Graphite Oxide Flame Retardants

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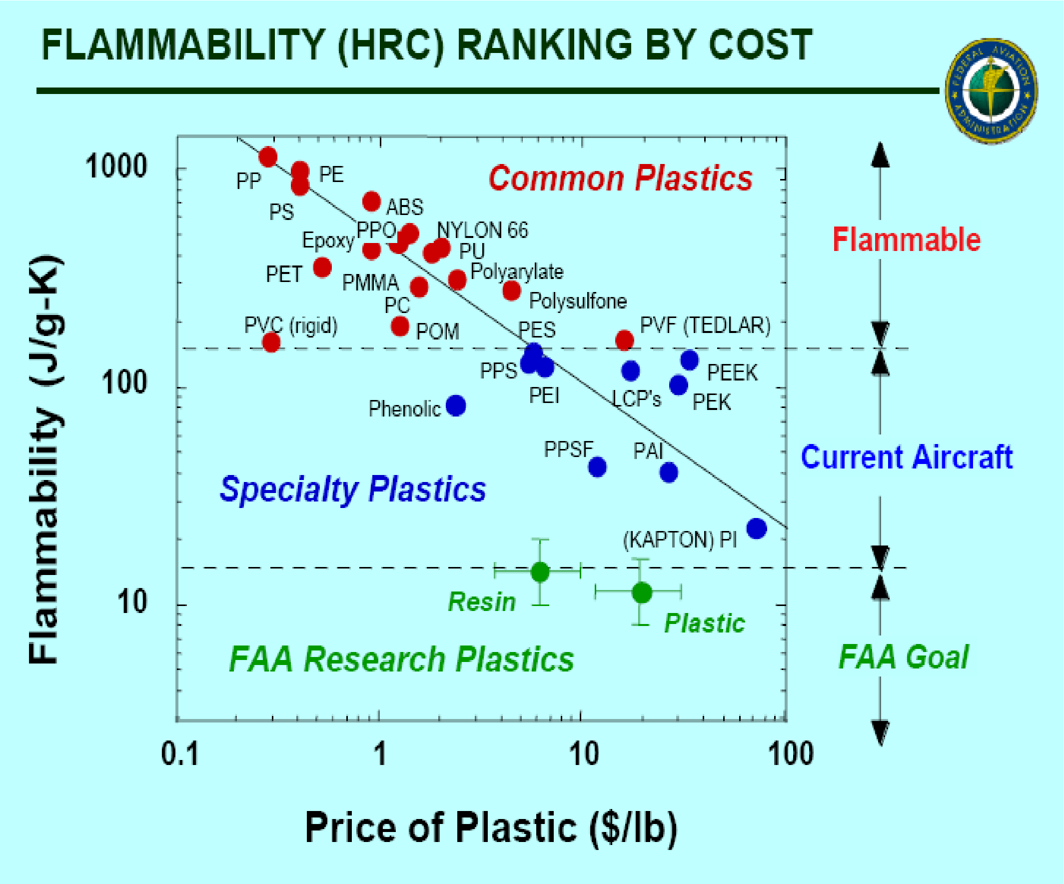
Outline

- Background
  - Combustion of polymers
  - Mechanism of flame retardancy
- Preparation of Materials
  - Graphite oxide (GO)
  - Characterization of GO
  - Silicone rubber/GO composites
  - Epoxy resin/GO composites
- Results
  - HVUL flame tests
  - Micro combustion calorimeter (MCC) testing
- Conclusions and future work

Hydrocarbon polymer systems

Most natural and synthetic polymer materials are flammable.



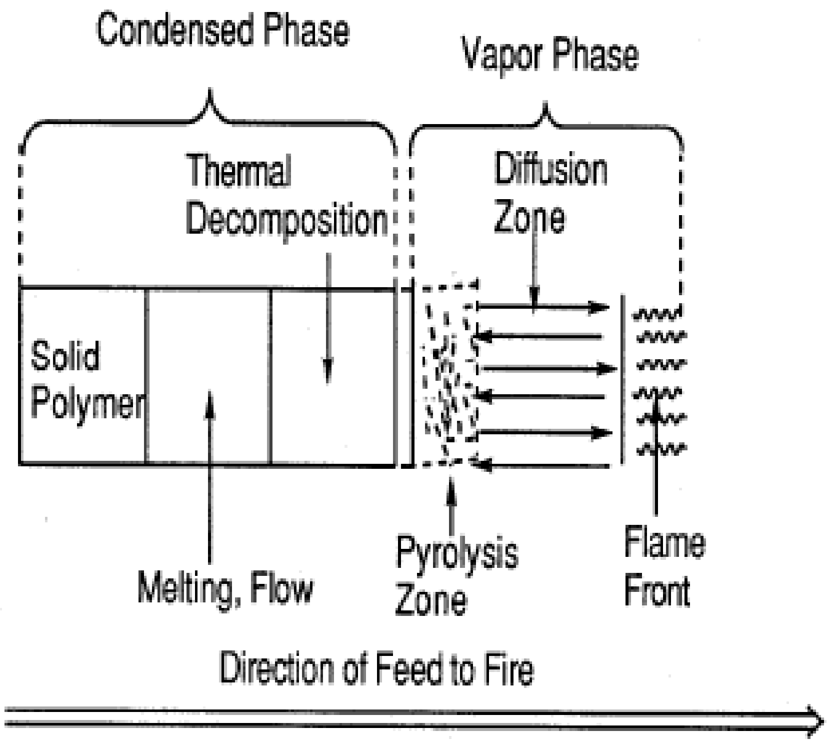
Two approaches:

1 Additive type

2 Reactive type

http://www.flameretardants.eu/objects/2/images/Pic_howdowork_1.gif

Schematic of polymer combustion



Stevens, M.P.; Polymer Chemistry: An Introduction, 3rd ed. Oxford, NY; Oxford University Press 1999. p 111.

- **Vapor Phase – halogenated compounds act as free radical traps which interrupt the burn cycle.**
- **Condensed Phase – high char forming and crosslinking materials can prevent fuel molecules from reaching the flame front and further depolymerization of the plastic.**

Mechanism of flame retardancy

A Endothermic degradation

$Al(OH)_3$ and $Mg(OH)_2$

B Gas phase radical quenching

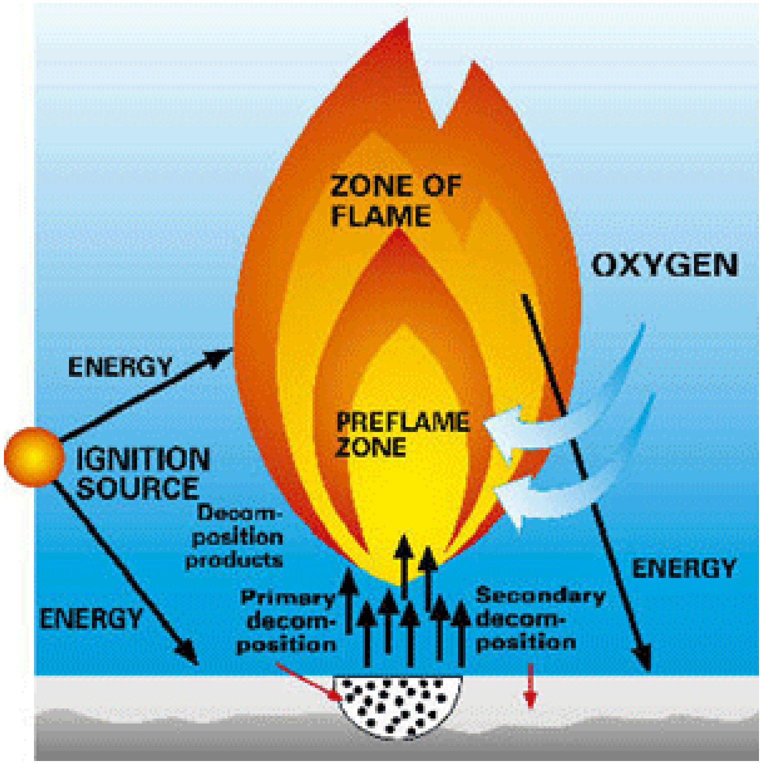
Halogen, phosphorus and antimony

C Thermal shielding: Char formation

Phosphorus, Intumescents

D Dilution of gas phases

Metal Hydroxides and Carbonates



Can Graphite oxides (GO) be a promising flame retardant additive?

(1) Formation of Char to block further heat transfer (C)

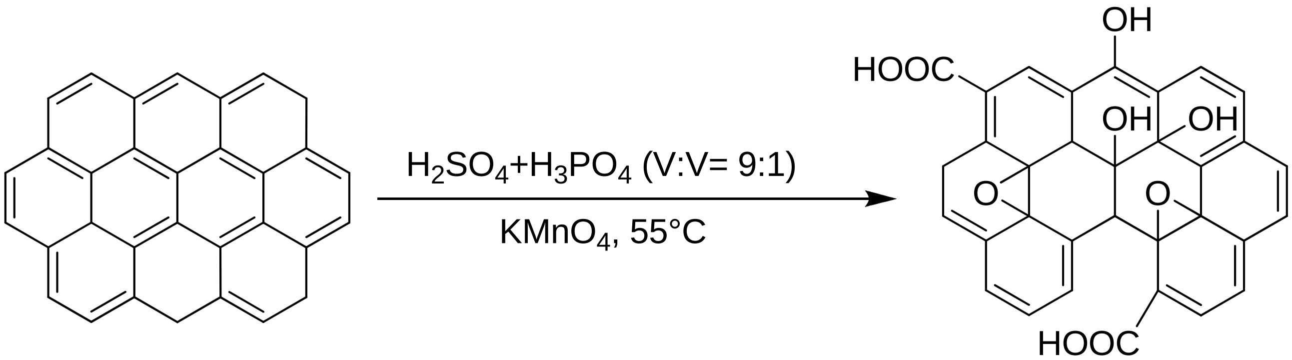
(2) Releasing of carbon dioxide (D)

Prog. Polym. Sci. **2002** *,27, 1661*

Flame retardant nano-additives

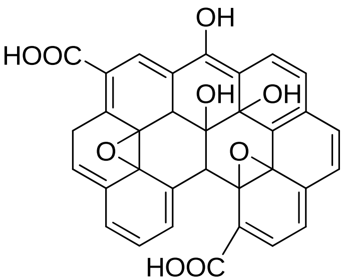
- Modification of materials at molecular to nanometer level
- Carbon nanotubes (CNTs) and nano-clays have shown effectiveness in reducing flammability – 0.1 – 5 wt % loadings
- Improved mechanical properties
- Works in condensed phase
  – Inhibit release of volatile compounds
- Exfoliated graphite oxide (GO)
  – Intumescent filler
  – Expands when heated
  – Barrier to block further heat transfer
  – Improved thermal stability for processing composites

Preparation of GO



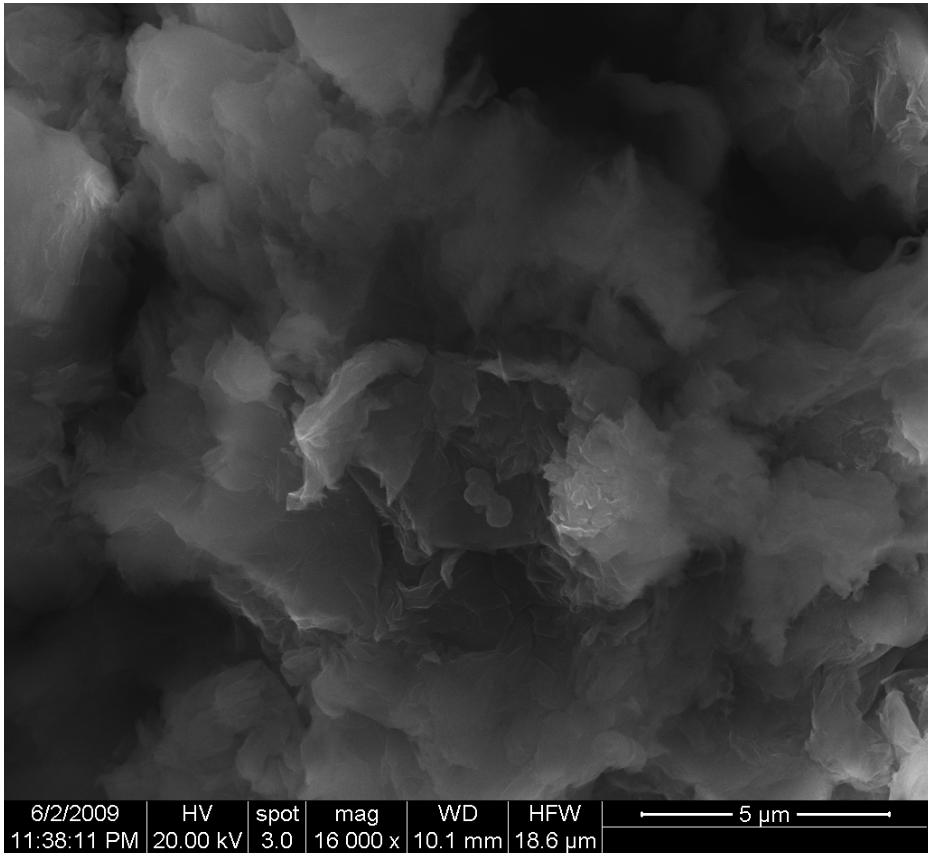
Graphite Oxide(GO)

Characteristics of graphite oxide



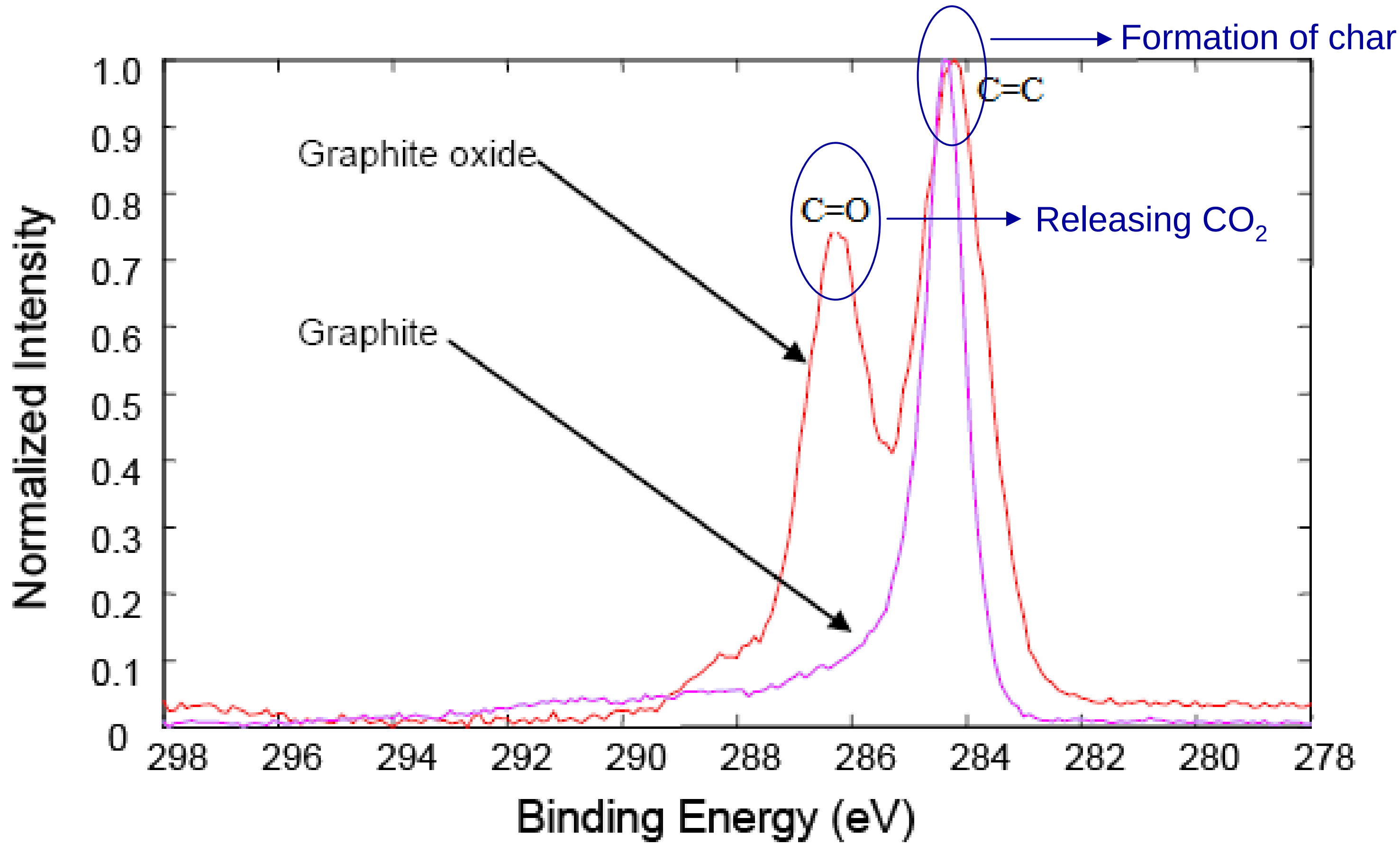
Graphite Oxide(GO)

Stacking



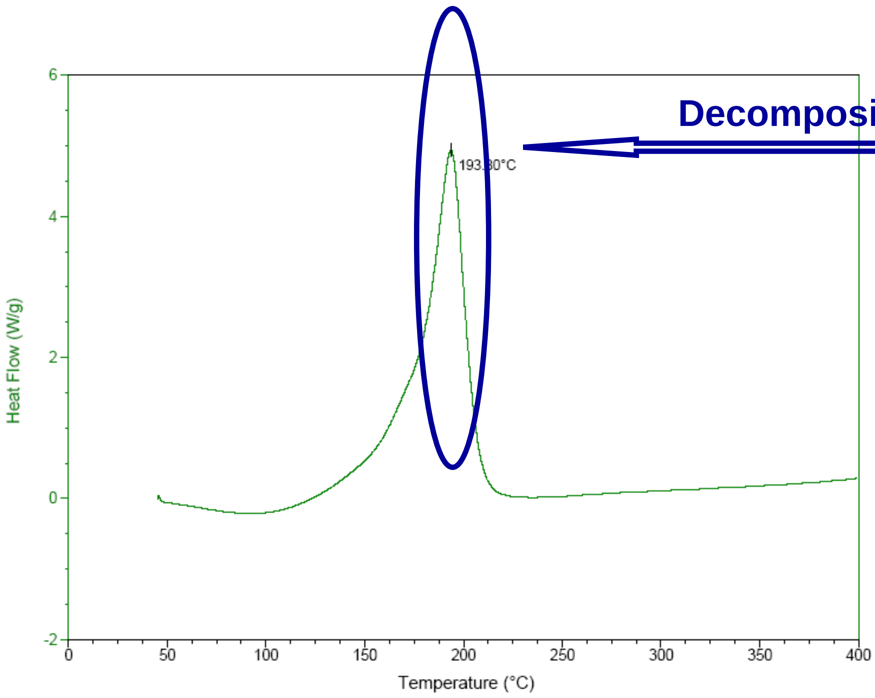
SEM image of graphite oxide

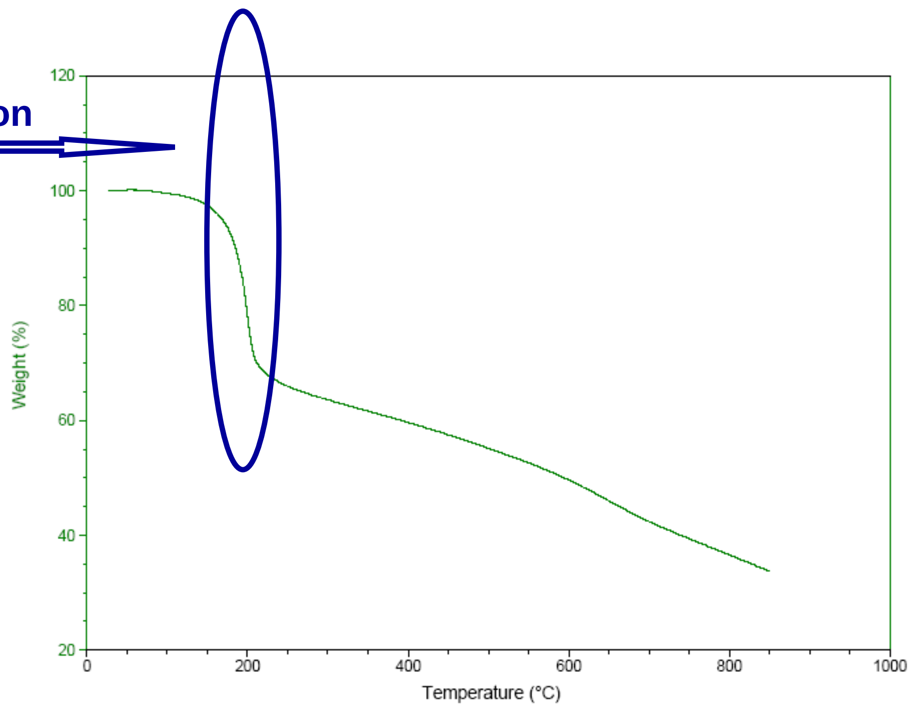
Characteristics of graphite oxide



X-Ray Photoelectron Spectroscopy (XPS) spectra of graphite and graphite oxide

Characteristics of graphite oxide





DSC curve of graphite oxide

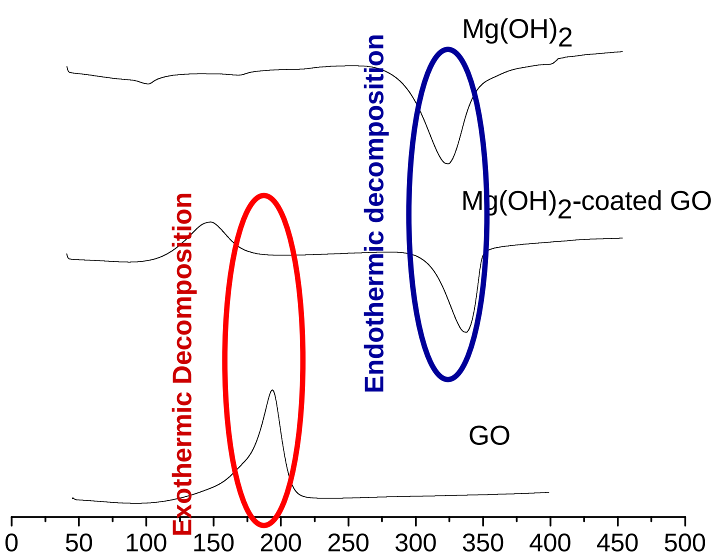
TGA curve of graphite oxide

Key: Protection of vicinal diols for processing at high temperature.

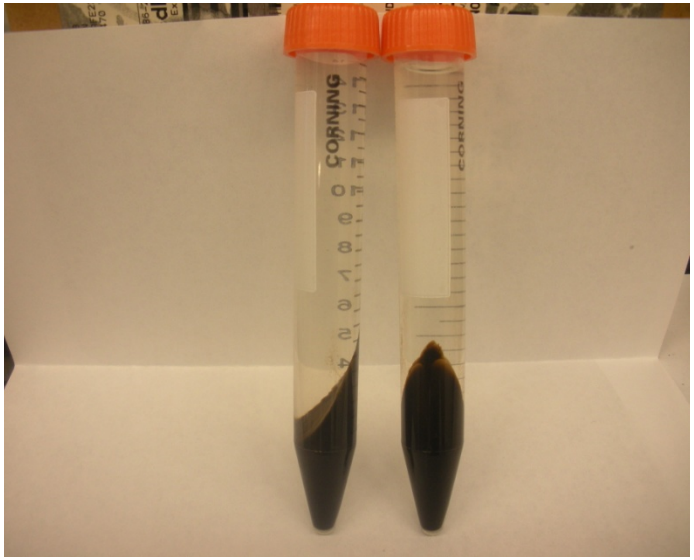
Stabilization of GO

Deposition of $Mg(OH)_2$ on GO

1g GO/50ml DI H_2O → (1.4g NaOH) → (3.49g $MgCl_2 \cdot 6H_2O$/10ml DI H_2O, Dropwiesly added) → (Centrifuge 15mins) → GO/$Mg(OH)_2$



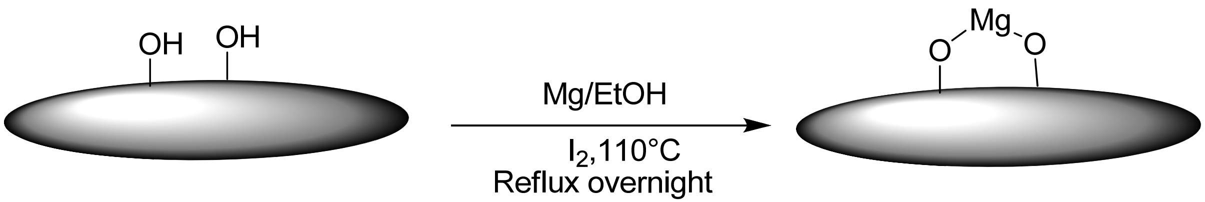
DSC curves of GO and GO derivatives: Exothermic decomposition vs endothermic decomposition

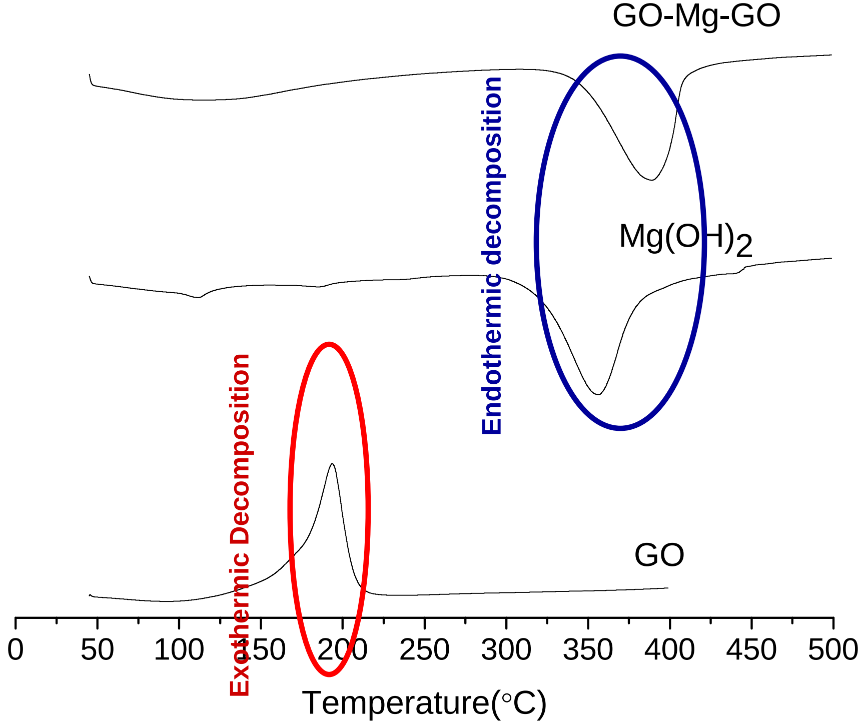


XGO precipitated from solution after centrifugation

Stabilization of GO

Protection of vicinal diols on GO

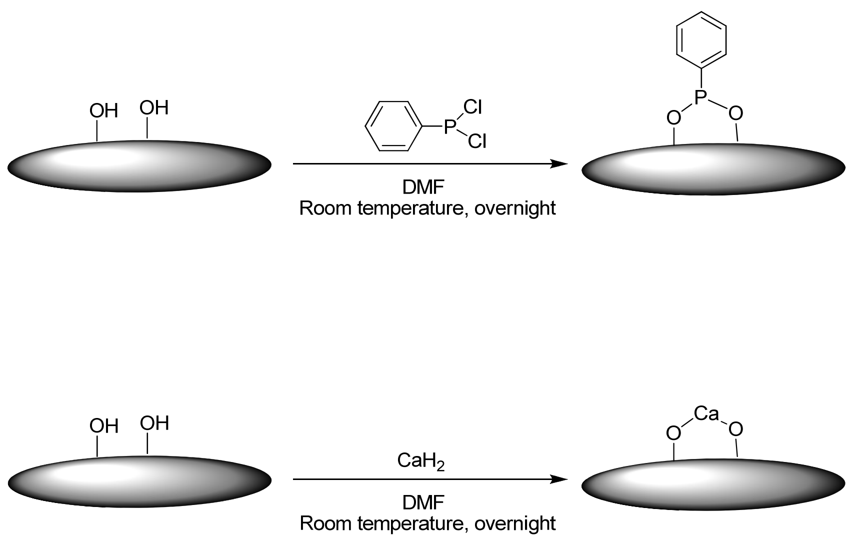


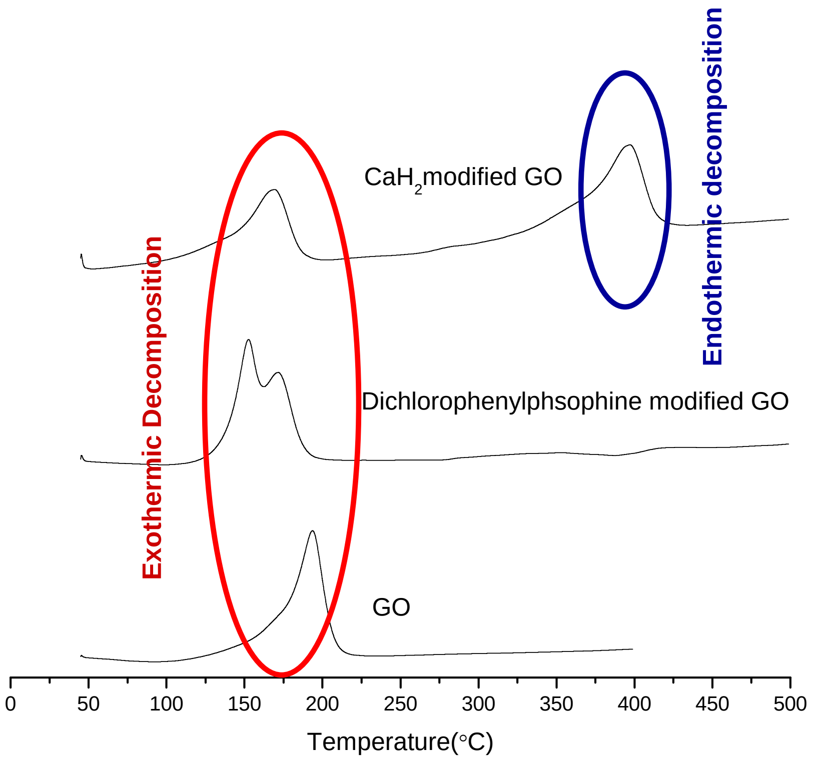


DSC curves of GO and GO derivatives

Stabilization of GO

Protection of vicinal diols on GO

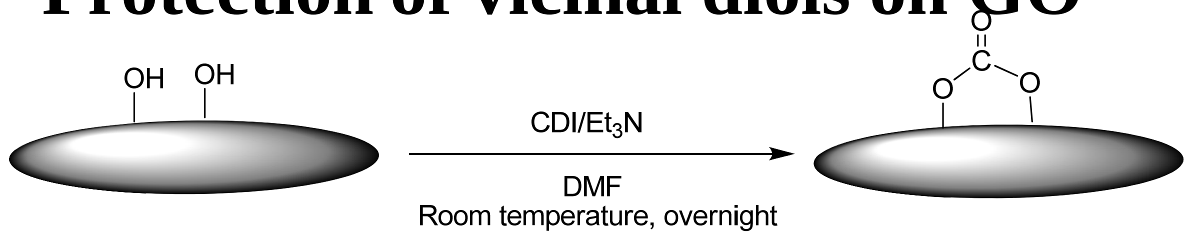


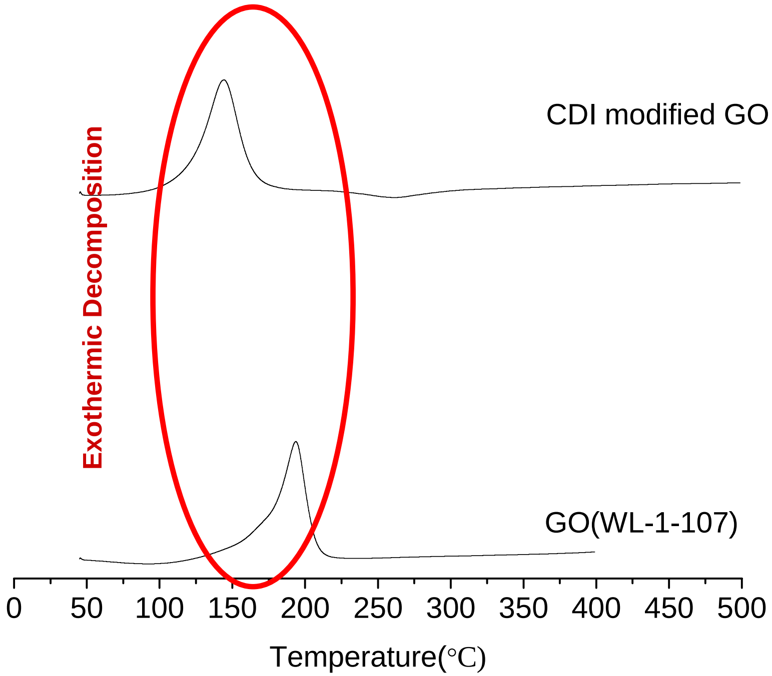


DSC curves of GO and GO derivatives

Stabilization of GO

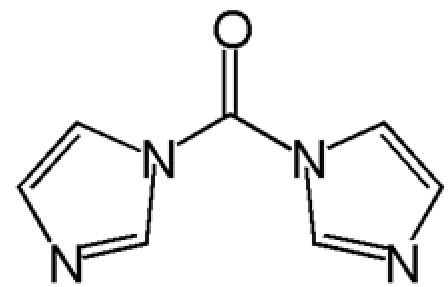
Protection of vicinal diols on GO





DSC curves of GO and GO derivatives

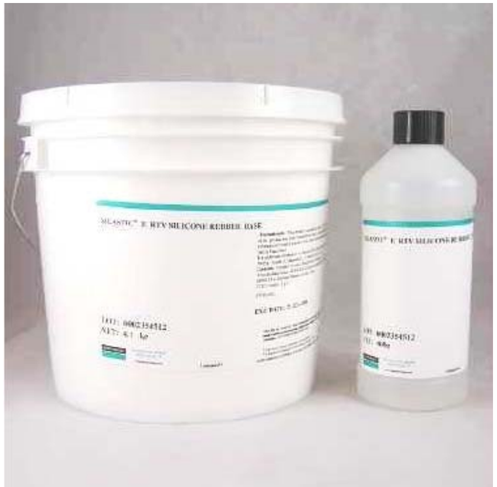
1,1'-Carbonyldiimidazole(CDI)



Polymer resin matrices studied here

AeroMarine 300/21
(inherently flammable epoxy)
[High heat release material]

Nusil silicone rubber R-2615A/B
(inherently flame retardant)
[Low heat release material]



Polymers can be cured at lower temperature to circumvent the decomposition of GO (150-200 °C).

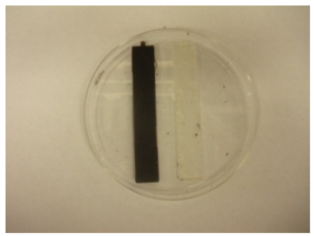
HVUL-94 flame tests

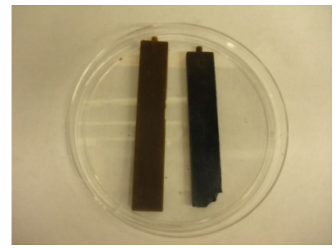
- Two bars of each sample were tested
- Each sample is exposed to flame for 10 s
- After the ignition, the flame is removed and the amount of time to extinguish is recorded.
- If the plastic self extinguishes in less than 10 s with no dripping onto a piece of cotton it is considered to be a V-0 material.
- ASTM D 3801-06

Silicon rubber/graphite oxide composites

Silicon rubber (Part A)
GO
Curing agent (Part B)

→ Bath Sonicator, 45mins → Degass, 1hr → 60°C, overnight → Silicon rubber/GO composites



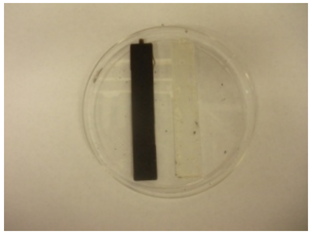


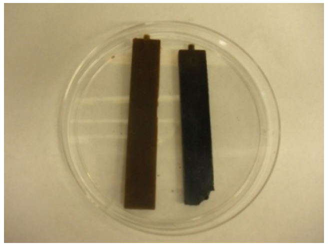
	Self-extinguish time 1	Self-extinguish time 2
Silicon Rubber (SR)	17s	18s
SR/GO (10phr)	12s	10s
SR/GO (15phr)	5s	6s

phr: parts per hundred parts of resin

Epoxy resin/graphite oxide composites

Epoxy resin + GO → (Bath Sonicator, 45mins) → (Curing agent, 30s; Degass, 1hr) → (60°C, overnight) → Epoxy resin/GO composites





	Self-extinguish time 1	Self-extinguish time 2
Epoxy resin (EP)	171s	168s
EP/GO (5phr)	163s	156s
EP/GO (10phr)	141s	141s

phr: parts per hundred parts of resin

Micro combustion calorimeter (MCC) testing

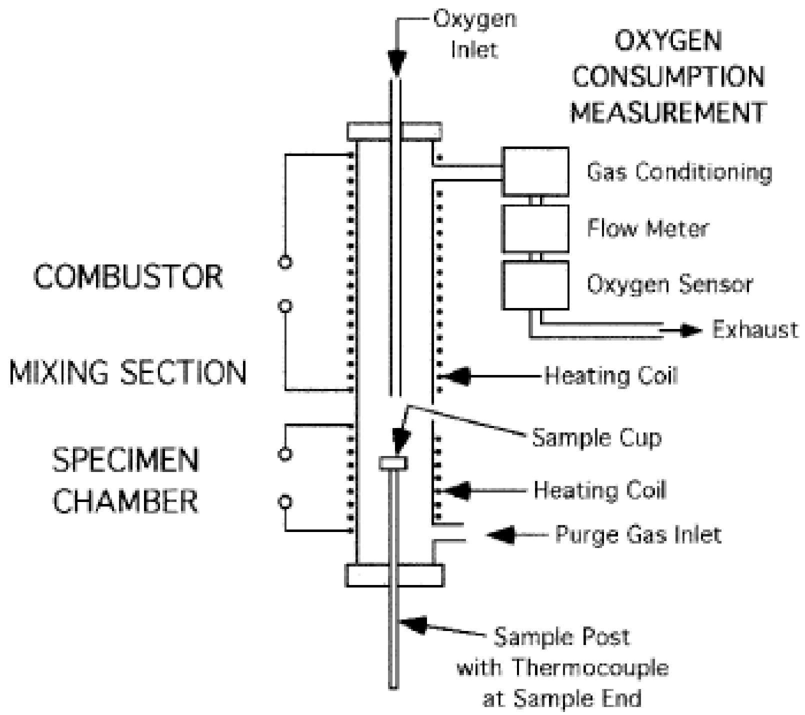
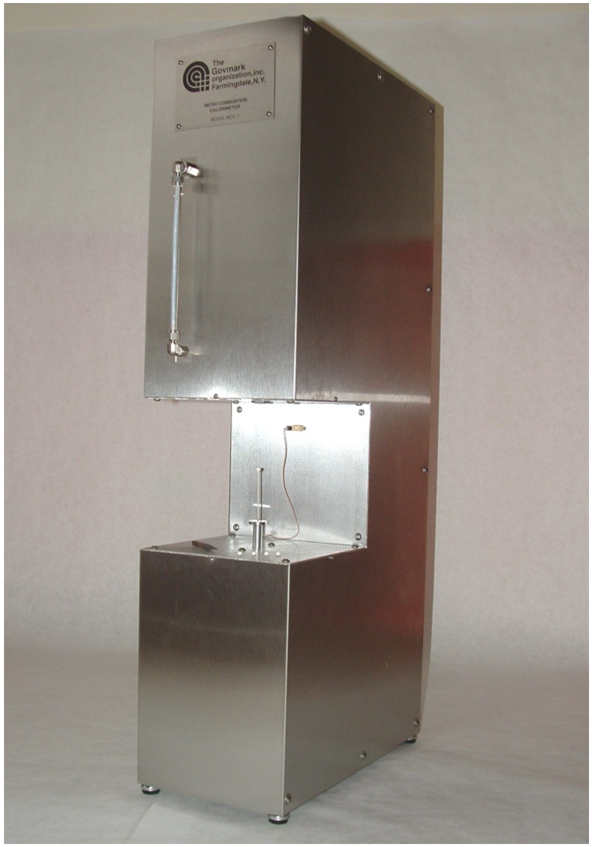
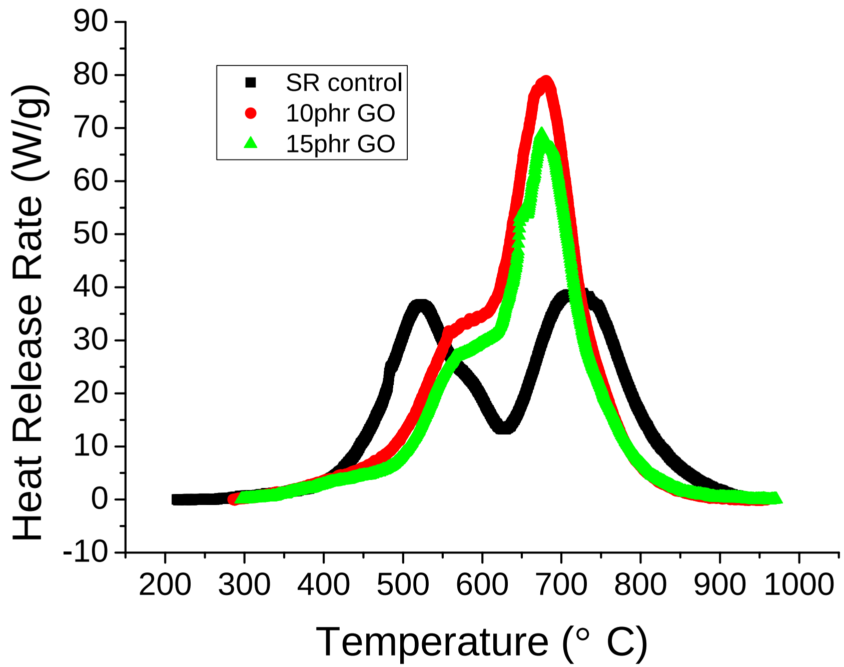


FIG. 1 Schematic Diagram of Apparatus



- **Performed by Dr. Alexander Morgan at the University of Dayton Research Institute.**
- **Measures inherent flammability of a material by oxygen consumption calorimetry.**
- **Epoxy resin samples were heated at a rate of 1 °C/s under nitrogen from 250 to 750 °C using method B of ASTM D7309 (pyrolysis under nitrogen), while silicone samples were tested from 200 to 1000 °C using method A of ASTM D7309 (pyrolysis under nitrogen).**

MCC testing of SR/GO composites



The addition of GO completely changes the thermal decomposition behavior of silicone rubber:

(1) two distinct peaks of thermal decomposition/heat release merge into a single peak with a lower temperature shoulder.

(2) HRR values go from 35-40 W/g to 60-70 W/g.

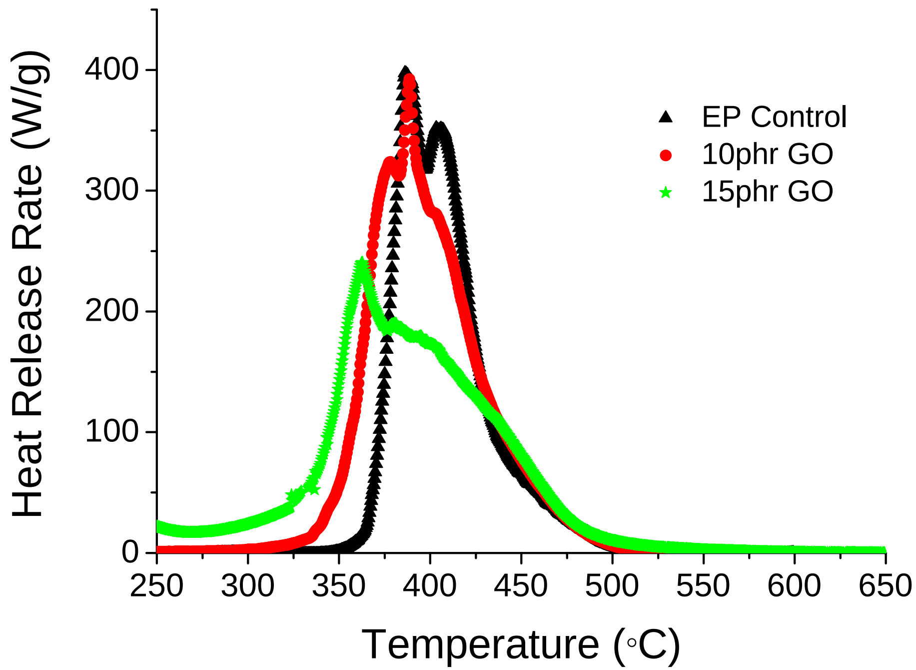
(3) At 10phr GO, the total HR increase slightly, but with 15phr GO, the total HR is less than that of the base polymer.

MCC testing of SR/GO composites

Sample	Char Yield (wt%)	HRR Peak(s) Value (W/g)	Total HR (kJ/g)	Char Notes
silicon rubber WL-2-181 A2	75.93	37, 38	10.5	kept shape, hard black chunk
silicon rubber WL-2-181 A3	72.63	37, 38	11.0	
silicon rubber WL-2-181 A4	76.06	35, 40	10.6	
silicon rubber WL-2-181 B1	50.32	32, 79	12.2	kept shape, hard black chunk
silicon rubber WL-2-181 B2	48.53	32, 69	11.6	
silicon rubber WL-2-181 B3	46.65	30, 73	11.5	
silicon rubber WL-2-181 C1	51.06	27, 69	10.3	kept shape, hard black chunk
silicon rubber WL-2-181 C3	50.33	26, 62	9.2	
silicon rubber WL-2-181 C4	50.97	24, 62	9.4	

WL-2-181A **Silicone rubber/GO composite (0phr GO)**
WL-2-181B **Silicone rubber/GO composite (10phr GO)**
WL-2-181C **Silicone rubber/GO composite (15phr GO)**

MCC testing of EP/GO composites



The addition of GO changes the thermal decomposition/heat release profile for the epoxy resin:

(1) 10 phr GO increases peak HRR slightly, but 15 phr GO decreases the peak HRR values.

(2) These peaks begin to merge into one larger peak with small shoulders

(3) Addition of GO inhibits the degree of crosslinking in the epoxy nanocomposites?

MCC testing of EP/GO composites

Sample	Char Yield (wt%)	HRR Peak(s) Value (W/g)	Total HR (kJ/g)	Char Notes
Epoxy resin WL-2-180 A1	4.45	389, 352	24.1	pan all black, shiny residue around edge
Epoxy resin WL-2-180 A2	4.68	394, 375	24.4	
Epoxy resin WL-2-180 A3	4.64	369, 351	23.9	
EP/GO WL-2-180 B1	5.31	323, 392, 281	23.5	pan all black, dull residue around edge
EP/GO WL-2-180 B2	4.97	373, 390, 265	24.8	
EP/GO WL-2-180 B3	5.10	357, 475, 294	24.2	
EP/GO WL-2-180 C1	8.22	24, 241, 190	26.3	pan all black dull residue on bottom
EP/GO WL-2-180 C2	7.94	22, 258, 252	26.2	
EP/GO WL-2-180 C3	8.79	24, 271, 250	25.7	

WL-2-180A Epoxy resin/GO composite (0phr GO)
WL-2-180B Epoxy resin/GO composite (10phr GO)
WL-2-180C Epoxy resin/GO composite (15phr GO)

Conclusions and future work

- To some extent, GO is a good flame retardant additive due to the following reasons:
  - slow down the mass loss rate

    may not see this effect in the MCC (too small of sample)
  - induce anti-dripping effects

- Decomposition of GO partially increases the heat releasing rate of the polymer matrix.
  - GO decomposition is exothermic

- Future work should be focused on fully understanding of curing process upon addition of GO.

- Effort should be made to combine GO with other flame retardant additives for synergistic effect.

Acknowledgements

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