Status Report PBI/NBR Heat of Reaction . . . 4/28/2010 . . . Randy Lee

I am still working on this effort. At this point however, it is my opinion that credible heats of reaction (or formation) cannot simply be calculated to a sufficient degree of reliability for macromolecules without additional testing and/or special software in order to estimate the 'relative group contributions' from the various functional groups and segments comprising the polymer. Such estimates can easily be accomplished for small molecules using established, readily available tables in handbooks and databases containing measured bond enthalpies and dissociation energies. However, for large molecular structures, bond energies for the various single and double bonds are usually several orders of magnitude lower or higher than the simple values provided in handbook tables. This is due to the fact that in larger molecules, each bond is substantially affected by the surrounding functional groups, local bonding links, and polymer size and structure.

This conclusion is supported by extensive work performed by several researchers in the field as well as the DOT, FAA and Office of Aviation Research who have physically measured the fire performance and combustion attributes for a number of polymers utilizing bomb calorimetry techniques. Through experimental correlations, these workers have undisputedly confirmed that group contributions in polymers are vastly different than those obtained from simple smaller molecules, which makes all these tables useless for such calculations. Van Krevalen has also published a textbook demonstrating how group contributions can be estimated for a variety of polymer properties, including reaction kinetics, energetics, specific heats, conductivities, densities, permeabilites, etc...

There is also an elaborate program developed by several universities and governmental agencies which facilitates these types of calculations. I have downloaded the open source software to develop such estimates, but there will likely be a learning curve. It is readily available as the program "GPYRO". I will pursue this tool as it will undoubtedly provide the means to estimate pyrolysis, combustion and ablative properties for other polymer systems of interest, such as phenolics, EPDM, epoxies and so on. At this point, I cannot give a schedule when more accurate and reliable estimates will be available using these more modern approaches.

As previously recommended (more than once), I believe that properly conducted DSC and TGA measurements will address your questions regarding the enthalpy changes of these materials, and give you a fairly precise answer right away. I would highly recommend the following characterization strategies and philosophy for executing DSC/TGA measurements. It is my belief that the thermochemical environment along the liners, insulators and ablative surfaces during the solid fuel burning process is that of a ‘depleted oxidation’ environment, since the oxidizer (perchlorate) is mostly consumed by reactions with the fuel (aluminum particles) and organic binder/matrix (NBR).

Unfortunately, these conditions probably have limited similarities to all the testing and analysis conducted by the DOT/FAA whose work was centered around flaming combustion (aerobic oxidative thermal degradation) in high oxygen environments with lesser contributions from smoldering combustion and char-producing pyrolysis (anaerobic non-oxidative thermal conversion). During RSRM/RSRMV-type solid fuel burn cycles, I believe these processes are reversed in order, so that thermal changes in the ablative materials are highly dominated by pyrolytic conversion with limited and localized levels of combustion (if these materials were chiefly undergoing oxidation, only gaseous CO_2 and H_2O would be produced with no char residue, and we know that does not happen).

Thus, I would recommend performing DSC and TGA tests (up to 4500°F or at least as high as the instruments will go) on: (a) raw PBI fibers, (b) raw chrysotile material (white asbestos), and (c) their corresponding NBR matrix composite forms (molded insulation samples). Additionally, it is highly recommended that the DSC/TGA testing be done using the following gaseous environments: (a) straight Ar to promote 100% pyrolysis (as a baseline), and (b) 3-5% O_2 in Ar mixture in attempts to simulate the average burn process along the material surfaces. Test results should include the raw data and first derivative curves. The derivative curves provide the most critical information and are required for successful evaluation (too many analysts leave this data out of their reports, particularly ATK and SRI). If you can arrange to have these tests performed in this manner, I believe the questions you have concerning the exothermic/endothermic differences between ASNBR and PBI/NBR can be extracted directly from the derivative data curves and you would not have to rely solely on a bunch of dubious calculations.

Recall that combustion is thermal oxidation, which completely volatilizes a material into CO_2 and H_2O. It is almost always an exothermic process (because the number and strengths of bonds being formed outweigh those being broken). On the other hand, pyrolysis is thermal cracking and is generally endothermic (but not always), producing solid carbon char (which tends to protect the virgin material underneath) and pyrolysis volatiles which have a cooling effect (H_2, O_2, N_2, CH_4, etc...). In both processes, almost all of the intermediate reacting species are free radicals (molecular fragments containing one or more unpaired electrons), as both combustion and pyrolysis are free radical-driven processes. During pyrolysis, secondary and tertiary reactions can convert the smaller alkanes which have left the surface, such as CH_4, into soot (solid carbon) particles, along with H_2, and/or H_2O and/or CO_2 and/or CO. These reactions often occur outside of the surface pyrolysis zone (the mesophase) and within the plume where other reactants and conditions become available. The production of carbon monoxide (CO) is what I consider to be the classic ‘partial oxidation’ product generated in these types of reactions.

During testing conducted by the DOT/FAA group, a couple hundred common polymers were evaluated (including PBI, PBO and Kevlar) and these workers eventually developed a parameter defined as the heat release capacity (HRC), which has become the industry standard for characterizing the flame resistance of polymeric materials. In this test, the polymer is pyrolyzed and the volatile gases expelled are subsequently combusted in a separate chamber to give the HRC, which is proportional to the heat of combustion, the char yield and the activation energy, and inversely related to the peak pyrolysis temperature. Thus, the HRC is the maximum heat released by combustion of the pyrolysis gas per degree rise per unit polymer in the mesophase. It is not yet clear how HRC values can be used to provide the answers we seek. For comparison purposes, a few selected HRC values for various representative materials are given below as developed by the DOT/FAA group . . .

	HRC (J/g-K)	Char (%)
Polyethylene (LDPE)	1676	0.0
Polyacrylonitrile Butadiene-Styrene (ABS)	669	0.0
Polyvinyl Alcohol (PVA)	533	3.3
Polymethyl Methacrylate (PMMA)	514	0.0
Polycaprolactone (Nylon 6)	487	0.0
Polyethylene Terephthalate (PET)	332	5.1
Epoxy novolac (DOW)	246	15.9
Bisphenol Cyanate Ester (Ciba)	239	26.4
Polybenzoxazole (PBO)	42	69.5
Polybenzimidazole (PBI)	36	67.5
Polyamideimide (Torlon)	33	53.6

Note that polymers which produce little or no char residue usually also have higher HRC values. As expected, PBI provides one the lowest flammability ratings and highest char yields of all the synthetic polymers available on the market. Polyazomethine (a developmental polymer not shown), yields 78% carbon char with 36 J/g-K HRC (I’d like to play around with some of that material). For PBI, the pyrolysis temperature ranges from about 1050° to about 1300°F with a peak decomposition temperature of about 1175° for the primary reactions and a secondary reaction peak around 1400°. The method of group contributions should confirm this, as well as DSC/TGA testing. It is the second phase where most of the H_2 is produced and which results in the final, thermally stable carbonaceous char. Because of the very strong mesogenic interactions between PBI chains, the material will behave much like a carbonaceous pitch, creating it's own LC mesophase in the 900°-1000°F range, converting into 'green' amorphous coke around 1400°-1500°, and ultimately graphitizing above 4000°- 4500° as it crystallizes.

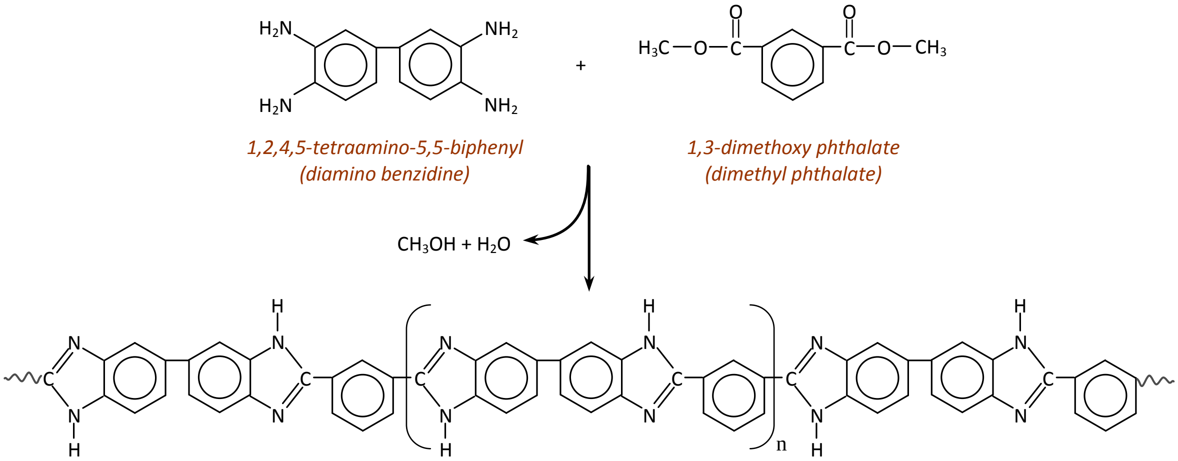
Using stoichiometic ratios, the table value of 67.5% char residue for PBI implies that only one of the carbon atoms in the unit structure is consumed during straight pyrolytic conversion which would likely be one of the imide ring carbons. If both imide ring carbons were abstracted (volatilized), such as might occur during a pyrolysis-dominated reaction with 1-2% oxidation, the following net reaction could be proposed . . .

$$\underset{\text{PBI chain unit}}{C_{14}H_{12}N_4\ (s)} \xrightarrow[\text{pyrolysis / partial oxidation}]{O_2} \underset{\text{carbon char}}{12\,C\ (s)} + \underset{\text{oxidation volatile}}{2\,CO\ (g)} + \underbrace{6\,H_2\ (g) + 2\,N_2\ (g)}_{\text{pyrolysis volatiles}}$$

While this is strictly hypothetical, it could conceivably be representative (on the average) of the thermodegradative process for PBI during a typical RSRMV burn process corresponding to ~98-99% pyrolysis with partial (incomplete) oxidation (both primary and secondary reactions inferred). The heat of this reaction could be estimated – if a reliable value for the heat of formation for a PBI unit could be obtained (such as that determined by bomb calorimetry, DSC or the group contribution technique described above). Such calculations are generally carried out by subtracting the sum of heats of formation for the reactants from the sum of heats of formation of the products as given by . . .

$$\Delta h_R = \sum_i n_p \Delta h^0_{f,p} - \sum_j n_r \Delta h^0_{f,r}$$

where p represents the products and r the reactants. The method of Van Krevalen permits estimation of the heat of monomer or unit formation via the additivity principle using group contributions as inferred earlier. However, that method is not yet available. While it may not be very precise, we can try an estimate using the heats of formation for the representative molecules which react to form each PBI unit, as in the reaction . . .



a PBI unit analogous to Celazole

Values for the heats of formation (Δh_f^0) for benzidine and dimethyl phthalate are available from the NIST database. Respectfully, these are ~ 107 and –684 kJ/mol. The heat of formation for carbon monoxide (CO) is known to be about –110 kJ/mol, and all the other products on the right side of the balanced equation given above can be taken as zero or negligible. Also, the net result of bonds broken and bonds formed during the benzidine-phthalate reaction comes out to about –36 kJ/mol. This results in a net heat of reaction of about +320 kJ/mol, or about 1038 J/g of virgin PBI, which is endothermic, as expected. Within localized anaerobic regions of the charring material where straight pyrolysis is occurring (with the production of methane instead of CO), and/or perhaps very late in the burn cycle when the oxidizer is almost completely depleted, it is possible the endothermic heat of reaction could be closer to the ~ 550-700 kJ/mol range (~ 1784-2270 J/g). On the other hand, in pockets where oxidation is prevalent (with the production of CO_2 or more CO), the endothermic enthalpy could be substantially lower.

However, these estimates may be ambiguous or premature and I am not certain I would base a strong argument on them at this time. For the sake of comparison however, would be interesting to explore what the energy changes associated with chrysotile might be as it undergoes the same burn cycle scenario. The HRC value for chrysotile is not readily available, and I am still working on a suitable method which might allow a more accurate comparison of the thermal properties between white asbestos and PBI. As you know, chrysoltile does not contain carbon and thus does not form a carbonaceous char. Rather, it is a magnesia/silica-based hydrate which undergoes several phase changes, dehydration, structural consolidation and eventually, volatilization as it is heated across the burn cycle temperature profile.

Specifically, chrysotile can be described as a hydrated magnesium silicate, or a magnesium silicate with bound water, $Mg_3(Si_2O_5)(OH)_4 = (MgO)_3 \cdot (SiO_2)_2 \cdot 2H_2O$. It is highly crystalline and thermochemically inert up to about 1000°-1100°F. In the 1100°-1500° range, the material undergoes dehydration and loses all its water as it becomes very porous. Indeed, asbestos provides its flame retardant / insulative properties by releasing this water. When dehydration ceases (above about 1500°), the insulative effects of asbestos rapidly diminish and become insignificant (i.e... it is only an insulator up to about 1500°F). For our application and purposes, we must be concerned with what happens to the fibers well beyond their normal and intended temperature ranges.

The dehydrated (anhydrous) form increases in amorphous character as it starts to segregate into rich Mg and Si dominated regions. Above about 1600°, the fibers recrystallize and decompose several times with increasing amorphous silica character along with the co-existence of fosterite, $(MgO)_2 \cdot SiO_2$ and estantite $(MgO)_2 \cdot (SiO_2)_2$. These oxide mixtures essentially undergo decomposition as they melt (incongruent melting) and this process continues until well above 2400°- 2600°F. Around 3000°, the silica fraction melts and liquefies, and above 4000°, silica completely vaporizes, leaving discontiguous particles of MgO as the last vestiges of the original asbestos fraction remaining (magnesia begins to melt somewhere above ~ 5000°). In contrast, above about 4000°, freshly carbonized PBI fibers undergo solid state crystallization (graphitization) which strongly remains intact before undergoing sublimation well above 6500°F.

Now the dehydration enthalpy for the original chrysotile fibers would have to be determined by calorimetry or one possibly of the other methods mentioned previously. Additionally, the latent heats of fusion and crystallization for all the various magnesia-silica alloys formed during the conversion process would be hard to ascertain. However, experimentally measured heats of dehydration of about 30 kJ/mol for one of the silica-based stellerite/zeolite compounds was found in the literature. This value may not be representative of the chrysotile system but for the sake of curiousity, it might be interesting to hypothetically utilize it as a rough indicator for this special case.

From certain perspectives, it may be conceivable to say that the net heats of endothermic melting and exothermic recrystallization across the transition process balance each other out, approximately . . . or the differences may be small enough to ignore for this first approximation. A representative energy change for the removal of water from the chrysotile structure might be given by ~ 70 kJ/mol or 0.25 J/g of chrysoltile (which includes ~ 40 kJ/mol corresponding to the heat of vaporization for water). A comparison of this value to the result obtained earlier for PBI could imply that the thermal conversion of PBI is substantially more endothermic than that of chrysotile, and this would be sensible. However, this approach is highly unrealistic and questionable at this point.

A couple of comments could be made regarding the differences between the PBI-NBR and ASNBR formulations (other comments may follow in subsequent updates). These two recipes are provided below along with a few of my comments concerning the constituent characteristics and general differences . . .

	PBI-NBR		**ASNBR**		
	Parts	%	Parts	%	
Polymer					
Nipol 1052	90	52.48%	100	45.65%	Butadiene elastomer with ~ 33% acrylonitrile co-monomer
Nipol 1312	10	5.83%			Slurry of NBR and fused silica particles; viscous liquid tackifier
Fiber					
PBI 1/8" fiber	15	8.75%			Poly(terephthalic acid)-benzene-1,2,4,5-tetraamine, $C_{14}H_{12}N_4$
Plastibest #20 (Asbestos)			40	18.26%	Chrysotile (white asbestos): Hydrated Mg silicate, $Mg_3(Si_2O_5)(OH)_4$
Fire-Retardants & Fillers					
Carbon Black N330	1	0.58%			Granulated, Activated, SA = 100 m^2/kg
Clay Nanomer 1.44PA	20	11.66%			Filler/Flame Retardant (aluminosilicate nanoplatelets)
HiSil 233			40	18.26%	Filler/Retardant (hydrated amorphous silica)
Processing Aids & Cure					
Agerite Stalite S	2	1.17%	2	0.91%	Amine Antioxidant (octylated diphenylamines)
Akrochem Resin P-133	17.5	10.20%			Resin Tackifier (thermoplastic alkyl phenolic resin)
Akrochem TMTM	0.1	0.06%			Cure Accelerator (Tetramethylthiuram Monosulfide)
TMTM (not sure about brand)			0.05	0.02%	
Eastman DOP	7.5	4.37%	12.5	5.71%	Plasticizer (Bis(2-Ethylhexyl) Adipate)
Industrene B (Stearic Acid)	1	0.58%	1.5	0.68%	Processing Aid (Lubricant; may also facilitate crosslink activation)
Kadox 920C Zinc Oxide	3	1.75%			Cure Activator (0.21 µ Pigment/Filler/Toughener/Sintering Aid)
Kadox 930C Zinc Oxide			5	2.28%	Cure Activator (0.33 µ Pigment/Filler/Toughener/Sintering Aid)
Naugex MBTS (ASNBR Altax currently)	1.5	0.87%	1.5	0.68%	Cure Accelerator (Benzothiazole, an aromatic sulfur generator)
Picco 6100			12.5	5.71%	Resin Tacktifier (aromatic, petroleum thermoplastic oligomers)
SBR			1.5	0.68%	Styrene Butadiene Rubber (increases hardness and crystallinity)
Crystex OT20 Sulfur			2.5	1.14%	Vulcanizing/Curing Agent (72% polysulfur in napthenic oils)
SCSD-70	2.9	1.69%			Vulcanizing/Curing Agent (70% polydispersion of Crystex in 30% SBR)
Total Parts	171.5	100.00%	219.05	100.00%	
Total Organics	81.9%	81.9%	60.4%	60.4%	
Total Inorganics	18.1%	18.1%	39.6%	39.6%	

As noted before, the polymer-to-fiber ratio for the PBI formulation is 6.0 and that for the AS system is 2.5, which implies a substantial difference in the packing fraction between the two and a notable surface area differential (fiber surface areas must appropriately correspond to the loading levels of specific processing aids for optimized formulation performance). More importantly however, compare the total organics in each mixture. Recall that PBI is organic while AS is not, and the PBI only accounts for about 10% of the organics in this formulation. As illustrated in the previous discussion, when subjected to pyrolytic conditions, the organic entities will behave quite differently than the inorganic constituents, generating a substantial cooling effect as the composite thermolytically degrades and pyrolysis volatiles leave the system.