Thermo-Gravimetric Analysis (TGA) of Combustion and Gasification of Styrene Butadiene Copolymer (SBR) and Polycyclic Aromatic Hydrocarbon (PAH) Formation

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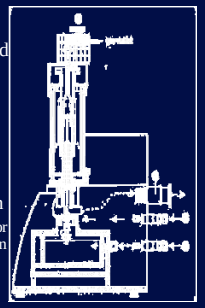
Abstract

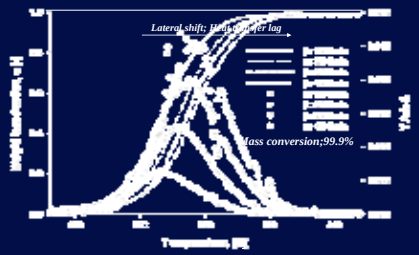
The thermal degradation (pyrolysis and combustion) of styrene-butadiene rubber has been studied thermo-gravimetrically using various heating rates (10, 20, 30, 40K/min) and various atmospheres (pure N_2, 3% H_2/N_2, air, 30%O_2/N_2). Calculation of kinetic parameters, A_0,E,n, for the different conditions provides some insight into possible degradation mechanisms and is explained. This work shows that only a one stage reaction is involved in the nitrogen and nitrogen/hydrogen atmosphere whereas a two stage reaction sequence (primary and secondary) are involved when oxygen is present. The results indicate that oxygen enhanced atmospheres have a significant effect on increasing combustion efficiency at the tested heating rates. A hydrogen-spiked atmosphere, surprisingly, did not have a significant effect on the gasification rates of SBR. In addition, this atmosphere resulted in a carbon residual that remained in the sample crucibles, something that was not observed in the other atmospheres, including nitrogen. The identification and quantification has been determined experimentally using gas chromatography/mass spectroscopy (GC/MS) coupled to Thermo-Gravimetric Analysis (TGA) unit. SBR samples were pyrolysed in TGA unit in a N_2 atmosphere. The identities and absolute concentrations of over 30 major and minor species has been established, including a large number of aromatics, substituted aromatics, and PAHs. The light hydrocarbon species also have been determined simultaneously and identified as H_2, C_2H_2, CH_4, C_2H_6, and C_4H_{10} with lower concentrations of other hydrocarbon gases. Significant amounts of benzene, toluene, and styrene were observed between 330oC and 400oC. The largest PAH detected was the family of $C_{24}H_{14}$ (molecular weight 302), benzo[ghi]perylene with peak concentrations reaching 0.05 ppmv.

Experimental Goals & Setup

- Determination of the effects on various atmospheres and heating rates (10,20,30,40K/min)
  - Pure N_2
  - 3% H_2 & 97% N_2
  - Air
  - O_2 enhanced (30% O_2 & 70%N_2)
  - 6.9% O_2 & 94.1% N_2
- Investigation of possible mechanisms
  - Pyrolysis
  - Combustion
- Calculation of Kinetic parameters using the modified Arrhenius equation and non-isothermal method.
  - Activation energy, E_a
  - Reaction order, n
  - Pre-exponential factor, A
  - Reaction constant, K
- Modified Arrhenius Equation
  - Including pre-exponential factor which depends on $T^{1/2}$ based on collision theory.



Results & Discussions

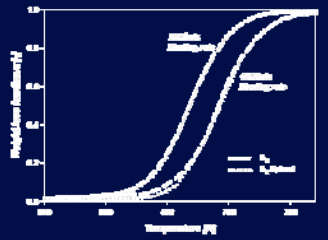


TG and DTG curves for the SBR sample in N_2 atmosphere at various heating rates

Slower temperature rates led to more mass loss at any given temperature due to the longer reaction times. Post test inspection of the crucible that contained the sample showed no sings of residual. The combined with the smooth decay curves in figure is a good indication that the SBR samples were pure and only contained the one co-polymer

Effect on TG of 3 % Hydrogen "Spiked" Atmosphere

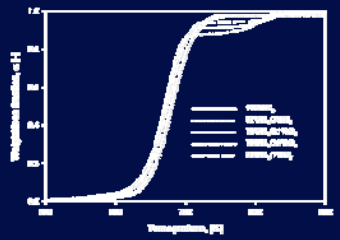
Our first attempt at improving the rate of degradation of the SBR was to inject or "spike" 3% hydrogen into the nitrogen atmosphere. It is expected tat the hydrogen would help break the carbon-carbon bonds on the co-polymer and yield more volatile cracked hydrocarbons. Unexpectedly, not only did not appreciably improve the degradation rate, but post test inspection of the sample crucible showed a significant amount black residual in the crucible.



The slower temperature ramp rate showed virtually no effect of the hydrogen. The higher ramp rate, however, possibly shows a difference, where the hydrogen spiked atmosphere seems to increase the degradation rate somewhat, albeit very small.

Comparison of hydrogen "spiked" atmosphere with pure N2

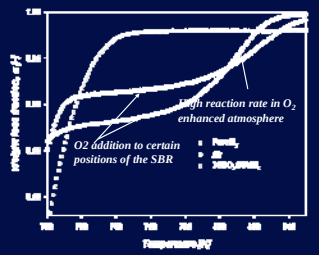
Two-Stage Oxidation in Air & O_2 enhanced Atmosphere



Comparison of pure N2, air, and O2 enhanced environment for a 20K/min ramp rate

The Air, O_2 enhanced atmosphere, in this case combusted, the SBR faster than it occurred in the pure N_2 experiment. In addition, there was no residual found at the completion of experiment. The results were similar for the other heating rates with differences in the mass amounts between the 2 reaction conditions becoming more pronounced with high the higher ramp rates, similar to that observed for the H_2/N_2 comparison. ***Beyond 425°C the air curve forms a plateau, which indicates no mass loss for some time. The occurrence of a plateau or more than one mass loss rate is normally associated with multiple mechanisms that are dominant at certain temperature***

The oxygen may insert in the double bond region of the SBR backbone, thus adding some weight to the compound. This insertion would ultimately lead to complete oxidation at higher temperature. The pure N_2 atmosphere has a smooth mass loss curve for the SBR. ***One explanation for this observation is that only enough energy needs to be imparted to gasify or release the compounds from the solid.*** This can occur through many processes, such as breaking the carbon bonds on the backbone or breaking the bonds between the backbone and the aromatic ring.

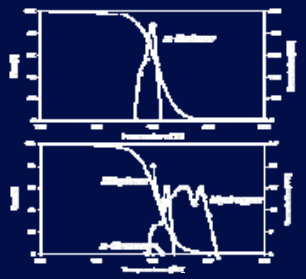


Comparison of pure N2, air, and O2 enhanced environment for a 20K/min ramp rate

Higher oxygen content has a faster reaction rate. ***This particular encouraging in light of the fact that aromatic species are considered a critical step in the formation of soot.*** Since the higher oxygen content atmosphere causes faster oxidation to occur, it is probable that the soot building sequence, which has its foundations in aromatic species formation, would be interrupted, thus yield a more complete burn with fewer emissions

Gas Analysis from TGA;

Pure N_2 Atmosphere, 20K/min

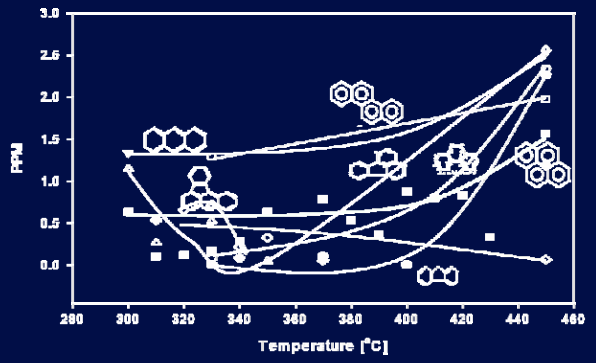


The hydrogen, which is observed by thermal degradation, would be a clue of *H-Abstraction C_2H_2-Addition* (HACA). The effluents from TGA are analyzed to identify *Polycyclic Aromatic HydroCarbon* (PAH), and then the PAHs are identified.

Major effluents from TGA

- *C_2's C_3's Hydrocarbon*
- *Polycyclic Aromatic Hydrocarbon (PAHs)*

PAHs Formation



Conclusion

Activation energy [J/mol]

Heating rate, β [K/min]	100% N_2	97% N_2 + 3% H_2	Air		O_2 enhanced	
10	2.06E+05	1.84E+05	1.60E+05	1.75E+05	1.80E+05	1.68E+05
20	2.01E+05	1.87E+05	1.62E+05	1.82E+05	1.84E+05	1.75E+05
30	2.04E+05	1.89E+05	1.64E+05	1.82E+05	1.85E+05	1.77E+05
40	2.06E+05	1.89E+05	1.65E+05	1.89E+05	1.87E+05	1.79E+05
AVG	**2.04E+05**	**1.87E+05**	**1.63E+05**	**1.82E+05**	**1.84E+05**	**1.75E+05**

Overall reaction order, n [-]

Heating rate, β [K/min]	100% N_2	97% N_2 + 3% H_2	Air		O_2 enhanced	
10	1.49	1.33	1.35	0.01	1.6	0.43
20	1.39	1.3	1.2	0.35	1.35	0.24
30	1.33	1.26	1.13	0.41	1.32	0.2
40	1.3	1.22	1.06	0.19	1.16	0.19
AVG	**1.38**	**1.28**	**1.19**	**0.24**	**1.36**	**0.27**

- **The two-stage combustion of SBR is probably due to the different oxidation rates of the unsaturated hydrocarbon backbone.**
- **The PAHs are observed by oxidizing benzene ring from the styrene.**
- **O2 enhanced atmospheres have promise for more efficient conversion of rubber waste rubber at high heating rates.**
- **Hydrogen does not seem to increase the degradation rate as much as expected.**