Biocatalytic Synthesis of Environmentally Safe FLAME RETARDANT Polymers

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

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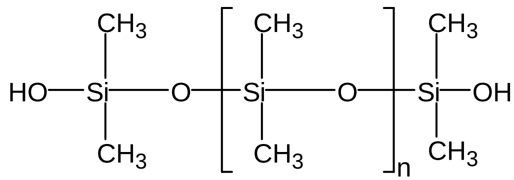
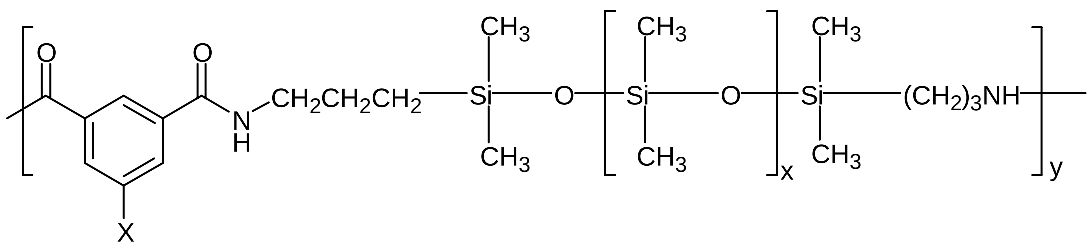
Problem Statement

- Success of military operations severely impacted by burn injuries (loss of personnel and high medical treatment costs – $10's of millions/year)
- Polymers such as Kevlar and Nomex offer a high degree of flame retardancy, but at a high cost
- Manufacture and processing requires the use of hazardous ingredients and solvents
- Highly insoluble and used as fibers, not easily coated onto objects
- Although current FR materials (Halogenated, Phosphorous, nitrogen and Inorganic compounds) additives such as halogenated, aluminium trihydroxide, antimony oxides may be a cost effective solution in many FR applications, but they have long term ecological problems due to the release of toxic gases upon combustion

Motivation
Environmentally-safe polymers



PDMS



1: X = OH; **2**: X = NH_2

To Save Lives while making or using the FR materials →

We do not want to kill people or cause damage to the environment. Do We?

Making the Materials
Advantages of Enzyme-Catalysis

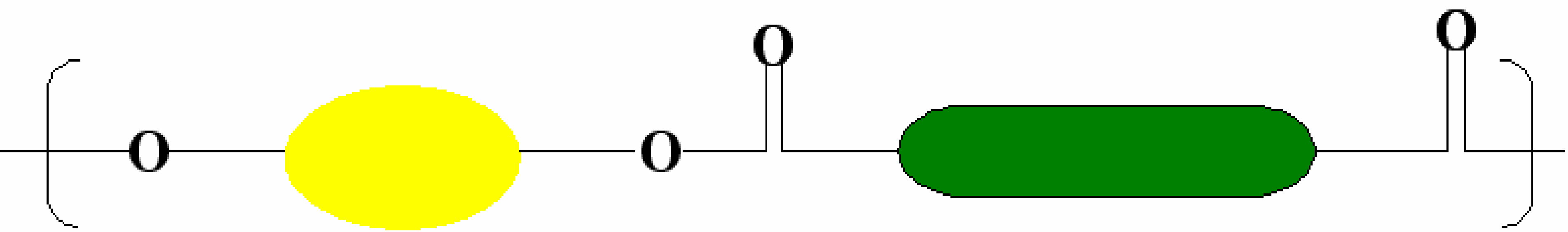
- **Mild reaction conditions**
- **Efficient and economical**
- **Environmentally benign**
- **Easy work up**
- **Regioselective**

Green Chemistry

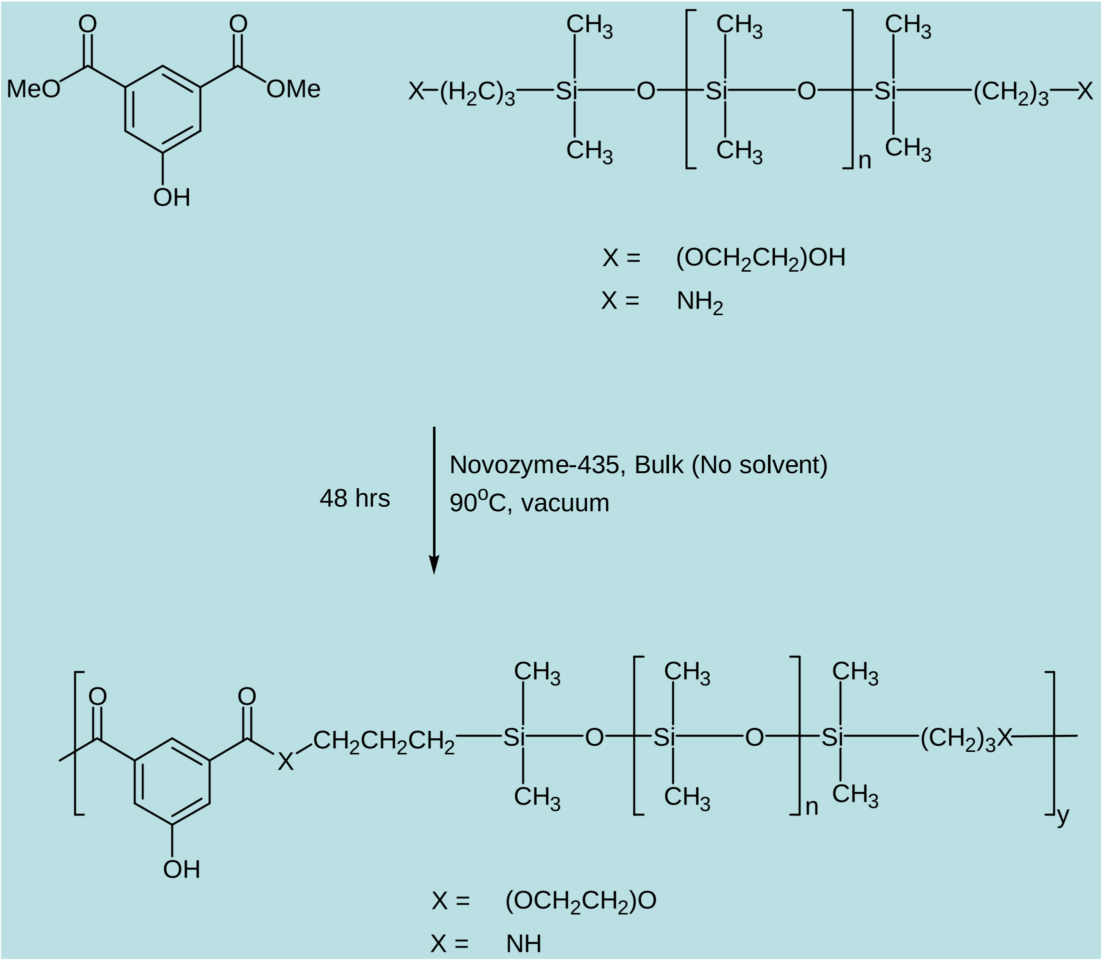
Why Lipases?

- Regio-, Chemo-, Enantio-, Diastereo-selectivity
- Proven track record of catalyzing trans-esterification, (trans)amidation and imidation reactions
- Flexible reaction conditions
  - Temperatures (40 – 90^{o}C)
  - No solvent required
  - If solvent necessary, its compatible

Condensation Polymerization

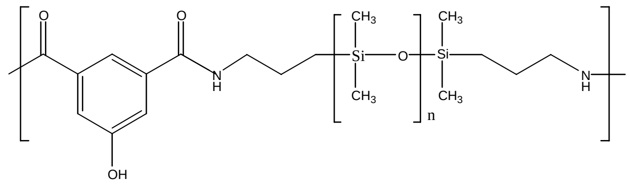


Lipase Catalyzed Synthesis of Siloxane Based Aromatic Co-Polymers

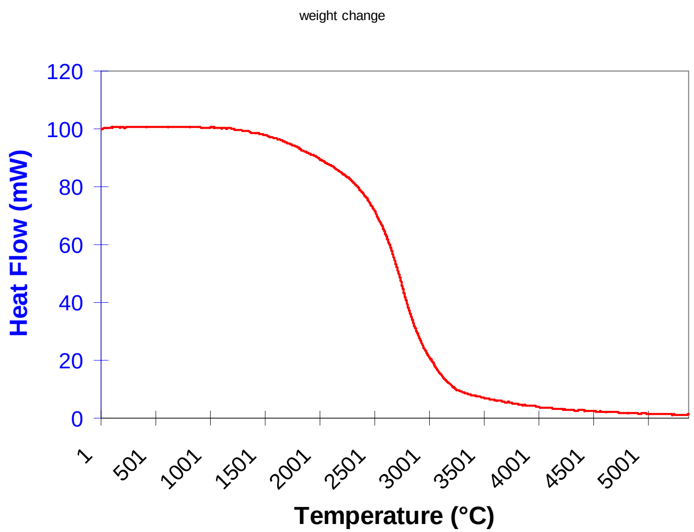


Kumar et al, *Adv. Mater.* **2004**, *16*, 1515.

Polysiloxane co-Polyamide



TGA	
T_{onset} (°C)	**403**
T_{max} (°C)	**462**
Char yield (%)	**10.2**
PCFC	
Heat release capacity (J/g.K)	**260**
Total heat release (KJ/g)	**21.2**



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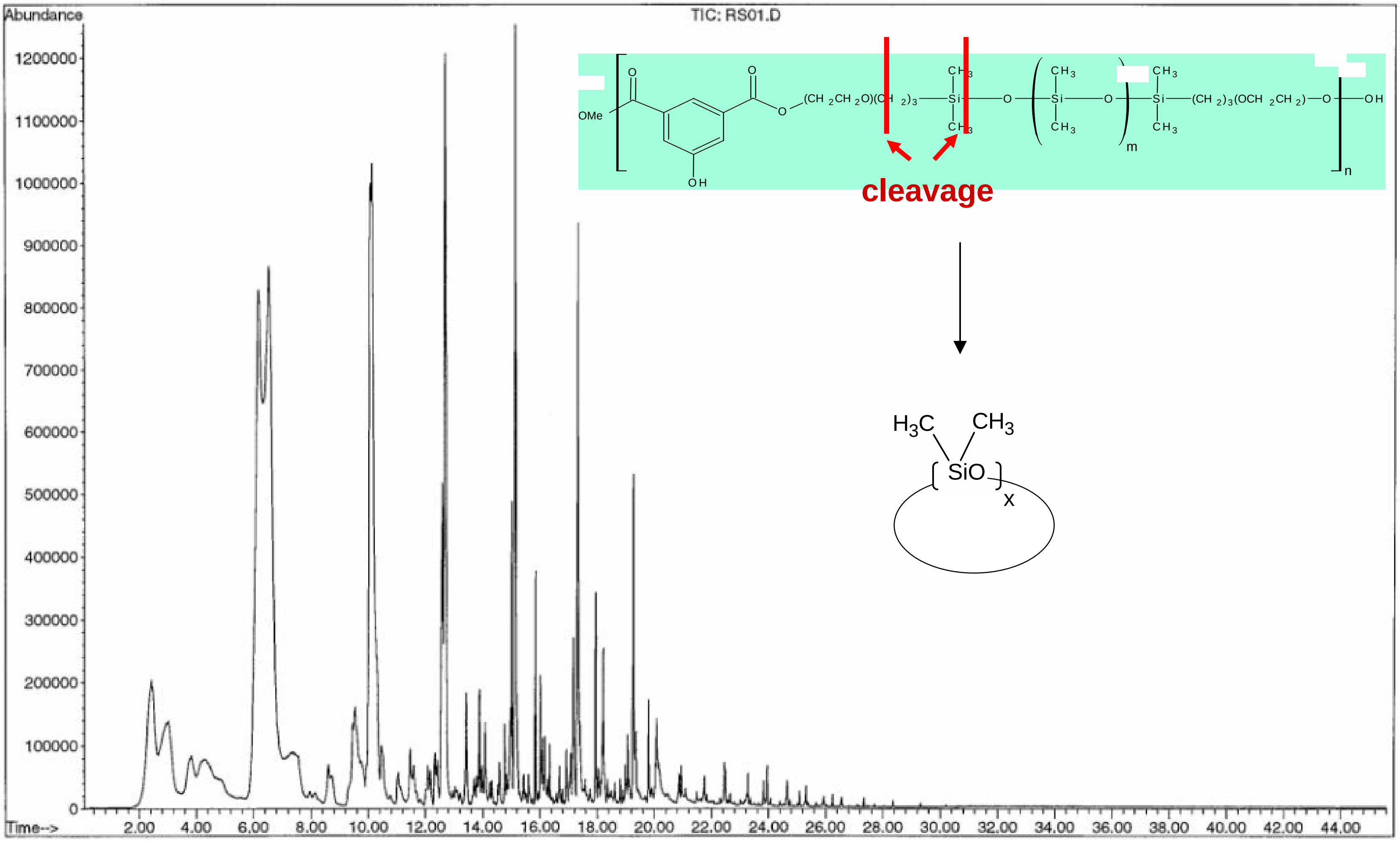
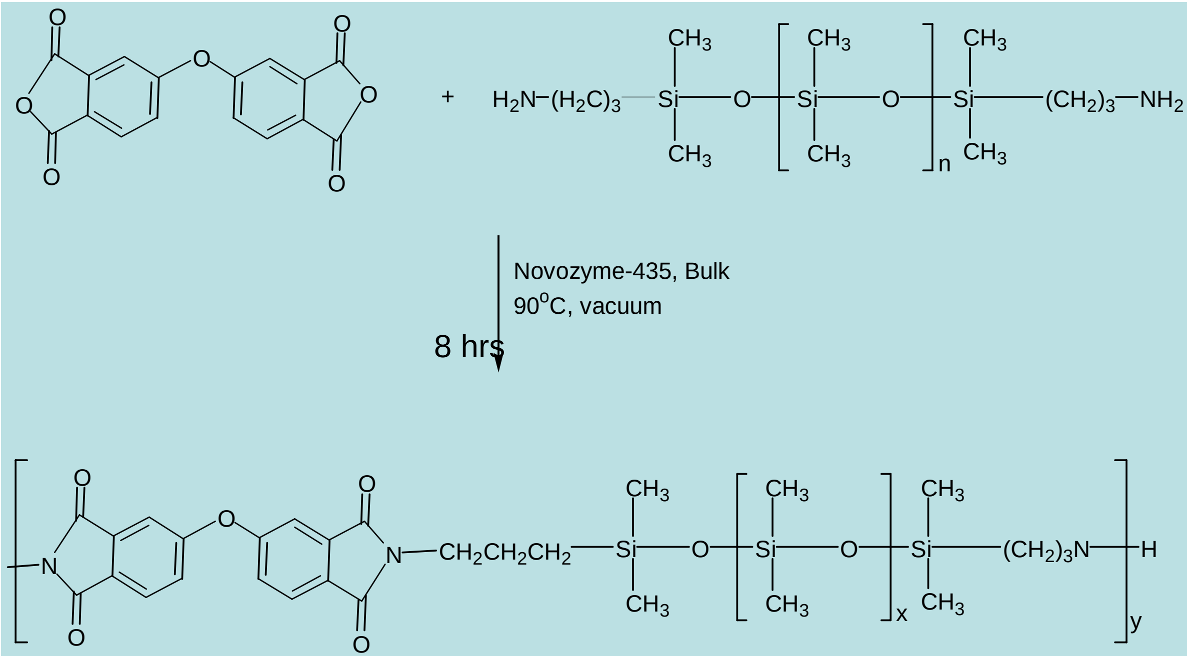
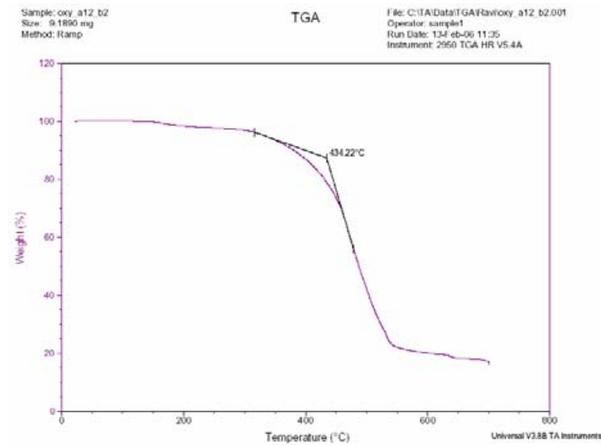
Py GC/MS of Siloxane copolyester



Enzymatic Synthesis of Polyimides





Direct Polyimide formation without polyamic acid intermediate

Yield = ~80%

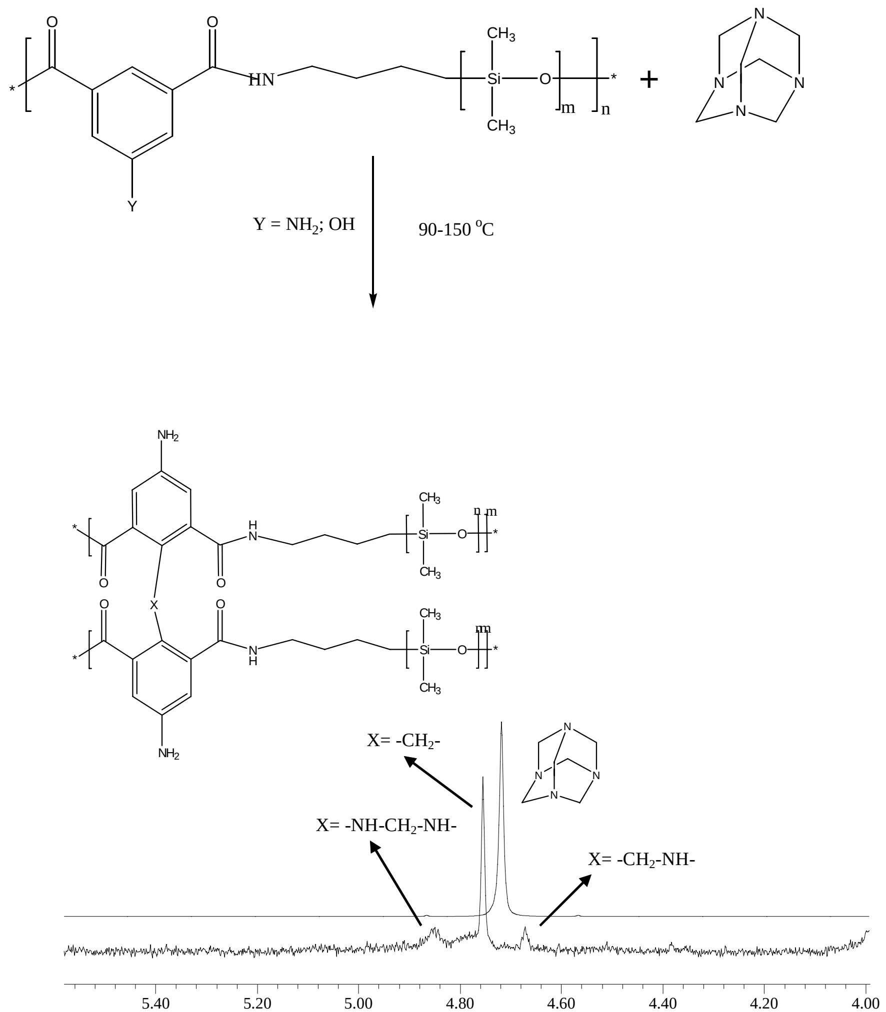
Only 8 hrs (48 hours for Polyesters and Polyamides)

Ave. GPC MW = 75K, PD = 1.7
(prior 20K was highest)

T_{dec} = 460 °C (10wt% wt loss) HRC = 313 J/g K

Mosurkal et al, *Macromolecules* **2007**, *40*, 7742.

Crosslinking of Polyamide

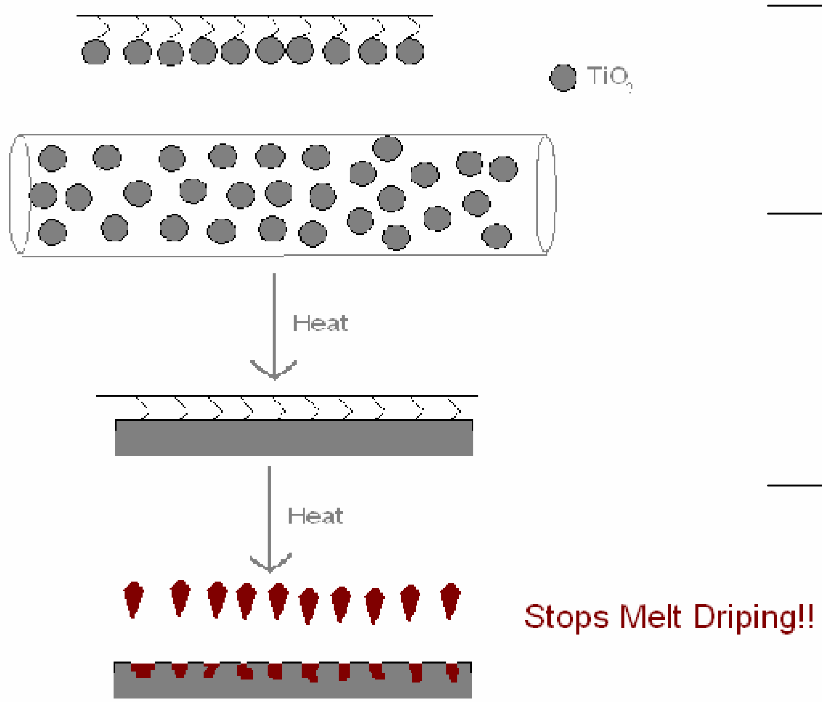


FR Properties of HMTA cross-linked Polyamide

Crosslinking %HMTA (by weight)	HR capacity (J/g*K)	char yield %
0%	194	11
1%	173	12.3
5%	156	14.4
10%	108	14.9
15%	125	12.5
20%	**90**	13.2

Mosurkal et al, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2006**, *47*, 1110.

Polymer-TiO_2 Nanocomposites for Improved FR materials



Covalent attachment of metal oxide nanoparticles (TiO_2) to FR polymer

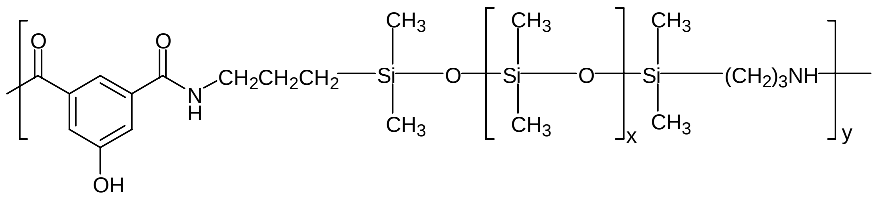
Nanoparticle incorporated into FR film or fiber

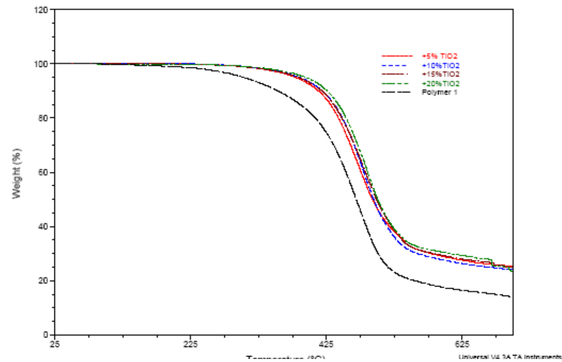
Upon heat, nanoparticles sinter to form porous metal oxide layer which serves to absorb polymer melt, suffocate heat and increase heat of decomposition.

Advantages

- Controllable covalent attachment of nanoparticle to the polymer
- Increase the heat of decomposition
- Suffocates heat
- Melt absorber – minimize melt drip
- Environmentally benign
- Inexpensive (paints, toothpaste, fillers)

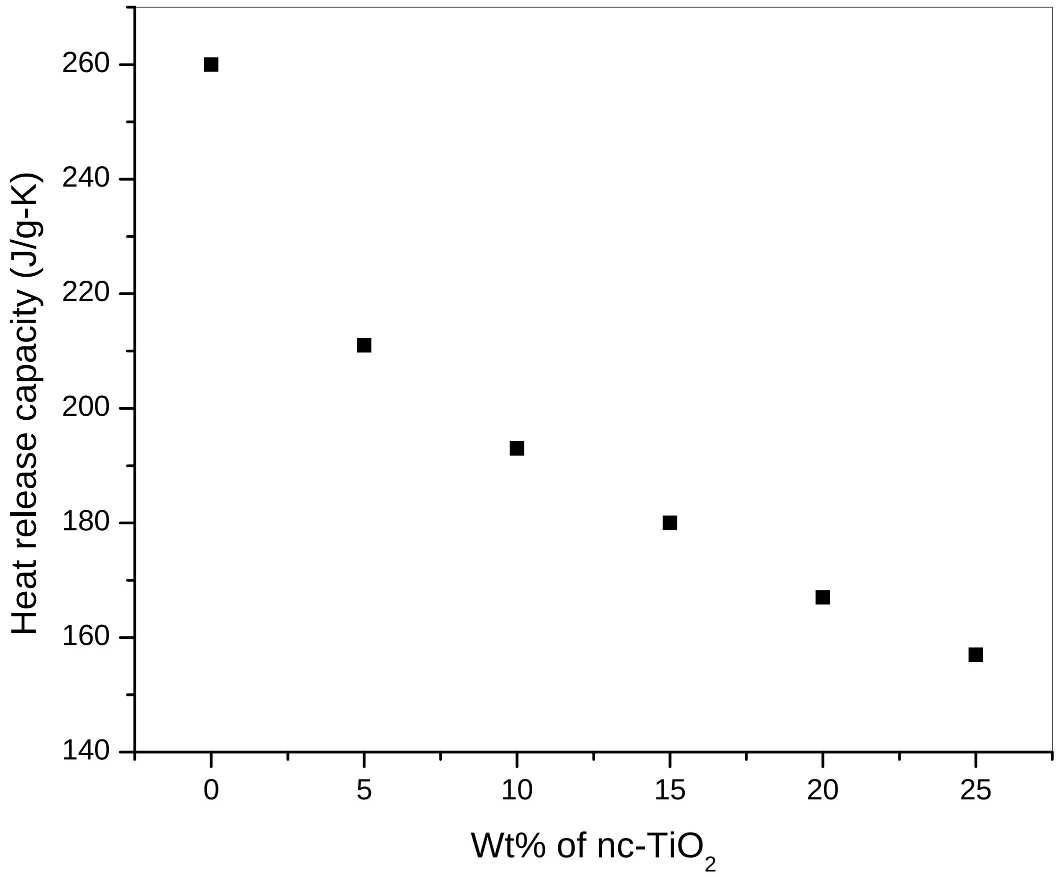
Poly-TiO_2 nanocomposites



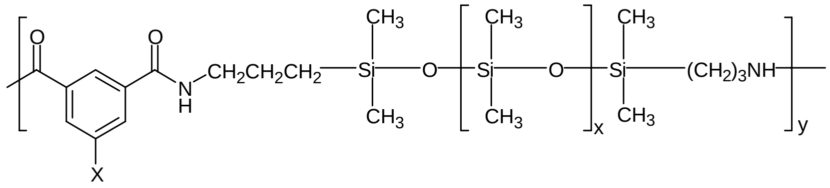


wt% of TiO_2	PCFC		TGA	
	HRC ($Jg^{-1}K^{-1}$)	Total HR (KJg^{-1})	T_{dec} (10% wt loss) (^oC)	Char Yield[b]
0	260.2	21.2	408	14.0
5	211.1	11.0	413	23.9
10	192.7	10.7	417	24.1
15	179.7	10.0	418	24.9
20	167.5	9.70	425	28.0

Heat release *vs.* Wt% of TiO_2



Comparison

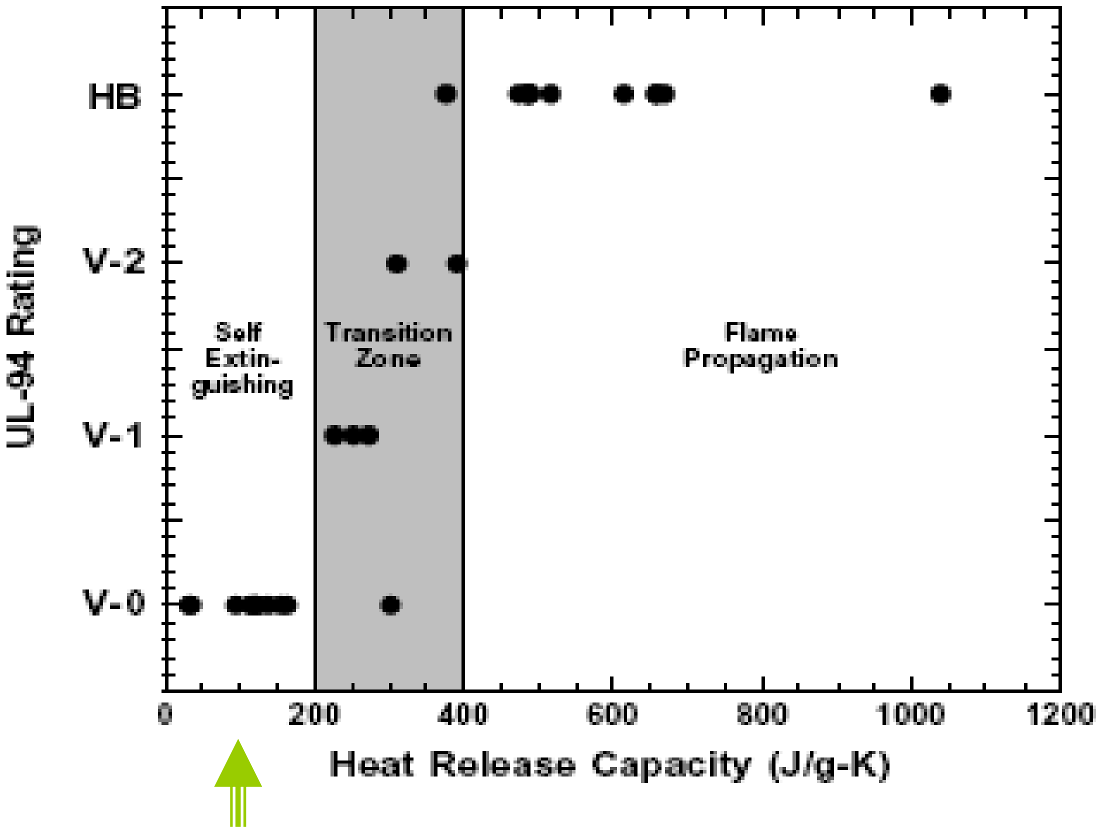


1: X = OH; **2**: X = NH_2

Polymer	PCFC		TGA	
	HRC ($Jg^{-1}K^{-1}$)	Total HR (KJg^{-1})	T_{dec}[a] (^oC)	Char Yield[b]
1	260.2	21.1	408	14.0
+TiO_2[c]	167.5	9.7	425	31.2
2	194.0	15.8	407	15.0
+TiO_2[c]	128.9	14.7	426	33.7

[a] at 10% weight loss; [b] at 700 ^{o}C; [c] 20wt% of TiO2

HR Capacity vs. UL-94 rating

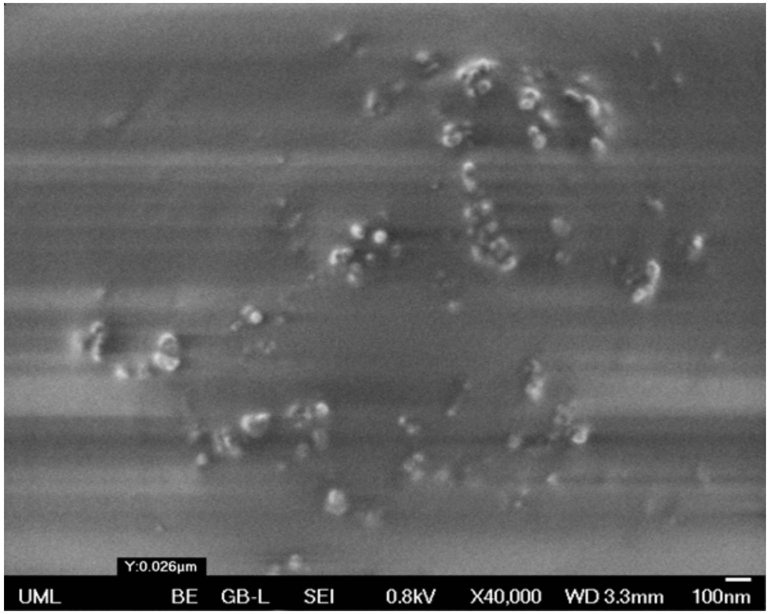


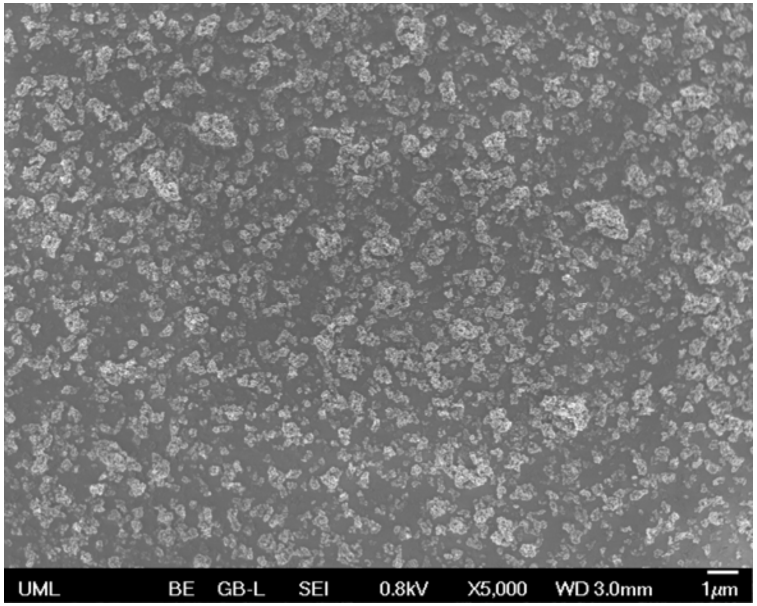
Our Best polymers

Ref: Lyon *et al*, FAA

SEM of Polymer 20wt% TiO_2

Thin film spincoated on ITO glass plate





Before Burn

After Burn

(500 ^{o}C /1hr)

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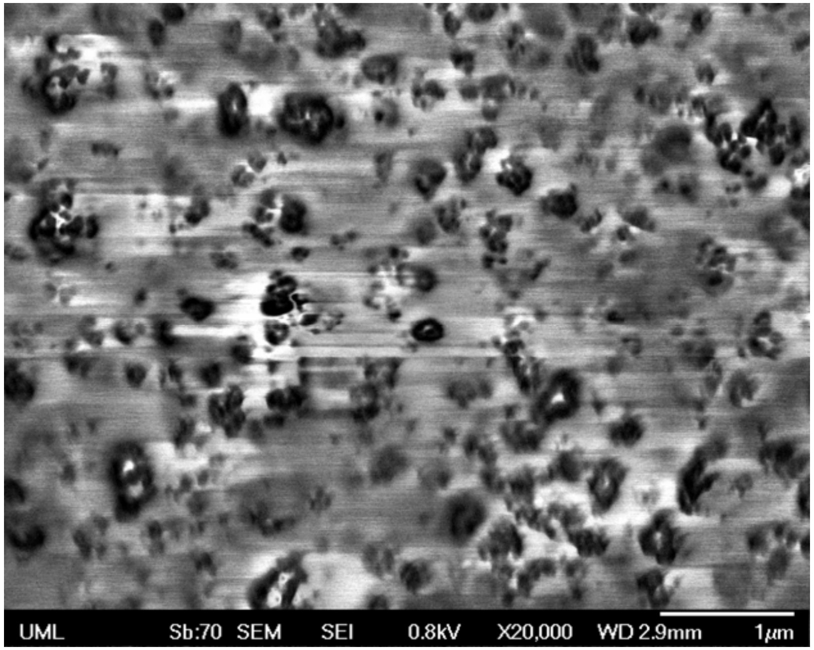
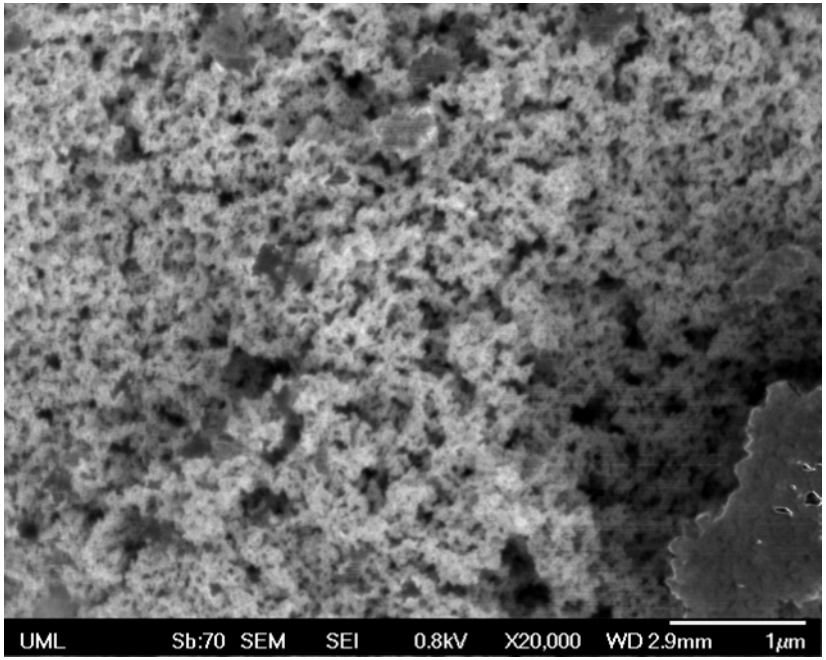
SEM images of Polymer-TiO_2 Char

Thick film spincoated on ITO glass plate and burnt at 500 ^{o}C for 1 hr





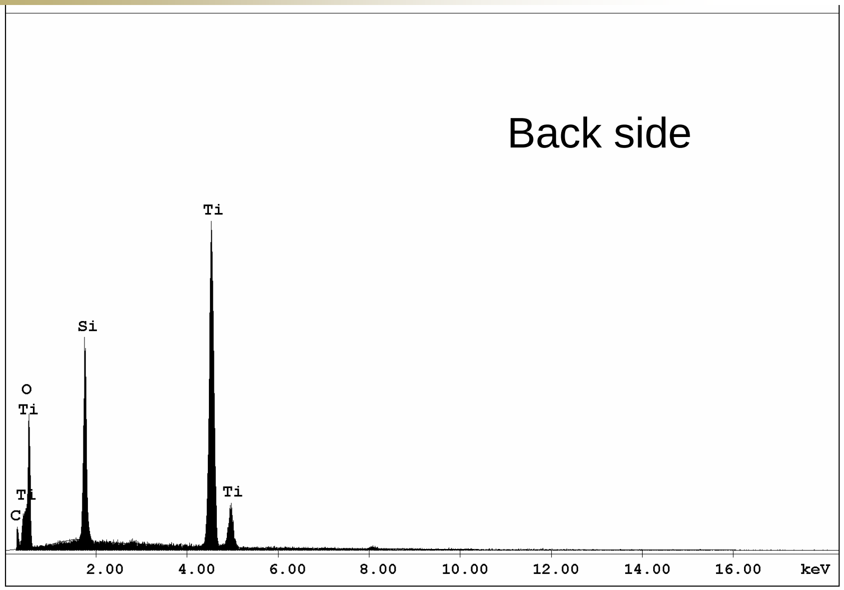
Char underneath surface (white)

Char-W

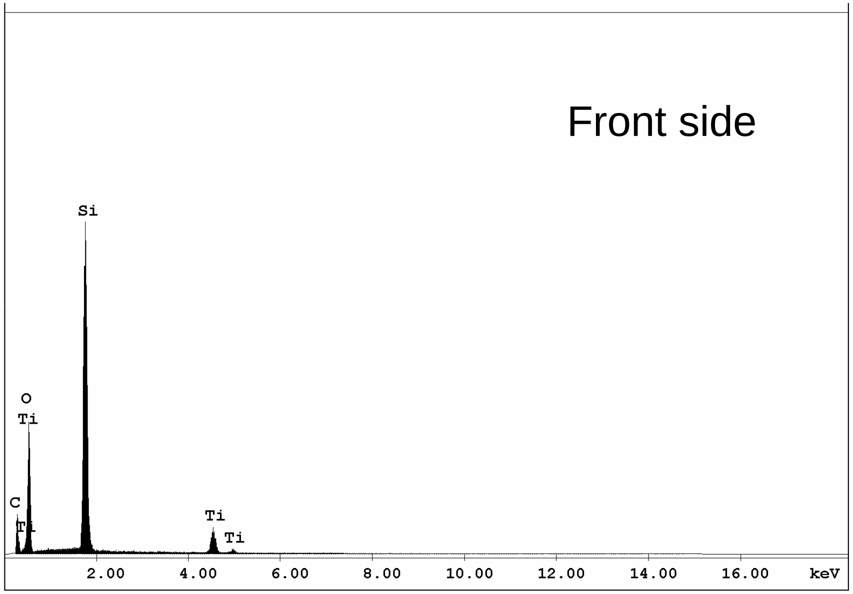
Char upside Surface (black)

Char-B

EDAX Composition



Char-W



Char-B

Atomic %

	C	O	Si	Ti
Char-W	13.8	57.7	9.2	19.3
Char-B	39.4	43.2	15.7	1.7

A12 - 20wt%TiO_2 on 3 x 1 in. fabric

Video Deleted

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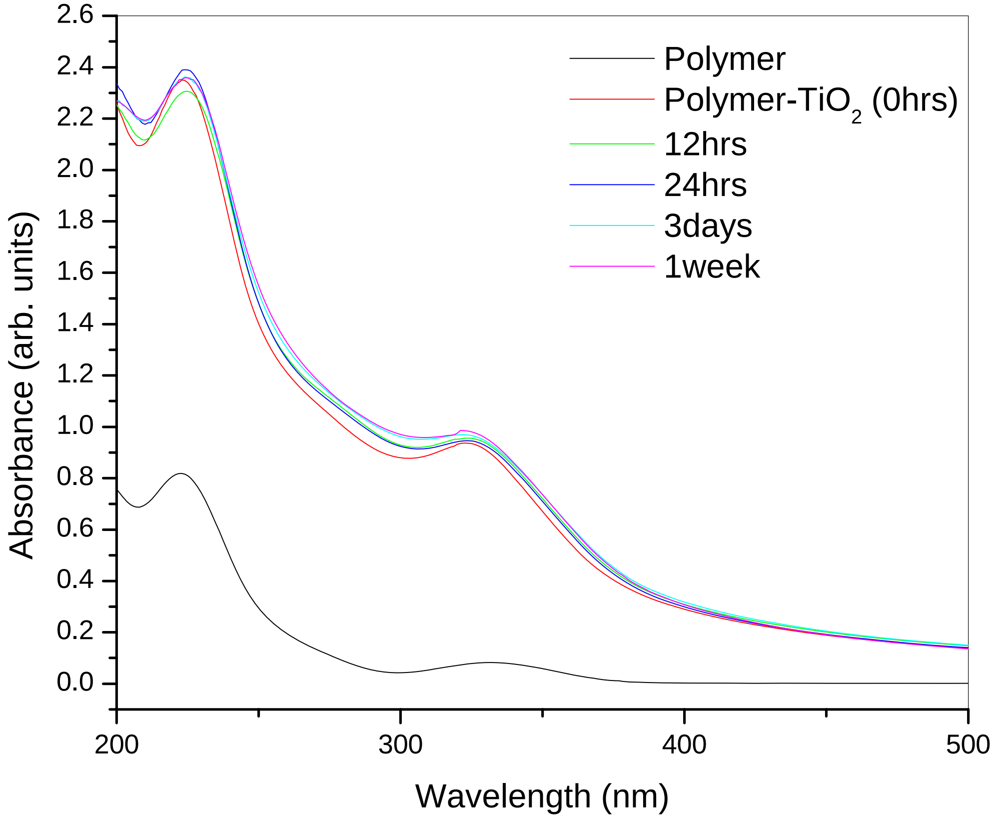
Burning of A12-TiO2 coated camouflage fabric
Self extinguish within 25sec.
No melt drip
Not ASTM standards

Protective swelled char formation around the fabric after burnt

When broken the protective Layer, fabric piece intact

Char is swelled and heat/mass transfer to the underlying material is hindered

Photostability with TiO2



Conclusions on TiO2-Polymer nanocomposites

- Increased thermal stability as TiO_2 limit the thermal conduction to the polymer inside and thus kinetics of degradation.
- Restricted mobility of polymer chains results from steric hindrance due to the presence of additive solid particles.
- Due to the increased viscosity of the melt with amount of TiO_2, the gas emission is hindered.
- Promotes char formation containing Si atoms (Silicate) on the surface which also hinders the heat transfer to the combustible gases.
- Photostability of the polymer in the presence of TiO_2 is good.

Comparison of FR Polymers

FR Material	Degradation Temp. (^oC)	Heat release Capacity (J/g.K)	Environ-mental effects	Process-ability	Synthesis	Cost
KEVLAR	500-550	302	No toxic byproducts?	Highly Insoluble difficult to coat	Hazard ingredients Multi-step	Too expensive to provide every Soldier
NOMEX	500-550	52	No toxic byproducts?	Highly Insoluble difficult to coat	Hazard ingredients Multi-step	Too expensive to provide every Soldier
Our Best Performing Polymers	**(Polyamide) 400 428** (Polyimide) 450**	**(Polyamide) 194 132** 90* (Polyimide) 313**	**No toxic byproducts No toxic byproducts**	**Highly soluble and easy to coat Highly soluble to partially soluble**	**Enzymatic Synthesis No solvents, 1-step Enzymatic Synthesis No solvents, 1-step**	**Potential to be very cost effective**

*cross-linked with 20% hexamethylenetetramine; **with 20% TiO_2 nanoparticles

Conclusion

Polysiloxane-copolymers are a promising alternative to halogenated and other expensive fire safe polymers

- **Flame retardancy comparable to well known FR polymers (high degradation temperatures, low heat release capacity)**
- **Environmentally benign synthesis**

  (single step, enzymes as catalysts and no solvents)
- **No toxic byproducts (cyclic siloxanes)**
- **Potentially processable for coatings, fibers, polymer blends**
- **Polymer-TiO_2 nanocomposites show improved FR and photostable**
- **SEM images showed that TiO_2 is helping to form Silicate char on the surface**
- **Potential to be low cost**

Acknowledgement

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- Mr. Kenneth D. Smith

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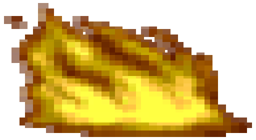
Environmental Quality Basic
Research (EQBR) Program



“Everything in this Universe burn at some temperatures, But if we can understand ‘why’ and ‘how’ a material burn, it may be possible to create an efficient, economical and more importantly environmentally safe Fire Proof material which can save lives”

EDAX composition

c:\edax32\genesis\genspc.spc
Label:Yale patient_2-1
kV:20.0 Tilt:0.0 Take-off:35.0 Det Type:SUTW+ Res:132 Amp.T:102.4
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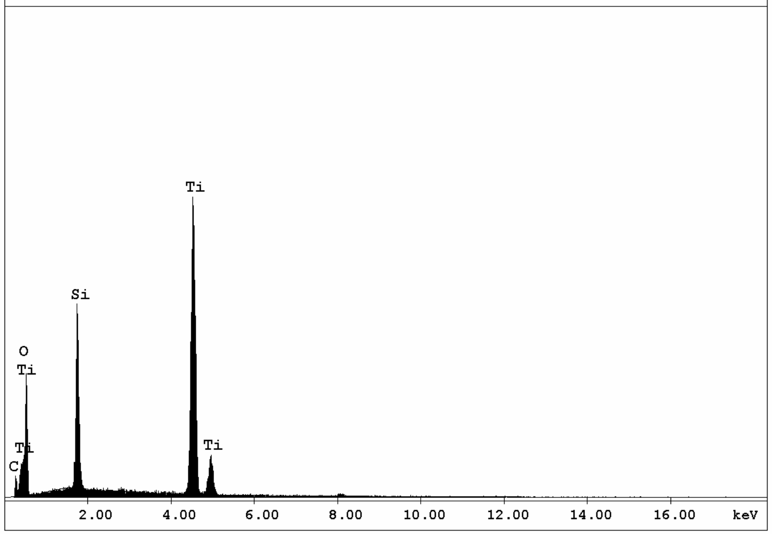

Weight % by Element

Filename	C K	O K	SiK	TiK
genspc.spc	28.03	40.98	26.22	4.77
genspc.spc	7.30	40.65	11.38	40.67

Atomic % by Element

Filename	C K	O K	SiK	TiK
genspc.spc	39.37	43.20	15.75	1.68
genspc.spc	13.80	57.71	9.20	19.29

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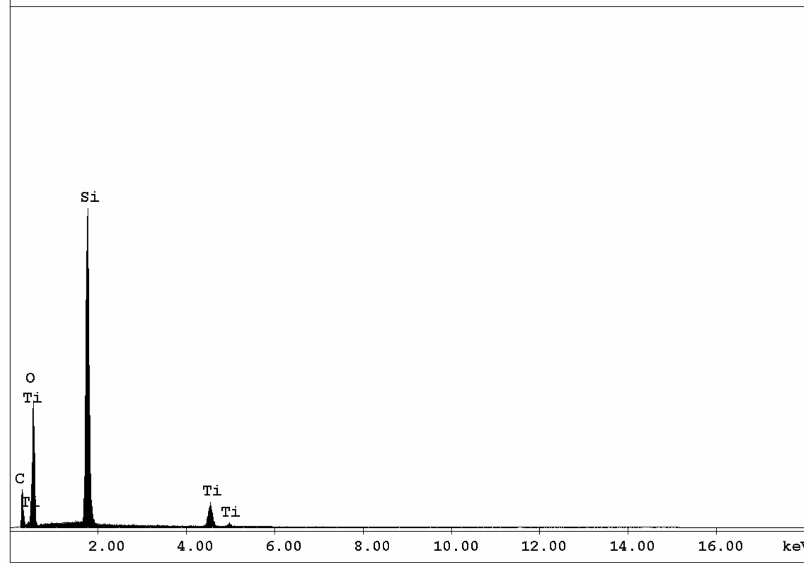

Weight % by Element

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