly poured while stirring in a large beaker of Et₂O. White flakes dropped to the bottom of the beaker, which were then filtered and washed many times with Et₂O. The white product was dried in vacuum overnight.

Ca-activated alumoxane was prepared by the reaction of lysine alumoxane (19.88 g) and Ca(acac)₂ in DI water (150 mL). The yellow solution was stirred overnight. Water was removed using a rotary evaporator, and the resulting bright yellow product was dissolved in ethanol. The ethanol mixture was added dropwise to Et₂O resulting in the precipitation of a white powder. The solvent was removed by decanting, followed by repeated washing with Et₂O. The resulting Ca-doped lysine-alumoxane was converted to the diacyrloyl derivative by the reaction of a toluene solution with acryl chloride in the presence of NEt₃. The mixture was constantly stirred and the pH of the solution was monitored until it reached ca. 10. The reaction was assumed to have been complete once the reaction stopped giving off heat. The product was isolated by removal of the volatiles and washing with water.
**Nanocomposite fabrication.** PPF and PPF-DA were mixed in CH$_2$Cl$_2$ in a 1:2 mass ratio. Alumoxane nanoparticles were then mixed into the polymer blend at loading concentrations of 0.5, 1, 2.5, and 5 wt. %. Solvent was removed by rotary evaporation and high vacuum drying. The crosslinking photoinitiator, BAPO was prepared in a 0.1 g.mL$^{-1}$ CH$_2$Cl$_2$ solution and added to the composite mixture at 0.5 wt. %.

Samples for flexural testing were prepared by injecting the nanocomposite mixture into silicon molds and crosslinking in an Ultralum UV light box. Samples were placed 20 cm below four bulbs producing light at 365 nm at 2 mW.cm$^{-2}$ intensity. Samples were removed from silicon molds after 5 minutes and exposed to UV light for another 30 minutes. Flexural testing samples were typically 50 mm long and 2 mm in diameter.

Samples for compressive testing were prepared by pouring polymer mixture with photoinitiator into cylindrical glass vials (6.5 mm diameter, 40 mm length). Samples were subjected to vacuum to remove air bubbles within the polymer and then placed in the UV light box. After 5 minutes, samples were released from the vials by breaking the glass, then returned to the light box for an additional 30 minutes. Samples were cut using a diamond saw into compression testing bars of approximately 6.5 mm diameter and 13 mm height.

**Materials Characterization.** IR spectra (4000 - 400 cm$^{-1}$) were obtained using a Nicolet 760 FT-IR infrared spectrometer. Particle size measurements were made on a Coulter N4 Plus Submicron Particle Sizer at scattering angles of 30° and 60°, using deionized water and a concentration of *ca.* 2 g.L$^{-1}$. SEM studies were performed on a JEOL JSM-5300 scanning microscope. Fracture plane samples from 3-point bending testing of 1 wt. % particle loading were sputter coated with approximately 20 nm of chromium and examined using a JOEL 6500F scanning electron microscope (ESEM).
Figure 3.11. Representative stress-strain curve for mechanical testing data. Modulus was calculated from initial linear slope (*). Fracture strength was derived from maximum stress prior to failure (#).

Mechanical Properties. Mechanical properties of solid nanocomposite samples were determined by an 858 Material Testing System mechanical testing machine with a sample size of five for each group. Flexural testing was conducted in accordance with ASTM D790M-92. Flexural testing samples were placed onto a 3-point bending apparatus with a support span of 4 mm. The cross-head was lowered at a rate of 10 mm.min\(^{-1}\) to the center of each specimen until failure. Force and displacement measurements were recorded and converted to stress and strain based on sample dimensions. Flexural modulus was calculated as the slope of the initial linear region of the stress-strain curve (Figure 3.11). Flexural fracture strength was calculated as the maximum stress applied prior to failure. ASTM D695-95. Cylindrical samples were placed between two plates as the cross-head lowered onto the sample at a constant rate of
1 mm/min until failure. Compressive modulus and fracture strength were calculated in the same manner as flexural properties.

Mechanical data are presented as means ± standard deviation for each experimental group (n = 5). Data analysis was carried out using JMP v.4 statistical software (SAS Institute, Cary, NC). Statistical significance within a data set was determined by single factor analysis of variance (ANOVA). Sample measurements at each nanoparticle loading were compared to pure polymer resin and statistically significant differences were assessed utilizing Dunnett’s Method. All tests were conducted with 95% confidence intervals (p < 0.05).

Reference


Chapter 4
Determination of the Mode and Efficacy of the Cross-Linking of Guar by Borate using MAS $^{11}$B NMR of Borate Cross-Linked Guar in Combination with Solution $^{11}$B NMR of Model Systems

Introduction

Thick gels of guar gum cross-linked with borax or a transition metal complex are used in the oil well drilling industry as hydraulic fracturing fluids.\(^1\) The polysaccharide guaran ($M_w \approx 10^6$ Da) is the major (>85 wt%) component of guar gum, and consists of a (1→4)-$\beta$-D-mannopyranosyl backbone with $\alpha$-D-galactopyranosyl side chain units attached via (1→6) linkages. Although the exact ratio varies between different crops of guar gum, the general structure is consistent with about one galactose to every other mannose (Figure 4.1).\(^2\)

![Figure 4.1. The repeat unit of guaran, a naturally occurring polysaccharide, consisting of (1→4)-$\beta$-D-mannopyranosyl units with $\alpha$-D-galactopyranosyl side chains attached to about every other mannose via (1→6) linkages.](image)
The synthesis of a typical boric acid cross-linked guar gel, with viscosity properties suitable for use as a fracturing fluid, involves mixing guar gum, water and boric acid, B(OH)_3, in a 10:2000:1 wt/wt ratio. Adjusting the pH to between 8.5 and 9 results in a viscous gel. The boron:guaran ratio corresponds to almost 2 boron centers per 3 monosaccharide repeat units. Such a large excess of boric acid clearly indicates that the system is not optimized for cross-linking, i.e., a significant fraction of the boric acid is ineffective as a cross-linking agent. Given the number of potential ligand sites through which boron could bind to guaran, it is important to understand if the inefficiency of borate in cross-linking guar gum is due to the lack of reactivity of boric acid and if competitive binding occurs between productive and unproductive sites for cross-linking.

The inefficiency of boric acid as a cross-linking agent for guar gum is not the only issue germane to the optimization of hydraulic fracturing fluids for “down hole” applications. Other factors include: the temperature stability of the cross-linked guar gel, the pH at which cross-linking occurs and is reversed, and the controllability of the viscosity of the cross-linked gel. There is much interest in the development of new cross-linking agents for down hole applications. Thus it is important to first understand the reasons for borates inefficiency as well as investigate alternative borate ligands to promote guar cross-linking at a lower pH. This chapter describes a ^11B NMR spectroscopic study using a series of model ligands and low molecular weight oligosaccharides.

In aqueous solution boric acid exists in a pH dependent equilibrium with the borate anion such that higher pH drives the reaction towards the formation of the borate (Eq. 4.1). In the presence of alcohols, diols, polyols, or polysaccharides, boric acid reacts to form alkoxide complexes. In the case of diols, the mono-diol [B(OH)₂L]⁻ (I) and the bis-diol [BL₂]⁺ (II) complexes are proposed to be formed in an equilibrium with the borate anion (Eq. 4.2).
Figure 4.2 shows the nomenclature used to assign specific structural units of the variety of species that were studied. For example, the acronym [B5] is used to denote a borate complex of a 1,2-diol forming a chelate 5-membered ring cycle, e.g., [B(OH)_2L]^-. Similarly, [B5_2] denotes a borate complex of two 1,2-diols both forming chelate 5-membered ring cycles, e.g., [BL_2]^-. 

A consideration of Figure 4.1 indicates the potential modes by which boron can bind to guaran. Monodentate coordination can occur via the oxygen groups on C-2, C-3, or C-6 of either the mannose backbone or the galactose side chain. In addition, the oxygen on the galactose C-4 is available for coordination. Examples of borate complexes derived from monodentate alcohols, [B(OR)_4]^-, are well known, although only a few have been structurally characterized, and they are generally prepared from non-aqueous solution. Given the chelate effect, it is more likely that any cross-linking involves bidentate coordination of a 1,2 or 1,3 diol. Although tridentate coordination is known for 1,3,5-triols the structure of guaran precludes this mode of coordination. Chelate binding to the backbone must occur exclusively in a 5-membered cycle formed with cis-1,2-diol, i.e., [B5_2]. In contrast, binding to the galactose side chain may occur by either cis- or
trans-1,2-diols forming a 5-membered cycle, or through the formation of a 6-membered cycle with a 1,3-diol, i.e., [B52] or [B56] or [B62].

![Chemical structures](image)

**Figure 4.2.** Schematic representation and nomenclature for the five structural types of diol complexes investigated in the present study.

It has been previously reported that both [B62] and [B56] complexation is involved in the cross-linking of guaran.\textsuperscript{16} This report is open to question, however, since the $\Delta S$ for the cross-linking reaction (Eq. 4.2) was calculated to be positive consistent with a *dissociative*, rather than the expected, *associative* process. Furthermore, these authors used *solution* $^{11}$B NMR methods to characterize a high molecular weight material with low solution mobility. This brings in to question exactly which species they were
observing, the cross-linked guaran or the remaining solution borate species? Other researchers have reported the presence of [B5] and [B6] complexation; however, no information on the nature of any cross-linking was reported.\textsuperscript{17} It is clear, therefore, that there is still much to be learnt about the cross-linking of guar.

A combination of $^{11}$B NMR spectroscopy and theoretical calculations has been used to gain a more complete understanding of this commercially important system. In order to interpret the $^{11}$B NMR spectra of boric acid with guaran and the guaran monosaccharides, a series of model ligands were first studied in order to identify the characteristic shifts associated with each of the binding modes of borate. In addition to boric acid, phenylboronic acid has been employed to determine the effect of complexation by substituents on boron.

**Results and Discussion**

Although the pH dependant speciation of boric acid (Eq. 4.1) has previously been extensively studied by $^{11}$B NMR spectroscopy,\textsuperscript{4} the concentration and pH dependence of the chemical shift makes the assignment of peaks in complex multi-component spectra difficult. Thus, base-line data was obtained under concentration conditions identical to those used for the model ligands and saccharides shown in Figure 4.3a. A similar dependence on the $^{11}$B NMR shift was measured (Figure 4.3b) for the pH dependant speciation of phenylboronic acid, PhB(OH)$_2$ (Eq. 4.3).

$$\text{PhB(OH)}_2 + \text{OH}^- \rightleftharpoons [\text{PhB(OH)}_3]^- \quad (4.3)$$

Below pH 7 the dominant species is PhB(OH)$_2$, and appears as a broad peak around 30 ppm. In contrast, above pH 10 the phenylborate anions, [PhB(OH)$_3$]$^-$, dominate, and appear as a sharp peak at 2.7 ppm. At intermediate pH values, the two species are in an equilibrium that is fast on the NMR time scale, resulting in a weighted average of the two
signals. It should be noted that boric acid appears as a 10% impurity in a commercial sample of phenylboronic acid.

Assuming the $^{11}$B NMR shift is directly proportional to the mole fraction of the total species present as the borate anion, $\chi_{\text{anion}}$ \{anion = [B(OH)$_4$]$^-$, or [PhB(OH)$_3$]$^-$\} the $^{11}$B NMR chemical shift at a given temperature, $\delta_{\text{obs}}$, may be used to calculate both $\chi_{\text{acid}}$ and $\chi_{\text{anion}}$, e.g., Eq. 4.4 and 4.5, respectively.$^{18,19}$ Using these equations the relative speciation as a function of pH may be calculated for both boric acid and phenylboronic acid, see Figure 4.4. The pH at which a 50:50 mixture of acid and anion for boric acid is \textit{ca.} 9.4, while that for phenylboronic acid is 9.0 consistent with the more Lewis acidic boron center in PhB(OH)$_2$.

$$\chi_{\text{acid}} = \frac{\delta_{\text{obs}} - \delta_{\text{anion}}}{\delta_{\text{acid}} - \delta_{\text{anion}}} \quad (4.4)$$

$$\chi_{\text{anion}} = \frac{\delta_{\text{acid}} - \delta_{\text{obs}}}{\delta_{\text{acid}} - \delta_{\text{anion}}} \quad (4.5)$$

The products of the reaction of various diols and saccharides to an aqueous solution (10% D$_2$O) of either boric acid or phenylboronic acid have been investigated. The $^{11}$B NMR spectra were collected across the pH range of 1 - 13. In each case, a single peak is observed at low pH due to the respective equilibria described by Eq. 4.1 and 4.3. As the pH is raised additional peaks are observed due to the formation of either [B(OH)$_2$L]$^-$ or [PhB(OH)L]$^-$'. In the case of boric acid a peak due to [BL$_2$]$^-$ is subsequently observed at higher pH.
Figure 4.3. The $^{11}$B NMR chemical shift (ppm) of (a) boric acid$^{20}$ and (b) phenylboronic acid as a function of pH.
Figure 4.4. The mole fraction of acid (■) and anion (□) forms of (a) boric acid and (b) phenylboronic acid as a function of pH.
Although the residual boric acid resonance is pH dependent, the peaks due to the diol complexes are pH independent\textsuperscript{20} indicating that \([\text{B(OH)}_2\text{L}]^-\) and \([\text{PhB(OH)}\text{L}]^-\) are not in equilibrium with a neutral trigonal species, i.e., Eq. 4.6 is not observed. This is in contrast to prior reports that suggest the possibility of such equilibrium.\textsuperscript{9}

\[
[\text{B(OH)}_2\text{L}]^- \rightleftharpoons \text{B(OH)L} + \text{OH}^- \quad (4.6)
\]

Variation of the diol:boric acid ratio indicates that \([\text{B(OH)}_2\text{L}]^-\), \([\text{BL}_2]^-\) and uncomplexed boron (boric acid and borate anion) are in equilibrium (Eq. 4.7 and 4.8).

\[
[\text{B(OH)}_4]^- + \text{LH}_2 \rightleftharpoons [\text{B(OH)}_2\text{L}]^- + 2\text{H}_2\text{O} \quad (4.7)
\]

\[
[\text{B(OH)}_2\text{L}]^- + \text{LH}_2 \rightleftharpoons [\text{BL}_2]^- + 2\text{H}_2\text{O} \quad (4.8)
\]

The equilibrium constants \(K_1\) and \(K_2\) may be determined at constant pH from the \(^{11}\text{B}\) NMR spectra of boric acid solutions using various concentrations of diol, (Eq. 4.9 and 4.10).

\[
K_1 = \frac{[\text{B(OH)}_2\text{(L)}]^-}{[\text{B(OH)}_4][\text{L}]} \quad (4.9)
\]

\[
K_2 = \frac{[\text{BL}_2]^-}{[\text{B(OH)}_2\text{(L)}][\text{L}]} \quad (4.10)
\]
$K_1$ and $K_2$ were determined from the appropriate plots. The values for $K_1$ and $K_2$ may be checked from the appropriate plot, and comparing to the product of $K_1$ and $K_2$ according to Eq. 4.11. The agreement of both values for $K_{12}$ suggests that there are no significant competing equilibria that must be considered. Obviously, in the case of phenylboronic acid only a single equilibrium is observed (Eq. 4.12) for which $K_1$ is defined (Eq. 4.13).

$$K_{12} = K_1 K_2 = \frac{[BL_2]^+}{[B(OH)_4^-][L]^2}$$

(4.11)

$$[\text{PhB(OH)}_3^-] + \text{LH}_2 \xleftrightarrow{K_1} \text{[PhB(OH)L]}^- + 2 \text{H}_2\text{O}$$

(4.12)

$$K_1 = \frac{[\text{PhB(OH)(L)}^-]}{[\text{PhB(OH)}_3^-][\text{L}]}$$

(4.13)

It is very important to note that in Eq. 4.7 – 4.13 it was assumed (as have previous researchers) that the borate anion is the reactive species. Furthermore, in determining $[B(OH)_4^-]$ prior reports have assumed that this value is equal to the total concentration of boron, i.e., $[B(OH)_4^-] + [B(OH)_3^-]$. Thus, previous reports have assumed that $B_{\text{total}}$ may be substituted for $[B(OH)_4^-]$ in Eq. 4.9 and 4.11. As discussed below, neither of these assumptions appears to hold true. However, the values for $K_1$ may be calculated assuming that $B(OH)_3$, $[B(OH)_4^-]$ or both react.

The formation of complexes with both 1,2- and 1,3-diols and either boron species is pH dependent. Raising the pH above ca. 7 results in the formation of boron-diol complexes. Complex concentration increases with increased pH, until complex dissociation occurs at high pH. An example of the pH dependence for complex formation is shown in Figure 4.5.
Figure 4.5. A plot of the pH dependence for complex (a) formation between phenylboronic acid (■) and (a) ethylene glycol and (b) catechol.
**Complexes with 1,2- and 1,3-diols.** The products of the reaction of various 1,2-diols or 1,3-diols with an aqueous solution of either boric acid or phenylboronic acid in an approximately 4:1 (boron:dial) ratio were investigated. This is a higher ratio than employed in synthesis of a typical boric acid cross-linked guar gel and thus should enhance complex formation making NMR characterization easier. A summary of chemical shifts, assignments and equilibrium constants for complexes with 1,2-diol and 1,3-diols is given in Table 4.1.

The reaction with cis-1,2-cyclohexanediol is typical of the 1,2-diols. For the reaction of cis-1,2-cyclohexanediol with boric acid, raising the pH above 7 results an additional peak at 5.3 ppm, while a second additional peak (8.6 ppm) is observed above pH 8.5. The intensity of both peaks increases with increased pH, until pH >11 at which the peak for non-coordinated borate is the only species observed. The low field peak is always a minor constituent. Based upon the relative intensity of the new peaks and prior work, the new peaks can be assigned at 5.3 and 8.6 ppm to [B5] and [B52], respectively. As with the cis-cyclohexanediol, borate can bind either one or two trans-cyclohexanediols.

The ΔH and ΔS for complexation of boric acid to cis- and trans-1,2-cyclohexanediol have been determined from the temperature dependence of the appropriate equilibrium constants (Table 4.2). The formation of [B5] and [B52] complexes (Eq. 4.7 and 4.8) are exothermic and similar in magnitude. It should be noted that if it is assumed that the borate anion, [B(OH)₄]⁻, is the reactive species then trans-1,2-cyclohexanediol complexation is favorable over coordination to the cis-1,2-cyclohexanediol. This is contrary to the theoretical calculations discussed below. In contrast, assuming B(OH)₃ is the reactive species (Figure 4.6 and Table 4.2) predicts the reverse trend, consistent with calculations and relative formation of the cis- and trans-1,2-cyclohexanediol complexation under similar conditions.
Table 4.1. Summary of $^{11}$B NMR data and association constants for borate-diol complexes.

<table>
<thead>
<tr>
<th>L</th>
<th>Borate</th>
<th>δ (ppm)²</th>
<th>Assignment¹</th>
<th>$K_{eq}$ (mol⁻¹ · dm³⁻¹)</th>
<th>pH ³</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOCH₂CH₂OH</td>
<td>B(OH)₃</td>
<td>5.6</td>
<td>[B5]</td>
<td>1.0 - 1.8</td>
<td></td>
<td>d, e,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1 - 0.65</td>
<td>f, g</td>
</tr>
<tr>
<td></td>
<td>PhB(OH)₂</td>
<td>9.3</td>
<td>[B5₂]</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>HOCMe₂CMe₂OH</td>
<td>B(OH)₃</td>
<td>4.7</td>
<td>[B5]</td>
<td>7.4</td>
<td>8.5</td>
<td>h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.6</td>
<td>[B5₂]</td>
<td>3.5</td>
<td></td>
<td>f</td>
</tr>
<tr>
<td></td>
<td>PhB(OH)₂</td>
<td>5.03</td>
<td>[B5]</td>
<td>8.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOCH₂CH₂CH₂OH</td>
<td>B(OH)₃</td>
<td>0.9</td>
<td>[B6]</td>
<td>0.72</td>
<td>11.5</td>
<td>h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>[B6₂]</td>
<td></td>
<td></td>
<td>d</td>
</tr>
<tr>
<td>neol-H₂</td>
<td>B(OH)₃</td>
<td>1.2</td>
<td>[B6]</td>
<td>1.2 - 5.8</td>
<td>9.0</td>
<td>f, h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.6</td>
<td>[B6₂]</td>
<td>0.05 - 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-C₆H₁₀(OH)₂</td>
<td>B(OH)₃</td>
<td>5.3</td>
<td>[B5]</td>
<td>1.14</td>
<td>9.5</td>
<td>f, h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.6</td>
<td>[B5₂]</td>
<td>0.79</td>
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</tr>
<tr>
<td>trans-C₆H₁₀(OH)₂</td>
<td>B(OH)₃</td>
<td>8.61</td>
<td>[B5]</td>
<td>6.14</td>
<td>8.5</td>
<td>h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13.7</td>
<td>[B5]</td>
<td>4.44</td>
<td>8.0</td>
<td>h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.33</td>
<td>[B5₂]</td>
<td>1.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-C₆H₄(OH)₂</td>
<td>B(OH)₃</td>
<td>7.6</td>
<td>[B5]</td>
<td>8.25</td>
<td>11</td>
<td>h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13.1</td>
<td>[B5₂]</td>
<td>1.64</td>
<td></td>
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<tr>
<td>fucose</td>
<td>PhB(OH)₂</td>
<td>11.7</td>
<td>[B5]</td>
<td>427</td>
<td>7.5</td>
<td>h</td>
</tr>
<tr>
<td></td>
<td>B(OH)₃</td>
<td>5.7</td>
<td>[B5]</td>
<td></td>
<td></td>
<td>h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.1</td>
<td>[B5₂]</td>
<td></td>
<td></td>
<td>h</td>
</tr>
<tr>
<td>Sucrose</td>
<td>B(OH)₃</td>
<td>1.3</td>
<td>[B6]</td>
<td></td>
<td></td>
<td>h</td>
</tr>
<tr>
<td></td>
<td>PhB(OH)₂</td>
<td>3.0</td>
<td>[B6]</td>
<td>65</td>
<td>9.0</td>
<td>h</td>
</tr>
<tr>
<td>Glucose</td>
<td>B(OH)₃</td>
<td>6.5</td>
<td>[B5]</td>
<td>63</td>
<td></td>
<td>i, j</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.3</td>
<td>[B5₂]</td>
<td>17</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.6</td>
<td>[B6]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>Borate</td>
<td>δ (ppm)</td>
<td>Assignment&lt;sup&gt;b&lt;/sup&gt;</td>
<td>$\text{Keq (mol}^{-1}\text{dm}^3$)</td>
<td>pH&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Ref.</td>
</tr>
<tr>
<td>-----------------</td>
<td>---------</td>
<td>---------</td>
<td>------------------------</td>
<td>-----------------------------------</td>
<td>--------------</td>
<td>-----</td>
</tr>
<tr>
<td>Cellobiose (glucose dimer)</td>
<td>B(OH)₃</td>
<td>5.3</td>
<td>[B5]</td>
<td>50 - 80</td>
<td>h, k</td>
<td></td>
</tr>
<tr>
<td>Mannose</td>
<td>B(OH)₃</td>
<td>1.6</td>
<td>[B6]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.3</td>
<td>[B6]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>PhB(OH)₂</td>
<td>8.25</td>
<td>[B5]</td>
<td>60 - 64</td>
<td>h, k</td>
<td></td>
</tr>
<tr>
<td>1-methoxy mannose</td>
<td>B(OH)₃</td>
<td>4.5</td>
<td>[B5]</td>
<td>12.4</td>
<td>l</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.1</td>
<td>[B52]</td>
<td>1.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>[B6]</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galactose</td>
<td>B(OH)₃</td>
<td>6.3, 5.7</td>
<td>[B5]</td>
<td>75 - 97</td>
<td>h, i</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.2</td>
<td>[B52]</td>
<td>3.0 - 3.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-methoxy galactose</td>
<td>PhB(OH)₂</td>
<td>7.8</td>
<td>[B5]</td>
<td>187</td>
<td>h</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B(OH)₃</td>
<td>4.6</td>
<td>[B5]</td>
<td>10.2</td>
<td>l</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.5</td>
<td>[B52]</td>
<td>1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.4</td>
<td>[B6]</td>
<td>7.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.6. The temperature dependence of the equilibrium constant, $K_{eq}$, for the formation of cis-[B5], assuming both B(OH)$_3$ and [B(OH)$_4$]$^-$ are reactive species (●, R = 0.996); assuming B(OH)$_3$ is the reactive species (●, R = 0.996); assuming [B(OH)$_4$]$^-$ is the reactive species (●, R = 0.997).

Initial complex formation between cis-1,2-cyclohexanediol and phenylboronic acid occurs at around pH 8.0 as indicated by a peak at 8.6 ppm assigned to [PhB5] (c.f., Figure 4.2). The intensity of this peak increases with increased pH, until pH 9.78 at which point a maximum is reached. Further increases in pH results in dissociation and the formation of the non-coordinated borate as the only species observed. The extent of complex formation between cis-1,2-cyclohexanediol and phenylboronic acid is higher than the analogous reaction with boric acid, as is confirmed by the relative $K_1$ values (Table 4.1). The formation of [PhB5] generally occurs at a lower pH that the analogous [B5] complex as shown below. The chemical shifts for the phenyl boronic acid [PhB5]
Table 4.2. Thermodynamic functions for borate-diol complexes.

<table>
<thead>
<tr>
<th>L</th>
<th>Borate</th>
<th>Complex</th>
<th>$\Delta H^a$ (kJ.mol$^{-1}$)</th>
<th>$\Delta S^a$ (J.K$^{-1}$mol$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$cis$-$C_6H_{10}(OH)_2$</td>
<td>B(OH)$_3$</td>
<td>[B5]</td>
<td>-21.1(1)$^b$</td>
<td>-63.5(3)$^b$</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-22.5(1)$^c$</td>
<td>-66.6(3)$^c$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-20.8(2)$^d$</td>
<td>-60.5(5)$^d$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[B52]</td>
<td>-20.6(6)</td>
<td>-68(2)</td>
<td></td>
</tr>
<tr>
<td>$trans$-$C_6H_{10}(OH)_2$</td>
<td>B(OH)$_3$</td>
<td>[B5]</td>
<td>-14.8(3)$^b$</td>
<td>-95(1)$^b$</td>
<td>e</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>-14.0(3)$^c$</td>
<td>-91(1)$^c$</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>-22.0(3)$^d$</td>
<td>-103(2)$^d$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[B52]</td>
<td>-19(1)</td>
<td>-87(3)</td>
<td></td>
</tr>
<tr>
<td>1-methoxy mannose</td>
<td>B(OH)$_3$</td>
<td>[B5]</td>
<td>-7</td>
<td>-2.2</td>
<td>f</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[B52]</td>
<td>-6.2</td>
<td>-16.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[B6]</td>
<td>-9.5</td>
<td>-16</td>
<td></td>
</tr>
<tr>
<td>1-methoxy galactose</td>
<td>B(OH)$_3$</td>
<td>[B5]</td>
<td>-7.8</td>
<td>-6.8</td>
<td>f</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[B52]</td>
<td>-3</td>
<td>-6</td>
<td></td>
</tr>
</tbody>
</table>

complexes are further down field, i.e., 7.8 – 13.8 ppm for [PhB5] versus 5.3 – 6.3 ppm for [B5]. This difference is consistent with the presence of the arene substituent, however, the [PhB6] chemical shifts (0.75 – 2.8 ppm) are similar to those observed for [B6] (0.9 – 1.6 ppm).

The reaction of 2,2-dimethyl propane-1,3-diol (neol-H2, III) with both boric acid and phenylboronic acid was investigated and the relevant equilibrium constants in the neol-borate system were determined (Table 4.1).

![Chemical Structure](image)

(III)

Complexation of boric acid with propane-1,3-diol has previously been reported, although no information as to the reaction equilibrium was reported. As in the case for the 1,2-diols, the shifts (Table 4.1) due to binding to boric acid ([B6] and [B62], cf. Figure 4.2) are independent of pH. In contrast to the [B5] species, the [B62] chemical shift is upfield of the [B6] moiety are both upfield of that of the non-coordinated borate shown in Figure 4.7. Although not present below pH 7, the concentration of the [B6] complex with boric acid increases rapidly as [B(OH)4]− become more prevalent in solution (from pH 8 to 9, as shown in Figure 4.2), reaching a maximum around pH 9.2. The reaction of phenylboronic acid with neol-H2 results in the immediate precipitation of a white insoluble powder. Borate ions are capable of simultaneously coordinating one neol and one cis-cyclohexanediol. As previously reported for similar mixed systems, the 11B
Figure 4.7. $^{11}$B NMR spectrum of neol-H$_2$ and boric acid in a 25:1 molar ratio at pH 11 showing the formation of the mono- and bis-chelate complexes, [B$_6$] and [B$_6$$_2$], respectively.

Figure 4.8. $^{11}$B NMR spectrum of cis-cyclohexanediol, neol, and boric acid in a 4:4:1 molar ratio at pH 9.0.$^{20}$
NMR shift of this species, [B56], appears between the peaks due to the two relevant bis-chelate species (Figure 4.8).

An interesting negative result is that under the condition studied, there is no complex formation between tetraethylene glycol (IV) and boric acid. This suggests that the potential for a chelate (V) is insufficient to promote complex formation. It may be concluded therefore, that it is unlikely for boron to bind to guaran via a primary alcohol and an ether moiety (in either the β-D-mannopyranosyl backbone with α-D-galactopyranosyl side chain, shown in Figure 4.1). Furthermore, large chelates or bridging monodentate complexation (VI) as a potential for guar gum cross-linking can be excluded.

\[
\text{(IV)}
\]

\[
\text{(V)}
\]

\[
\text{(VI)}
\]

**Ab initio calculations.** In order to better understand the relative stability of *cis*- and *trans*-dil complexation to boron, the importance of reducing *versus* non-reducing hydroxyl groups, and the relative stability of 5- and 6-membered chelates, *ab initio*
Figure 4.9. Schematic representations of model compounds investigated by *ab initio* calculations.
calculations at the HF/6-31G** level (Experimental section) on a series of model compounds have been performed, as shown in Figure 4.9.

The energies of borate complexed to two cis-cyclohexanediols, cis-[B52], to one cis- and one trans-cyclohexanediol, cis-trans-[B52], and to two trans-cyclohexanediols, trans-[B52], were calculated along with the associated uncomplexed ligands (as shown in the Experimental section). The calculated B-O bond distance, and intra-ligand O-B-O angle for the chelating diols (104.98°) in trans-[B52] are within the experimental error of the crystallographically determined parameters in (DMSO)Na{B(O2C6H10)2}∞ [105.4(4)° and 106.0(4)°].12 The variation in the inter ligand O-B-O angles is, however, significant and presumably a consequence of the sodium ions coordinated to the [B(O2C6H10)2]+ anion in [(DMSO)Na{B(O2C6H10)2}]∞ (VII). Thus, while trans-[B52] exhibits four equivalent O-B-O angles (111.64 – 111.83°) while the analogous angles in [(DMSO)Na{B(O2C6H10)2}]∞ are grouped into those associated with the sodium cations [105.7(5)° and 107.5(5)°] and those that are not [116.0(7)° and 116.6(6)°].

![Diagram of cis-cis complex](VII)

The total energies of the optimized structures of the model compounds were determined at the B3LYP level using 6-31G** basis set (Table 4.3). The cis-cis
<table>
<thead>
<tr>
<th>Compound</th>
<th>Total energy (Hartrees)</th>
<th>Relative energy (kJ.mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{trans-}C(<em>6)H(</em>{10})(OH)(_2)</td>
<td>-386.19391982</td>
<td>0</td>
</tr>
<tr>
<td>\textit{cis-}C(<em>6)H(</em>{10})(OH)(_2)</td>
<td>-386.17672626</td>
<td>+45.1</td>
</tr>
<tr>
<td>\textit{cis-[B52]}</td>
<td>-795.301336820</td>
<td>0</td>
</tr>
<tr>
<td>\textit{cis-trans-[B52]}</td>
<td>-795.296048641</td>
<td>+13.9</td>
</tr>
<tr>
<td>\textit{trans-[B52]}</td>
<td>-795.292468570</td>
<td>+23.3</td>
</tr>
<tr>
<td>\textit{cis-2,3-(OH)(_2)C(<em>5)H(</em>{10})O}</td>
<td>-422.06979306</td>
<td>0</td>
</tr>
<tr>
<td>\textit{cis-3,4-(OH)(_2)C(<em>5)H(</em>{10})O}</td>
<td>-422.06522515</td>
<td>+12.1</td>
</tr>
<tr>
<td>\textit{cis-[B(2,3-5)]}</td>
<td>-597.6966119</td>
<td>0</td>
</tr>
<tr>
<td>\textit{cis-[B(3,4-5)]}</td>
<td>-597.6883323</td>
<td>+21.7</td>
</tr>
<tr>
<td>\textit{cis-[B(2,3-5)(_2)]}</td>
<td>-867.0780825</td>
<td>0</td>
</tr>
<tr>
<td>\textit{cis-[B(3,4-5)(_2)]}</td>
<td>-867.0565407</td>
<td>+56.5</td>
</tr>
<tr>
<td>\textit{[B(1,2-5)]}</td>
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<tr>
<td>\textit{[B(1,3-6)]}</td>
<td>-520.28639831</td>
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<tr>
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<td>0</td>
</tr>
<tr>
<td>\textit{[B(1,3-6)(_2)]}</td>
<td>-712.24128888</td>
<td>+15.1</td>
</tr>
</tbody>
</table>

\(^a\) All calculations performed at the B3LYP level using 6-31G** basis sets.
conformation cis-[B52] was found to be most energetically favorable, being 13.9 kJ·mol⁻¹ more stable than cis-trans-[B52], and 23.3 kJ·mol⁻¹ more stable than trans-[B52]. A comparison of the relative stability of the uncomplexed cis- and trans-cyclohexanediols shows that the relative ΔHᵣ also follow the order cis-[B52] > cis-trans-[B52] > trans-[B52]. A trend that is consistent with boric acid, rather than the borate anion, being the reactive species.

A consequence of the availability of the reducing hydroxyl groups in simple monosaccharides (see below) is the observation of unusually large equilibrium constants (K₁ and K₂) for the binding of borate (shown in Table 4.1).²³ However, it has been reported that the equilibrium constants for borate binding to 1-methoxy mannose and 1-methoxy galactose (i.e., in which the basic hydroxide is blocked) are comparable to those of simple diols (Table 4.1).¹⁷ To quantify the effect of increasing the acidity of the hydroxyl groups, ab initio energy calculations were performed on cis-tetrahydropyran-2,3-diol (VIII) and cis-tetrahydropyran-3,4-diol (IX) and their borate complexes (Figure 4.9). The choice of these ligands was based upon the desire to compare two categories of isoelectronic complex in which the basicity of one of the diols is increased due to the adjacent oxygen.

![Diagrams of VIII and IX](https://example.com/diagrams.png)
Complexation through the reducing cis-diol group in cis-[B(2,3-5)] is thermodynamically favored compared to complexation through the non-reducing cis-diol moiety in cis-[B(3,4-5)], as shown in Table 4.3. Optimization and energy calculations were also performed with the reducing (more acidic) and non-reducing (less acidic) cross-linked species for both the cis- and trans- conformations, i.e., cis-[B(2,3-5)₂], cis-[B(3,4-5)₂], cis-[B(2,3-5)₂], and cis-[B(3,4-5)₂] (Table 4.3). As expected, cross-linking through the reducing hydroxyl groups in the cis-conformation, cis-[B(2,3-5)₂], is most stable. This result indicates that the acidity of the hydroxyl groups has a larger effect on the energies of the cross-linked complexes than the conformation.

In an effort to understand the effect of increasing the chelate ring size on the stability of the mono-diol, [B(OH)₂L]⁻ (I) and the bis-diol, [BL₂]⁻ (II), complexes, ab initio energy calculations were performed on borate complexes of the methylether of propane-1,2,3-triol (IX). The choice of the methyl ether mitigates taking intra-molecular hydrogen bonding into account. A comparison of both the mono-chelates, [B(1,2-5)] versus [B(1,3-6)] (Figure 4.9), and the associated bis-chelates, the five membered chelates are more stable than the six membered analogs, i.e., [B(1,2-5)] > [B(1,3-6)] and [B(1,2-5)₂] > [B(1,3-6)₂] (Table 4.2). This order is confirmed by previously published experiments.¹¹

\[
\text{HO} \quad \text{OH} \\
\text{OH} \\
\text{(IX)}
\]

**Complexes with mono- and poly-saccharides.** In addition to investigating the interaction of boric acid and phenylboronic acid with the guaran monosaccharides,
mannose and galactose, the complexation with the monosaccharide L-fucose (6-deoxy-L-galactose), and the disaccharides, cellobiose (β-D-1,4-glucose dimer), and sucrose was studied. Schematic representations of the monosaccharides examined are shown in Figure 4.10; a summary of the $^{11}$B NMR chemical shifts and equilibrium constants is given in Table 4.1.

Fucose is related to the galactose monosaccharide (Figure 4.10c and b, respectively), that forms the guaran polymer, but with hydrogen in place of the primary alcohol on the C-6 position. Thus, coordination of boric acid to fucose is limited to either cis- or trans-[B5] coordination. In contrast, cellobiose and sucrose are used to characterize the chemical shift due to complexation to either trans-[B5] or [B6] in a saccharide. Unlike cellobiose, the reducing hydroxyl group in sucrose is used to link the glucose and pentose sub-units (Figure 4.1).

The complexation of boric acid to fucose occurs as [B5] and [B52] (Table 4.1). In addition to the peak due to non-coordinated borate, the $^{11}$B NMR spectrum of boric acid and cellobiose (at pH 9) shows two peaks due to trans-[B5] and [B6], $\delta = 5.3$ and 1.6 ppm, respectively. Any peak due to boron cross-linking two 5-membered rings, trans-[B52], is obscured by the broad non-coordinated borate peak. However, no cross-linking is observed at pH 8.0. There are no cis-diol groups in cellobiose, and therefore the existence of a peak at 5.3 confirms that coordination through trans-moieties is possible in sugars with uncomplexed reducing hydroxyl groups. The $^{11}$B NMR of boric acid and sucrose shows only a single mode of coordination, [B6]. A similar, but more extensive coordination is observed between phenylboronic acid and sucrose (Table 4.1).

β-Mannose monosaccharides comprise the backbone of the guaran polymer. In solution, mannose exists as a mixture of α- and β-anomers. $^{13}$C NMR reveals that the β-anomer dominates (≈ 80%) in the sample used in these studies. $^{11}$B NMR of an aqueous solution of mannose and boric acid reveals three different types of species in addition to the non-coordinated borate. These may be assigned by comparison to the spectrum of
Figure 4.10. Schematic representation of (a) β-mannose (b) α-galactose, (c) fucose, (d) cellobose and (e) sucrose.

boric acid with *cis*-cyclohexanediol and neol as well as the other saccharides studied (Table 4.1). The $^{11}$B NMR shifts for these species are essentially independent of pH. The peak at 6 ppm due to [B5] is actually due to at least three distinguishable species. At pH
8.5, a peak at 6.3 ppm is the major species, with two shoulders at 5.3 ppm and 5.7 ppm being present. At pH 9.5, the shoulders become sharper and more readily distinguished from the major species. As may be seen from Figure 4.10a there are four possible ways in which boron can coordinate to mannose to produce 5-membered rings, [B5]: a cis interaction between C-2 and C-3, a trans interaction between C-3 and C-4, and two possible coordination modes through the reducing hydroxyl group on C-1 (cis for \(\beta\)-mannose and trans for \(\alpha\)-mannose). Assuming that these four modes are discernable by \(^{11}\)B NMR, and given the lower concentration of \(\alpha\)-mannose and the favorability of cis versus trans complexation it may be that the missing peak is either the trans C1-C2 in \(\alpha\)-mannose or the trans C3-C4 complex.

Galactose monosaccharides are attached via 1->6 linkages to approximately every other mannose in the backbone of guaran. In solution, galactose exists in equilibrium between both \(\alpha\)- and \(\beta\)-anomers. \(^{13}\)C NMR indicates that there is a slight excess of \(\alpha\)-anomer present (\(\approx 55\%\)). \(^{11}\)B NMR reveals three types of species are present in solutions of galactose and boric acid (Table 4.1), as observed with mannose.\(^{20}\) As with mannose, the peak at \(ca. 6\) ppm in spectra of galactose and boric acid is actually due to multiple [B5] species. At most pH values, a peak at 5.7 ppm dominates. Above pH 8, two shoulders, at 5.2 ppm and 6.3 ppm, are observed. At higher pH, these are narrower and are readily distinguished from each other. Interestingly, the peak at 5.7 ppm decreases with increased addition of galactose.\(^{20}\) The formation of [B6] is much less favored for galactose than mannose. In fact, the amount of [B6] formed is too low to give a reliable plot for the determination of K[B6]. The effect of the relative concentration of the galactose [B5] and [B5\(\_2\)] (\(\delta = 10.7\) ppm) complexes with galactose concentration is similar to that observed for mannose.\(^{20}\)

The reaction of phenylboronic acid with the guaran monosaccharides, mannose and galactose shows the presence of [B5] complexation with a significantly larger K[B5] (Table 4.1). Importantly, as was observed for 1,2-cyclohexanediol, the initial formation of
the [B5] complexes occurs at a lower pH that for boric acid. This observation offers a potential for improved cross-linking agents.

**Complexation with guar.** Prior work on the guar gum/borate system has employed solution $^{11}$B NMR despite the obvious problems associated with the insolubility and high molecular weight of the cross-linked guar resulting in broadening. The MAS $^{11}$B NMR spectrum of guar cross-linked with an excess of boric acid at pH 9.2 was determined (Experimental section).

Two peaks are observed in the $^{11}$B NMR spectrum of the boric acid/guar gel. A peak at 4.6 ppm ($W_{1/2} = 220$ Hz) can be assigned to [B5] or [B56] complexation while that at 9.0 ppm ($W_{1/2} = 190$ Hz) is due to [B52] cross-linking. Under the conditions employed (boric acid:guar = 4:1) the two peaks are of close to equal intensity.

The $^{11}$B NMR spectrum of the product from the reaction of phenyl boronic acid and guar exhibits a single broad resonance at 1.8 ppm ($W_{1/2} = 320$ Hz). This resonance is outside of the range expected for [B5] but within the range of [B6], however, the extremely weak signal (only just observed above the background of the probe, as shown in the Experimental section) and the lack of potential cross-linking obviating any definitive assignment.

**Molecular mechanics calculations.** Although the calculations on the model systems described above provide insight into the relative stability of the various potential cross-linking modes (i.e., [B52] versus [B62]) they do not provide information with regard to the potential cross-linking in the guaran system. Due to the complexity of the guar gum system a relatively simplistic geometry optimization using the molecular mechanics method MMFF94 was undertaken (Experimental section). This study is limited to symmetrical complexes, i.e., those in which the boron is bonded to the same group on each guaran polymer chain.
As may be seen from Figure 4.11 – 4.15, cross-linking via the mannose backbone groups occurs via the cis-[B₅₂] complex. However, two isomers are possible, wherein the boron binds to a mannose that is either connected (Figure 4.11) or not (Figure 4.12) to a galactose. Each isomer results in the orientation of the guaran backbones parallel to each other. Observation of space filling representations indicates that binding to the backbone results in significant steric strain (although some of this is presumably mitigated by the potential for hydrogen bonding between the adjacent guaran chains.

Figure 4.11. Computer generated structure of cis-[B₅₂] cross-linking two small sections of guaran polymer via the 2,3-diols of the mannose backbone. The borate is coordinated to a mannose linked to a galactose, and the mannose backbones are oriented parallel. Atoms are color coded as follows: carbon (grey), oxygen (red), hydrogen (white), and boron (yellow).
**Figure 4.12.** Computer generated structure of *cis*-[B5₂] cross-linking two small sections of guaran polymer via the 2,3-diols of the mannose backbone. The borate is coordinated to a mannose not linked to a galactose, and the mannose backbones are oriented parallel. Atoms are color coded as follows: carbon (grey), oxygen (red), hydrogen (white), and boron (yellow).

**Figure 4.13.** Computer generated structure, viewed along one of the poly-mannose backbone chains, of a *trans*-[B5₂] cross-linking two small sections of guaran polymer via the 2,3-diols of the galactose side chain. The mannose backbones are oriented perpendicular. Atoms are color coded as follows: carbon (grey), oxygen (red), hydrogen (white), and boron (yellow).
**Figure 4.14.** Computer generated structure of a *cis*-[B5₂] cross-linking two small sections of guaran polymer via the 3,4-diols of the galactose side chain. The mannose backbones are oriented at approximately 45° to each other. Atoms are color coded as follows: carbon (grey), oxygen (red), hydrogen (white), and boron (yellow).

**Figure 4.15:** Computer generated structure of [B6₂] cross-linking two small sections of guaran polymer via the 4,6-diols of the galactose side chain. The mannose backbones are oriented at approximately 40° to each other. Atoms are color coded as follows: carbon (grey), oxygen (red), hydrogen (white), and boron (yellow).
Cross linking via the galactose side chains can occur via either trans- or cis-[B5₂] complexes or [B6₂] (Figure 4.13 - 15, respectively). The cis-[B5₂] and [B6₂] isomers (Figure 4.18 and 19) involving the galactose side chains result in an overall configuration in which the steric interactions between the two guaran polymer chains are minimized.

**What is the mode of complexation of borate with guar?** A key issue in the structural characterization and understanding of the guar/boric acid system is the assignment of the $^{11}$B NMR spectral shifts associated with various complexes. A summary of chemical shifts and equilibrium constants for boric and phenyl boronic acid systems is given in Table 4.1. A graphical representation of the observed shift ranges for boric acid chelate systems is shown in Figure 4.16. As is clearly observed, the chemical shifts for the different chelate ([B5] and [B6]) and chelate cross-linked ([B5₂] and [B6₂]) species are distinct allowing for easy assignment.

![Diagram of B(OH)₃ and B(OH)₄⁻ shifts](image)

**Figure 4.16.** $^{11}$B NMR spectroscopic shifts of chelate alkoxide compounds in comparison with boric acid and borate anion.

Based upon the data shown in Figure 4.16, the peak at 9.0 ppm to [B5] coordination has been assigned, while the second peak observed (4.6 ppm) is in the range of both [B5] and [B5₆] coordination. However, since no peak associated with [B6₂] is observed (which would be expected based upon the results for cis-cyclohexanediol and
neol mixtures, shown earlier), and the peaks are of near equal intensity, it can be proposed that the resonance at 4.6 ppm is due to [B5] coordination. These results directly contradict prior studies.

Jasinski et al. reported the presence of two peaks in the solution $^{11}$B NMR spectrum of guar-boric acid. The peaks at 6.1 and 2.1 ppm were assigned as being due to [B56] and [B62], coordination, respectively. A comparison of these resonances with Figure 4.16 shows that their assignment is not consistent with the assignment in this study and other solution $^{11}$B NMR studies. The most intense peak observed by Jasinski et al. (6.1 ppm) is undoubtedly due to [B5] coordination, while the lower intensity peak (2.1 ppm) is within the range associated for [B6] coordination. Given the discrepancy between our results and those of Jasinski et al., it is worth further discussion.

Firstly, Jasinski reported a binding constant for the formation of a cross-linked guar (i.e., $K_{12}$, in Eq. 4.11) in the range 83 to 130. This is significantly larger than the values observed for [B52] and [B62] cross-linking (Table 4.1) and also higher than determined in this study for the highly reactive basic (and hence for reactive) hydroxides in the monosaccharides (shown earlier and in Table 4.1). Secondly, Jasinski et al. calculate a $\Delta H$ for [B56] cross-linking of 21 kJ.mol$^{-1}$ and 30 kJ.mol$^{-1}$ for [B62]. These values suggest that [B62] cross-linking is 9 kJ.mol$^{-1}$ more stable than [B56], with [B52] presumably being less stable still since it was not thought to occur. In contrast, it was calculated in this study that the [B62] cross-linking is 15.1 kJ.mol$^{-1}$ less stable than [B52] (Table 4.3). Finally, and possibly more telling, they calculated a positive $\Delta S$ for an associative reaction (Eq. 4.2). In order to explain the observation of a positive $\Delta S$ by Jasinski et al., one must consider the reactions that are present and whether the products are in solution or solid state, then determine which species were observed in their solution $^{11}$B NMR experiment.

Using Eq. 4.2 as a model reaction, the cross-linking of guar (G) can be represented by the equilibria shown in Eq. 4.14.
\[
\begin{align*}
K_1 & \\
[B(OH)_4]^{-} + 2G & \rightleftharpoons [B(OH)_2G]^{-} + G & \rightleftharpoons [BG_2]^{-} \quad (4.14)
\end{align*}
\]

Uncomplexed borate ion would be expected to be soluble under the conditions reported, and thus observable by solution \(^{11}\)B NMR spectroscopy. The molecular weight of the guar used by Jasinski et al. was \(2 \times 10^6\) Da and was found to have a solubility of 63 g.L\(^{-1}\). This solubility would allow observation by solution \(^{11}\)B NMR of any boron that was coordinated but not cross-linked. In contrast, since a single cross-linking reaction will increase the molecular weight significantly (at least by a factor of two), and the increased viscosity observed for cross-linked guar suggest that many cross-linking reactions take place per strand of guar, the cross-linked guar is unlikely to be soluble under the conditions studied. In addition, any material that is "soluble" would be of sufficient molecular weight such that tumbling in solution would be slowed so that any NMR peak would be broadened to the point of being unobserved. Therefore, while \([B(OH)_4]^{-}\) and \([B(OH)_2G]^{-}\) would be observed by solution \(^{11}\)B NMR, \([BG_2]^{-}\) would only be observed by solid state MAS \(^{11}\)B NMR. This conclusion is in agreement with our assignment of Jasinski's data.\(^{16}\)

The reaction of boric acid with guar would yield the species shown in Eq. 4.14. For a typical complexation reaction (Eq. 4.2) and as is observed through a study of a wide range of model compounds, the \(\Delta S\) for each reaction (complexation and cross-linking) would be negative. This has been observed both by Pezron et al.,\(^{17}\) and in this study. Increasing the temperature would result in the dissociation of boron from the guar, i.e., the equilibria shown in Eq. 4.14 would shift to the left. If the \(^{11}\)B NMR experiment only observed \([B(OH)_4]^{-}\) and \([B(OH)_2G]^{-}\), and their relative quantities would change. It would be expected that their relative intensity as compared to "non-coordinated" borate would decrease, as was observed by Jasinski.\(^{16}\) Thus, at higher temperatures Jasinski et al. were
not measuring the *increase* in cross-linking, but the *increase* in the formation of soluble non-crosslinked (but complexed) guar.

Reassignment of Jasinski’s solution $^{11}$B NMR spectrum as being due to soluble non-crosslinked guar, in which boron is complexed by [B5] (major) and [B6] (minor) coordination, is consistent with both the chemical shifts and the temperature dependence of the peak intensities.

**What is the coordination site of boron on guar?** If it is concluded that boron coordinates to guar predominantly via [B5] coordination, and cross-links via [B$^{5+}$] coordination, then the next question concerns the coordination site.

As may be seen from Figure 4.1, guaran provides four potential binding [B5] sites: via the 2,3-*trans*-diols or 3,4-*cis*-diols of the galactose side chain and via the 2,3-*cis*-diols of the mannose backbone in which the mannose is either linked or not to a galactose (Figure 4.11 - 14). With a galactose (side chain) to mannose (backbone) ratio of approximately 2:1, these four potential sites are approximately equimolar.

In aqueous solutions, assuming that boric acid is the reactive species (see below), there is a preference to cross-linking via *cis*-cyclohexanediols over *trans*-cyclohexanediols (Table 4.1 and 4.2) and *ab initio* calculations (Table 4.3) show that the boron cross-linking through *cis*-dial groups is favored over cross-linking through *trans*-dial groups. It should be noted that coordination to *trans* moieties is only observed in aqueous monosaccharide solutions due to the presence of more acidic hydroxyl groups (shown above). 24,25 Thus, based upon the relative thermodynamic stability, it would be expected that coordination of boron via the 3,4-*cis*-dial of the galactose side chain and the 2,3-*cis*-diols of the mannose backbone be preferred over the 2,3-*trans*-diols of the galactose side chain. This is also consistent with geometry optimization calculation using the molecular mechanics method MMFF94 (shown above). Based upon steric congestion about the boron center and the packing of the two adjacent guar chains, the relative
preference for cross-linking is proposed to be: 3,4-\textit{cis}-diol of the galactose side chain $> 2,3$-\textit{cis}-diols of the mannose backbone in which the mannose is linked to a galactose $> 2,3$-\textit{cis}-diols of the mannose backbone in which the mannose is not linked to a galactose. Therefore, it can be proposed that the preferred cross-linking site on guaran would be the 3,4-\textit{cis}-diols of the galactose side chain. However, complexation without cross-linking (i.e., \textbf{B5}) would show a preference for the $2,3$-\textit{cis}-diols of the mannose backbone on statistical grounds.

\textbf{Boric acid versus borate anion: Which reacts with diols?} Based upon a study with ethylene glycol, van Duin \textit{et al.}, proposed that simple diols react with the anion rather than boric acid.\textsuperscript{9} They postulated that the maximum formation of $[B(OH)_2L]^-$ and $[BL_2]^-$ occurs at a pH higher than the $pK_a$ (boric acid), which is determined to be 9.07 (Figure 4.4a). This postulate was made because the concentration of the glycol/borate complexes increased with increasing pH. Unfortunately, their study was limited to a pH of 12. This study has shown that if this pH range is extended, the formation of the borate complexes is reversed and $[B(OH)_4]^-$ is the only boron containing compound observed at high pH. A similar trend is also observed for phenyl boronic acid (e.g., Figure 4.5). In contrast to the results for glycol, van Duin \textit{et al.},\textsuperscript{9} proposed that optimum pH for the formation of glycolic acid complexes is under the condition where $pK_a$ (glycolic acid) $< \text{pH} < pK_a$ (boric acid). Under these conditions it is the boric acid, $B(OH)_3$, not the borate anion, $[B(OH)_4]^-$, that reacts to form the complex. There has thus existed an unusual situation in subsequent literature\textsuperscript{10,11,23} where carboxylic acids are assumed to react with boric acid, but alcohols react with the borate anion.

A comparison of the relative speciation of boric acid/borate as a function of pH (Figure 4.4) and the formation of various complexes suggests that this latter condition is actually appropriate for diols such as glycol. This is in contrast to the proposal of van Duin \textit{et al.}\textsuperscript{9} For example, an overlay of the data in Figure 4.4b and Figure 4.5a shows that
at the pH for maximum complex formation *ca.* 50% of the boron would be expected to exist as boric acid. Furthermore, the decrease of complex with increased pH closely follows the competitive formation of the boron anion, \([\text{B(OH)}_4]^−\). Additionally, if the borate anion, \([\text{B(OH)}_4]^−\), was the reactive component with a diol such as glycol, then increases in pH above 9-10 should result in *increased* complex formation since this maximizes the availability of \([\text{B(OH)}_4]^−\). This is not observed and it can be proposed that the formation of \([\text{B(OH)}_2\text{L}]^−\) most likely occurs via the reaction of boric acid rather than borate. There are several areas of supporting evidence for our proposal.

The conversion of boric acid to borate (Eq. 4.1) must occur through attack of hydroxide or the deprotonation of a coordinated water ligand,\(^{26}\) either of which is related to the pK\(_a\) of water. The formation of \([\text{B(OH)}_2\text{L}]^−\) from \(\text{B(OH)}_3\) would be expected therefore to occur via a similar initial reaction (attack by RO\(^−\) or deprotonation of coordinated ROH) followed by a subsequent elimination of \(\text{H}_2\text{O}\) and the formation of a chelate coordination, and would therefore be related to the pK\(_a\) of the alcohol. Thus the pH at which \([\text{B(OH)}_2\text{L}]^−\) is formed relative to \([\text{B(OH)}_4]^−\) will depend on the relative acidity of the alcohol. The pK\(_a\) of a simple alcohol (e.g., MeOH = 15.5, EtOH = 15.9) are close to the value for water (15.7) and the lowest pH at which \([\text{B(OH)}_2\text{L}]^−\) is formed should be comparable to that at which \([\text{B(OH)}_4]^−\) forms, as can be seen from Figure 4.4b and 5a, this is indeed observed. The dependence of borate binding with the acidity of resins has been recently reported.\(^{27}\)

Given the above, the pH at which complexation occurs would be expected to be lower the more acidic the alcohol. This is indeed observed. As may be seen from a comparison of Figure 4.5a and b, the pH at which complexation occurs for catechol (pH > 4) is significantly lower than for ethylene glycol (pH > 7). This difference is consistent with the relative pK\(_a\) of an alcohol (*ca.* 15.5) versus a phenol (10.0). The complex between catechol and phenyl boronic acid occurs at a lower than the pH (> 4) than that at which the borate anion, \([\text{PhB(OH)}_3]^−\), is observed (pH > 6), suggesting that the neutral
phenyl boronic acid is the reagent rather than the anion (Eq. 4.15). A similar reaction is expected for boric acid (Eq. 4.16).

\[
\text{PhB(OH)}_2 + \text{LH}_2 \xleftrightarrow{\text{H}_2\text{O}} [\text{PhB(OH)\text{L}}^-] \quad (4.15)
\]

\[
\text{B(OH)}_3 + \text{LH}_2 \xleftrightarrow{\text{H}_2\text{O}} [\text{B(OH)}_2\text{L}^-] \xleftrightarrow{-2 \text{H}_2\text{O}} [\text{BL}_2]^-. \quad (4.16)
\]

It can be proposed therefore that the formation of \([\text{B(OH)}_2\text{L}^-]\) as compared to \([\text{B(OH)}_4]^-\) is a competition between the reaction of \(\text{B(OH)}_3\) with \(\text{RO}^-\) and \(\text{OH}^-\) (Scheme 4.1). The inability of alcohols to form complexes (despite potential chelate via an ether group, i.e., IV) has been observed and this suggests that the chelate effect is the factor that enables the formation of \([\text{B(OH)}_2\text{L}^-]\). With regard to boron cross-linking of guaran, the presence of multiple available chelate 1,2-diol sites is the saving grace for this system. Given the aqueous nature of the system, and the competition between complex and borate formation, the chelate effect and the intramolecular elimination of water, are the only driving forces for cross-linking (Scheme 4.1).

Scheme 4.1. Proposed competition between hydroxide and 1,2-diol for complexation to boron in the aqueous boric acid/diol system.
How can the efficiency of boric acid cross-linking of guar be enhanced? From the forgoing it can be summarized that the cross-linking of guar by borate is highly inefficient. The reasons for this are four-fold: a) the reactive reducing hydroxyl groups on both mannose and galactose monomers are consumed in the (1 $\rightarrow$ 4) polymerization of mannose and the (1 $\rightarrow$ 6) attachment of galactose (Figure 4.1); b) $[^{B_6}_2]$ cross-linking is preferred on steric grounds, but the sterically more demanding $[^{B_5}_2]$ conformation is favored energetically, and is actually the mode observed; c) an excess of borate is required since the equilibrium constants for the formation of $[^{B_5}]$ are low ($1 - 10 \text{ mol}^{-1}\text{dm}^3$) and the cross-linking reaction, $[^{B_5}_2]$, are between 15-50% of the value for $[^{B_5}]$; d) the competition between hydroxide and the alcohol for complexation to boron arising from the similarity in $pK_a$ for water and the diol. Based upon the $K_{eq}$ values it may be estimated that only 1% of the boric acid in a typical guar system are actually involved in cross-linking. Clearly, the structure of guar is not optimized for cross-linking with boric acid. Furthermore, based upon the solvent, pH and speciation required for complexation (see below) boric acid is itself not an optimum cross-linking agent.

It would be desirable to have an alternative material to guar, one in which a basic hydroxide was available on the side chain. Since this would require finding an alternative low cost polysaccharide with suitable molecular weight characteristics, or chemically modifying guar at great expense, it is more reasonable to propose the use of alternative, more efficient, cross-linking agents.

Based upon the steric hindrance inherently based upon the $[^{B_5}_2]$ unit between two guar polymers (shown above), and the observation that binding is more efficient that cross-linking, a di-boron moiety (e.g., $X$) would have significant advantages. In particular, the presence of a spacer or linker unit would minimize steric interaction between guar chains, i.e., $XI$ versus $XII$ for boric acid. If a phenyl borate cross-linking species ($XIII$) were used then the pH at which a defined amount of boron compound is active for cross-linking would be reduced by approximately half a pH unit; significant
with respect to competition with hydroxide (shown below). This in turn would result in a reduction in the use of base in the field, a significant environmental impact.

(X)

(XI)

(XII)

(XIII)

As an alternative approach the Barron lab is currently investigating the use of borate functionalized nanoparticles as more efficient, thermally stable cross-linking agents. Each
borate moiety attached to the nanoparticle acts independently, allowing cross-linking to occur via several one-step processes rather than depending on a two-step mechanism (Eq. 4.2). This is undoubtedly the mechanism by which hydrolyzed alkoxides of various metals function as cross-linking agents. 28, 29, 30

A final issue to take into account is the water: diol ratio used for hydraulic fracturing fluid applications. At a guaran:H₂O:B(OH)₃, ratio of 10:2000:1 wt/wt, there is approximately a 10³ molar excess of water available for reaction as compared to diol on the guaran chain. Given the competition between hydroxide and the diol, a significant decrease in the water content would provide more efficient cross-linking per boron. However, this approach is limited by solubility and practical considerations.

**Conclusions**

Using ¹¹B MAS NMR spectroscopy and in comparison with model compounds, it has been shown over here that boric acid cross-links guaran (the major constituent of guar gum) via [B₅₂] coordination. Based upon steric constraints we propose that preferential cross-linking the guaran polymer occurs via the 3,4-cis-diols of the galactose side chain.

Unfortunately, despite its commercial applications, it is hardly possible to conceive of a less efficient method than the guar-boric acid system. The most reactive sites on the component saccharides (mannose and galactose), at the 1-position, are precluded from reaction by the nature of the guar structure (Figure 4.1). The comparable acidity (pKₐ) of the remaining guaran alcohol substituents and the water solvent, results in a competition between cross-linking and borate formation. The large water content of a typical fracture fluid compounding this last issue. Furthermore, a significant fraction of the boric acid is ineffective in cross-linking guar. As a consequence of the modest equilibrium (Kₑq) the majority of the boric acid is present in its un-complexed forms (boric acid or borate), or simply complexed to the guar polymer ([B₅]),. It should be remembered that the results discussed herein are for samples at ambient or near ambient
temperatures, down-hole temperatures can be significantly higher, leading to less cross-linking. Therefore, the large excess of boric acid required to provide the viscosity desired by the oil well drilling industry for hydraulic fracturing fluids is a combination of these factors. In answering the questions posed in the introduction, the inefficiency of boric acid to cross-link guar gum is not due to the lack of reactivity of boric acid, but to the competition between diol-complex and borate formation, and it appears that all sites have potential for cross-linking, although steric congestion is a possible factor for cross-linking via the backbone.

**Experimental Section**

$^{11}$B NMR spectra were collected at 64.2 MHz on a Bruker Avance 200 spectrometer using a 8.1 μs 90° pulse, 0.5 s FID acquisition time and a 1.0 s acquisition delay. All chemical shifts were referenced to an external BF$_3$(Et$_2$O) standard at 0.0 ppm. pH measurements were made with an Orion 230A pH meter with an accuracy of 0.1 pH units. All chemicals were used as received without further purification. Unless otherwise stated DI water was used for all solutions. Solid state $^{11}$B NMR spectra were collected in a 7mm rotor at 64.2 MHz on a Bruker Avance 200 spectrometer using 0.5 μs pulse length and a hpdec ($^{11}$B pulse with 1H decoupling) pulse program, 0.032 s FID acquisition time, a 5 s acquisition delay and a spinning rate of 4000 Hz. All chemical shifts were referenced to Na[BPh$_4$] $\delta$ = -6.3 ppm.$^{31}$

**Solution NMR sample preparation.** To determine the characteristic $^{11}$B NMR shifts of borate with diols, samples were prepared using 10 % D$_2$O as the lock solvent and the pH was adjusted with NaOH to between 8.5 and 9. In general, excess of the diol (ca. 4:1 mol ratio of diol to borate) was employed to ensure that a sufficient amount of cross-linked species was formed to allow detection. All spectra were collected at room temperature. Solutions used to determine the equilibrium constants in the borate-neol, cis-cyclohexandiol, mannose and galactose systems were prepared as follows. Three stock
solutions were prepared: 1) boric acid (0.504 g, 0.0326 M) and NaCl (10.227 g, 0.7 M) in a deionized water/D$_2$O mix (200 mL water, 50 mL D$_2$O); 2) NaOH (0.8 g in 100 mL, 0.2 M) and NaCl (4.09 g, 0.7 M); 3) NaCl (4.09 g in 100 mL, 0.7 M). The boric acid solution (5 mL) was added to a vial containing the weighed amount of the diol or sugar. The pH was adjusted to either 9 or 11 using the stock NaOH/NaCl solution. The stock NaCl solution was used to bring the total volume of the solution to 10 mL by the total weight, taking into account the NaCl, boric acid, and weight of the sugar present. For example, the solution containing a 4:1 mol ratio of neol to boric acid was prepared by first weighing neol (0.068 g, 0.65 mmol) into a clean vial, adding the stock boric acid/NaCl solution (5.0 g H$_2$O/D$_2$O mix + 0.21 g NaCl + 0.01 g boric acid = 5.22 g total) then adjusting the pH using the NaOH/NaCl solution, then raising the total weight of the solution using the NaCl solution (total expected weight = 10 g H$_2$O/D$_2$O + 0.41 g NaCl + 0.01 g boric acid + 0.068 g neol = 10.5 g). This method resulted in solutions that were 0.0163 M boric acid/borate ion, the same concentration used to cross-link guar, and 0.7 M NaCl to keep the total ionic concentration of the solution approximately constant. In most cases, the concentration of the diol was varied from 0.00815 M to 1.63 M. The same stock solutions were used to determine the extent of cross-linking in the neol-borate system as a function of pH. The concentration of neol was fixed (0.4075 M, 25 : 1 neol : borate ratio) and the pH was varied from 7 to 11.

The determination of the $^{11}$B NMR shifts of phenylboronic acid with diols, samples were prepared using 10 % D$_2$O as the lock solvent and the pH was adjusted with NaOH to the required pH. All spectra were collected at room temperature. In general, excess of the diol (> 4:1 mol ratio of diol to phenylboronic acid) was employed to ensure that a sufficient amount of cross-linked species was formed to allow detection. Solutions used to determine the equilibrium constants in the phenylboronic acid - ethyleneglycol, catechol, cis-cyclohexane 1,2-diol, trans-cyclohexane 1,2-diol, pinacol, tetrathyleneglycol, mannose and galactose systems were prepared as follows. Three stock
solutions were prepared: 1) phenylboronic acid (3.97 g, 32.6 mM) and NaCl (10.227 g, 0.70 M) in a deionized water/D$_2$O mixture (200 mL water, 50 mL D$_2$O); 2) NaOH (0.8 g in 100 mL, 0.2 M) and NaCl (4.09 g, 0.70 M); 3) NaCl (4.09 g in 100 mL, 0.70 M). The phenylboronic acid solution (5.0 mL) was added to a vial containing a weight amount of the diol or sugar. The pH was adjusted using the NaOH/NaCl solution. The stock solution was used to bring the total amount of solution to 10 mL by the total weight, taking into account the NaCl, phenylboronic acid and the weight of the sugar present.

**Solid state NMR sample preparation.** Boric acid (1.0 g) was mixed with guar (2.0 g) in water (50 mL) resulting in a porridge-like solution. The initial pH of 5.28 was adjusted to 9.2 by the addition of aqueous NaOH (0.2 M). At which point it was not possible to stir the mixture anymore. MAS $^{11}$B NMR was run on this solid. A similar preparation was employed for phenyl boronic acid.

**Computational methods.** *Ab initio* calculations utilized non-local, gradient corrected density functional theory. For these molecules, relativistic effects were trivial and hence not taken into account. The 6-311++G basis set for carbon, hydrogen, oxygen and boron, yielded structures that were closest to X ray crystallographic parameters for [(DMSO)Na{B(O$_2$C$_6$H$_{10}$)$_2$}]$_{\infty}$. This basis set features single first d and p polarization functions as well as diffuse functions. Electron correlation effects were taken into account using Becke’s three-parameter hybrid gradient-corrected functional of Lee, Yang, and Parr (B3LYP). This functional was used for all geometry optimizations. The Gaussian98 Revision A.5, program was used for single point energy calculations and geometry optimizations.

Molecular mechanics calculations were performed using Spartan (02 Windows) running on a PC. The final structures are optimized using molecular mechanics method MMFF94.
References.


30 G. J. Rummo, Oil & Gas Journal, 1982, 80, 84.


Appendix A

Vacuum Bagging

The basic principal of a vacuum setup is that before the resin starts to cure, all the components and the mold are sealed in a plastic bag from which the air is then removed.\textsuperscript{1,2} This squeezes the laminate into the mold with the theoretical maximum pressure of one atmosphere. This ensures void free or virtually void free components, even when component shape is quite complex, better inter-laminar bond strength, and improved laminate consolidation. In short, the benefits are improved quality and mechanical properties.

The mold in the series of experiments in Chapter 2 was a thin 18" x 12" stainless steel plate (bottom) and the vacuum bag itself (top). Before each experiment, the stainless steel mold was cleaned well to make sure that it was free from any sharp corners or spikes of reinforcing fibers that might puncture or damage the vacuum bag. A thin layer of external mold release was brushed on to the bottom mold and then allowed to dry. Five pieces of alumoxane-coated fiber were stacked one on top of the other. Resin and hardener were applied to the fiber as described in Method 4 (Chapter 2). A piece of perforated release film was placed on top of the top most fiber layer. Release film is a thin, non-stick plastic film, which is used to separate the laminate from the stack of vacuum materials after curing. A perforated form was used in this case to allow the bleed-through of resin.

A piece of felt-like non-woven polyester material called the breather fabric was placed on top of the perforated release film. This served two purposes. Firstly, it ensured that the air in the vacuum bag was removed easily, by providing a pathway for the air and any volatiles that need to escape during the cure process. Secondly, the material acted as an absorbent layer for excess resin.
The vacuum bagging material that was used was a nylon film that has very low gas permeability and thus maintained a good vacuum. The bagging film was made into actual bags with the aid of sealing tape. This rubber based adhesive tape, roughly 2 cm in width, is adhesive coated on both sides with a removable backing paper on one face. It was placed onto the bottom mold and once in position the backing was removed and the bag material was stuck to it.

Finally, in order to connect the pipe from the house vacuum to the vacuum bag, a ‘through-bag connector’ was used. It is a length of metal pipe which fits into the metal pipe, with a ring of sealing tape wrapped around it, which is then stuck to the sealing tape on the periphery of the bag. The bag material was then tucked tightly around the pipe to form a good seal.

![Diagram of vacuum bag materials sequence](image)

Figure A.1. Vacuum bag materials sequence

References


Appendix B

NMR of Boron

Boron has two NMR-active isotopes, $^{10}\text{B}$ and $^{11}\text{B}$. The nuclear properties of boron are listed in Table B.1. In general, $^{11}\text{B}$ is the preferred nucleus for NMR, being more receptive, having a non-integral spin, and a smaller electric quadrupole moment. The standard reference used in boron NMR is BF$_3$.Et$_2$O at $\delta = 0$ ppm. Boron-containing glasses or ceramics are often present in the manufacture of spectrometer probes, and boron may be present in solution NMR sample tubes. Both sources create a broad background signal which can be a problem in very dilute solutions.

**Table B.1.** Summary of the properties of boron nuclei.

<table>
<thead>
<tr>
<th></th>
<th>$^{10}\text{B}$</th>
<th>$^{11}\text{B}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Receptivity relative to $^{1}\text{H}$</td>
<td>0.0039</td>
<td>0.133</td>
</tr>
<tr>
<td>NMR frequency (MHz)*</td>
<td>10.7</td>
<td>32.1</td>
</tr>
<tr>
<td>Natural abundance (%)</td>
<td>19.6</td>
<td>80.4</td>
</tr>
<tr>
<td>Spin, $I$</td>
<td>3</td>
<td>$3/2$</td>
</tr>
<tr>
<td>Quadrupole moment, $Q$, (10$^{-28}$ m$^2$)</td>
<td>0.074</td>
<td>0.0355</td>
</tr>
</tbody>
</table>

* Relative to $^{1}\text{H}$ at 100 MHz.

**Reference**

Appendix C

Publications


Patent

Presentations


Review