In class we used TTIP (titanium tetraisopropoxide) to crosslink hydroxyl terminated PDMS (polydimethyl siloxane). Often, PDMS is crosslinked using TEOS (tetraethoxy silicate). TEOS or TTIP can also be used to make a ceramic gel in a sol-gel reaction. This is the first step in the production of an aerogel.

1) a) Give the structure of TTIP.  
b) Give the structure of TEOS  
c) Show the reaction scheme (including stoichiometry) for hydrolysis of TEOS or TTIP.  
d) Show the reaction stoichiometry for the condensation of tetra hydroxy silicate or titanate to silica (SiO$_2$) or titania (TiO$_2$).  
e) Explain how water can act as both a catalyst and a reactant in the hydrolysis/condensation reaction of TEOS.

2) In crosslinking reactions to produce a rubber from hydroxyl terminated PDMS and TEOS or TTIP, HMDSO or HMDS (hexamethyldisiloxane) is often added to reduce the functionality of TEOS or other crosslinking agents.  
a) Give the structure of HMDSO (guess if you do not know, it has two silicon atoms bonded by an oxygen).  
b) Show the hydrolysis reaction scheme for HMDSO.  
c) Show the condensation production of hydrolyzed HMDSO with a hydroxyl group such as on tetrahydroxyl silicate (hydrolyzed TEOS) or hydroxyl terminated PDMS.  
d) How can this condensation reaction reduce the functionality of the network? (Functionality means the average number of bonds at a crosslink site.)  
e) Why is PDMS rubber used as an aerospace sealant materials?

3) In class we also made a silly putty from hydroxyl terminated PDMS mixed with boric acid.  
a) Give the structure of boric acid.  
b) Show the hydrolyzed structure of boric acid in water.  
c) If boric acid (61.8 g/mole and 1.44 g/cc were used in a stoichiometric ratio with hydroxyl terminated PDMS of 20,000 g/mole 0.965 g/cc) roughly how much tetrafunctional Boric acid would be needed to end link the PDMS chains? (Give a guesstimate assuming boric acid is trifunctional; PDMS is bifunctional.)  
d) How does this compare with the amount of Boric acid needed to make a reasonable silly putty material?  
e) Guess at the reason for the difference in amounts.
c) in "c" 4 water molecules are used; while in "d" 2 water molecules are produced so 2 water molecules act as catalysts and are regenerated while 2 water molecules act as reactants and are consumed.
2) a) 

\[
\begin{align*}
\text{Si} & \quad \text{Si} \\
\text{Si-O-Si} & \quad \text{Si} \\
\text{Si} & \quad \text{Si}
\end{align*}
\]

b) 

\[
\text{Si} - \text{O-Si} - + \text{H}_2\text{O} \xrightarrow{\text{hydrolysis}} 2 \left( \text{Si-0H} \right)
\]

\[
\text{Si} \left( \text{CH}_3 \right) \left( \text{OH} \right)
\]

c) 

\[
\text{Si} \left( \text{OEt}_4 \right) + 4 \left( \text{Si} \left( \text{CH}_3 \right) \left( \text{OH} \right) \right) \xrightarrow{\text{C}} 4 \left( \text{EtOH} \right) + 4 \left( \text{Si} \left( \text{CH}_3 \right) \left( \text{OH} \right) \right)
\]

\[
\text{Si} \left( \text{CH}_3 \right) \left( \text{OEt} \right) + 4 \left( \text{Si} \left( \text{CH}_3 \right) \left( \text{OH} \right) \right) \xrightarrow{\text{C}} 4 \left( \text{EtOH} \right) + 4 \left( \text{Si} \left( \text{CH}_3 \right) \left( \text{OH} \right) \right)
\]

d) The -0Si\left(\text{CH}_3\right)_{\text{Si}} bond does not further bend in the network.

e) Low Tg and high decomposition temperature lead to:

\[
\begin{align*}
\text{Si} - 127^\circ\text{C} & \quad \text{Si} \\
\text{Si-C} & \quad \text{Si}
\end{align*}
\]

\[
\text{a wide range where properties are stable:} -55^\circ\text{C} \text{ to } 200^\circ\text{C}
\]
3) a) 
\[
\begin{align*}
\text{H}_2\text{O} & \xrightarrow{+\text{H}^+} \text{H}^+ + \text{H}_{\text{aq}}^+ \\
\text{B} & \xrightarrow{-\text{OH}} \text{B} - \text{OH} \\
\text{N} & \xrightarrow{+\text{H}_2\text{O}} \text{NH}_4^+ + \text{H}_2\text{O}
\end{align*}
\]

b) 
\[
(\text{H}_2\text{O} + \text{OH}^-)
\]

\[
\text{H}^+ +
\]

c) 
\[
3 (\text{H}_2\text{O} + \text{OH}^-) + 2 (\text{OH}^-) \text{Assume tri-functional}
\]

\[
\frac{0.965 \text{ g/l}}{1.99 \text{ g/l}} \times \frac{2 (61.8 \text{ g/mole DA})}{3 (20,000 \text{ g/mole PAMS})} = 0.0014 \text{ Volume Ratio}
\]

\[
0.014 \text{ oz by mole DA} \\
i.e. \text{almost none}
\]

d) We added quite a bit. Silly Paul, has more DA than PAMS.

e) DA must bond weakly along the chains perhaps with the Si atoms, then bond weakly positively charged to link the chains.