

Thermal characteristics of fibers

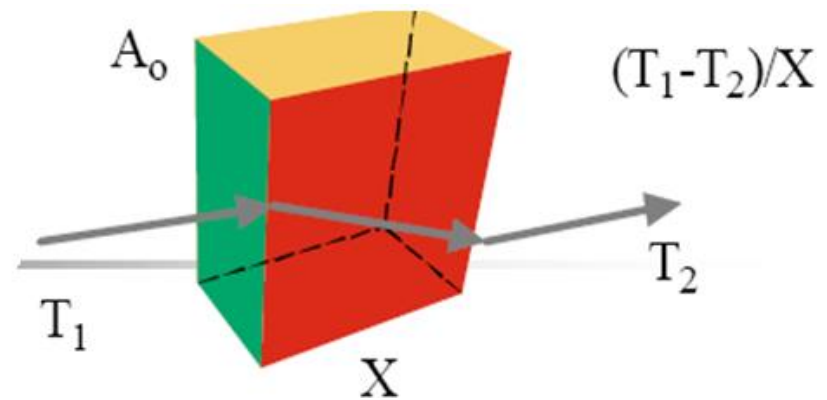


- Heat to textile material causes both **physical and chemical changes**.
- For thermoplastic fibers, the physical changes occur at the second order transition (T_g), and melting temperature (T_m), while the chemical changes occur at pyrolysis temperatures (T_p) at which thermal degradation occurs.

When a textile is ignited, the rate of rise in temperature depends on;

- a) The specific heat of the fiber,
- b) Its thermal conductivity
- c) The latent heat of fusion (for melting fibers) and
- d) The heat of pyrolysis.





Thermal conductivity

- Thermal conductivity is expressed as coefficient of thermal conductivity λ [$\text{Wm}^{-1}\text{K}^{-1}$]. This coefficient is a proportionality parameter in equation for steady thermal flow across plate of area A_o . Rate of thermal flow is proportional to difference of input T_1 and output T_2 temperatures of both ends and plate thickness X

$$\frac{Q}{t} = -\lambda * A_o * \frac{(T_1 - T_2)}{X}$$

- Q is amount of heat transported through plate till time t . Air has very low thermal conductivity 0,003 [$\text{Wm}^{-1}\text{K}^{-1}$].



The ability of a material to transport heat.

Fourier's Law

$$q = -\lambda \frac{dT}{dx}$$

heat flux (J/m²-s) → q

← $\frac{dT}{dx}$ temperature gradient

← λ thermal conductivity (W/m/K)



- **Atomic perspective:** Atomic vibrations and free electrons in hotter regions transport energy to cooler regions.



Factors affecting thermal conductivity

Thermal conductivity mainly depends on;

1. Temperature
2. Degree of crystallinity
3. Density of polymer
4. Orientation of chain segments
5. Structure

Typical value of thermal conductivity of some

SL	Fibers	Thermal conductivity (<i>mW / m. K</i>)
01	Silk	50
02	Wool	54
03	Cotton	71
04	Polyester (PET)	140
05	PVC	160
06	Nylon	250
07	Polyethylene	340



Thermal Conductivity: Comparison

Material	λ (W/m-K)	Energy Transfer Mechanism
<ul style="list-style-type: none"> <u>Metals</u> 		
Aluminum	247	atomic vibrations and motion of free electrons
Steel	52	
Tungsten	178	
Gold	315	
<ul style="list-style-type: none"> <u>Ceramics</u> 		
Magnesia (MgO)	38	atomic vibrations
Alumina (Al ₂ O ₃)	39	
Soda-lime glass	1.7	
Silica (cryst. SiO ₂)	1.4	
<ul style="list-style-type: none"> <u>Polymers</u> 		
Polypropylene	0.12	vibration/rotation of chain molecules
Polyethylene	0.46-0.50	
Polystyrene	0.13	
Teflon	0.25	

Selected values from Table 19.1, *Callister & Rethwisch 8e.*



The ability of a material to absorb heat.

- **Quantitatively:** The energy required to produce a unit rise in temperature for one mole of a material.

heat capacity
 (J/mol-K)

$$C = \frac{dQ}{dT}$$

energy input (J/mol)

temperature change (K)

- Two ways to measure heat capacity:

C_p : Heat capacity at constant pressure.

C_v : Heat capacity at constant volume.

C_p usually $>$ C_v

Specific Heat capacity

$$C = Q/m \cdot \Delta T$$

How much each unit of mass is stored

- Heat capacity has units of $\frac{\text{J}}{\text{mol} \cdot \text{K}}$ $\left(\frac{\text{Btu}}{\text{lb} - \text{mol} \cdot ^\circ\text{F}} \right)$

- Fibers specific heat capacity is frequently expressed as specific heat at constant pressure C_p [$\text{Jkg}^{-1}\text{K}^{-1}$].
- Specific heat at constant pressure is defined as heat Q required for heating of 1 kg of fiber to increase their temperature up to 1 degree of Kelvin. This quantity is dependent on the molecular and super molecular structure of fibers, temperature and rate of heating. Specific heat at constant pressure is expressed as

$$C_p = \left(\frac{\partial Q}{\partial T} \right)_p \text{ [Jkg}^{-1}\text{K}^{-1}\text{]}$$

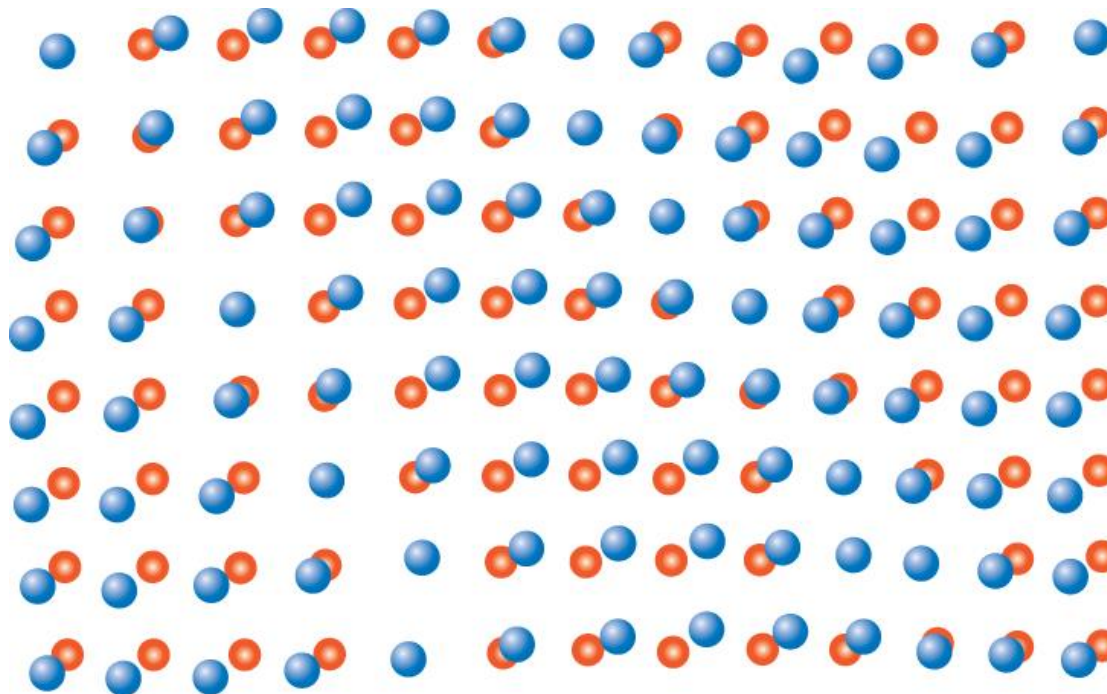
Fibers have nearly constant value $C_p=1,5$ [$\text{Jg}^{-1}\text{K}^{-1}$].



Atomic Vibrations (Vibrational Heat Capacity)

Atomic vibrations are in the form of lattice waves or phonons.

In most solids, the principal mode of absorption of thermal energy is by the increase in the vibrational energy of the atoms.

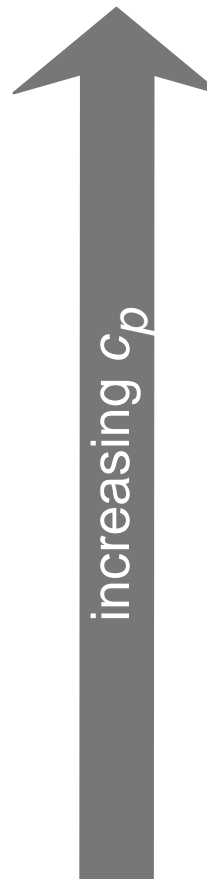


- Normal lattice positions for atoms
- Positions displaced because of vibrations





Specific Heat: Comparison



Material	c_p (J/kg-K) at room T
• <u>Polymers</u>	
Polypropylene	1925
Polyethylene	1850
Polystyrene	1170
Teflon	1050
• <u>Ceramics</u>	
Magnesia (MgO)	940
Alumina (Al ₂ O ₃)	775
Glass	840
• <u>Metals</u>	
Aluminum	900
Steel	486
Tungsten	138
Gold	128

c_p (specific heat): (J/kg-K)
 C_p (heat capacity): (J/mol-K)

• Why is c_p significantly larger for polymers?



Materials change size when temperature is changed.



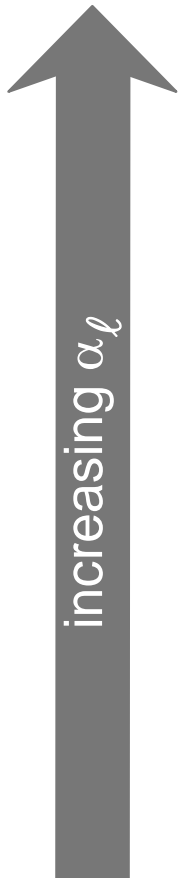
$$\frac{l_{\text{final}} - l_{\text{initial}}}{l_{\text{initial}}} = \alpha_l (T_{\text{final}} - T_{\text{initial}})$$

α_l is the linear coefficient of thermal expansion (1/K or 1/°C).
 The fractional increase in length of a material due to rise in temperature by 1 °C



Coefficient of Thermal Expansion: Comparison

Material	α_ℓ ($10^{-6}/^\circ\text{C}$) at room T
Polymers	
Polypropylene	145-180
Polyethylene	106-198
Polystyrene	90-150
Teflon	126-216
Metals	
Aluminum	23.6
Steel	12
Tungsten	4.5
Gold	14.2
Ceramics	
Magnesia (MgO)	13.5
Alumina (Al ₂ O ₃)	7.6
Soda-lime glass	9
Silica (cryst. SiO ₂)	0.4



Polymers have larger α_ℓ values because of weak secondary bonds

Q: Why does α_ℓ generally decrease with increasing bond energy?



It measures the ability of a material to conduct thermal energy relative to its ability to store thermal energy. It has the SI unit of m^2/s . Thermal diffusivity is usually denoted by α
The formula is:

$$\alpha = \lambda / (c \times \rho)$$

where

λ is thermal conductivity ($\text{W}/(\text{m}\cdot\text{K})$)

ρ is density (kg/m^3)

c is specific heat capacity ($\text{J}/(\text{kg}\cdot\text{K})$)



Pyrolysis

- PYRO – HEAT
- LYSIS - BREAK DOWN

What is Pyrolysis?

“Pyrolysis is thermal cracking in the absence of oxygen.”

Cedric Briens

“Pyrolysis is the thermal decomposition of organic material at elevated temperatures, in the absence of gases such as air or oxygen.”

Greenpeace

Heat introduced, O₂ excluded

An endothermic reaction

- Pyrolysis is a chemical reaction.
- This reaction involves the molecular breakdown of larger molecules into smaller molecules in the presence of heat.
- Pyrolysis is also known as thermal cracking, cracking, thermolysis, depolymerization, etc.



The Pyrolysis effects within different temperature zone

Pyrolysis Zones

Zone A: Up to 392° F (200° C)

Wood is dried and small amounts of decomposition take place

Zone B: 392° - 536° F (200° - 280° C)

A large number of complex chemical compounds are generated through decomposition and charring begins

Zone C: 536° - 932° F (280° - 500° C)

Rapid pyrolysis takes place, releasing and/or generating a wide range of complex chemical compounds. Secondary reactions between these products can take place and charcoal is formed.

Zone D: > 932° F (500° C)

Surface temperature of charcoal is sufficient to induce secondary reactions such as combination of free carbon and carbon dioxide (simple asphyxiant) to produce large amounts of carbon monoxide (toxic and flammable)

Ignition Temperatures ^[35]

Fixed Carbon: 765° F - 1094° F (407°-590° C)

Hydrogen: 1076° - 1094° F (580 - 590° C)

Methane: 1202° - 1382° F (650° - 750° C)

Ethylene: 1008° - 1018° F (542° - 548° C)

Ethane: 968° - 1166° F (520° - 630° C)

Benzene: 1097° - 1364° F (740° C)

Carbon Monoxide: 1191° - 1216° F (644° - 658° C)

Listed ignition temperatures are based on the range of temperatures (low to high) listed in multiple reference sources. Ignition temperature is also influenced by the oxygen concentration in the atmosphere.

Pyrolysis of wood results in production of a far greater number of complex chemical compounds. The materials listed are simply a representative sample of the more common of these substances.



Fibre	T _g (°C) Glass Transition	T _m (°C) Melting	T _p (°C) pyrolysis	T _c (°C) combustion	**H KJ/g	*LOI* (%)
Wool	-	-	245	600	27	25.0
Cotton	-	-	350	350	19	18.4
Viscose	-	-	350	420	19	18.9
Triacetate	172	290	305	540	-	18.4
Nylon 6	50	215	431	450	39	20.0-21.5
Nylon 6.6	50	265	403	530	32	20-21
polyester	80-90	255	420-477	480	24	20-21.5
Acrylic	100	>220	290	>250	32	18.2
Polypropylene	-20	165	469	550	44	18.6
Modacrylic	<80	>240	273	690	-	29-30
PVC	<80	>180	>180	450	21	37-39
PVDC	-17	180-210	>220	532	11	60.0
PTFE	126	>327	400	560	4	95.0
Oxidised acrylic	>640	-	55	-	-	-
Nomex	275	375	310	500	30	28.5-30
Kevlar	340	560	590	>550	-	29
PBI	>400	-	>500	>500	-	40-42

* LOI - Limited of Index (%), **Heat of Combustion - Kcal/g

Lists of T_g,
Melting and
Pyrolysis
temperatures
and LOI%



$$\lambda \approx K * \rho * C_v * v_z$$

Rate of sound spread in polymer v_z

polymer	λ [Js ⁻¹ m ⁻¹ K ⁻¹]	$C_v \cdot 10^3$ [Jkg ⁻¹ K ⁻¹]
PP	0,172	2,14
PVC	0,168	0,96
PES	0,218	1,13
elastane	0,147	1,70

Semicrystalline

polymers- thermal conductivity is dependent on the densities of amorphous ρ_a and crystalline ρ_K phases.

Thermal conductivity of crystalline phase at usual temperature is six times higher than thermal conductivity of amorphous phase .

$$\lambda_c = \lambda_a \left[1 + 5,8 * \left(\frac{\rho_K}{\rho_a} \right) - 1 \right]$$



Melting points of some Thermoplastic textile fibres

Fibre type	Trade names	Melting point (T _m °C)
Polyester	Terylene, Dacron, Trevira, Thermastat, Coolmax, Patagonia	255
Polypropylene	Meraklon, Leolene, Ulstron	150
Polyamide	Nylon 6, Nylon 6-6, Tactel	250
Poly Vinylidene Chloride	Damart Thermolactyl, Rhovyl	Shrinks 95
Modacrylic	SEF, Velicren, Teklan,	175
Spandex (Elastic Fibres)	Lycra, Vyrene	250





Difference between T_g & T_m

SL	T_g	T_m
01	Characteristic of the amorphous phase	Characteristic of the crystalline phase
02	It is the secondary transition.	It is the primary transition.
03	It involves a change of phase from a solid state to rubber state.	It involves a change of phase from a solid to liquid.
04	Below T_g : Disordered amorphous solid with immobile molecules	Below T_m : Ordered crystalline solid
05	Above T_g : Disordered amorphous solid in which portions of molecules can wiggle around	Above T_m : Disordered melt
06	<p>Glass transition temperature</p> <p>Heat</p> <p>Temperature</p> <p>Amorphous polymer</p>	<p>Melting temperature</p> <p>Heat</p> <p>Temperature</p> <p>Crystalline polymer</p>

T_g & T_m of some polymers:

SL	Polymer	T_g ($^{\circ}C$)	T_m ($^{\circ}C$)
01	Nylon 6	50	250
02	Nylon 6:6	50	270
03	Polyester	64	269
04	PET	69	264
05	Tri-acetate	73	306
06	PVC	81	310
07	PAN	97	314
08	Poly styrene	100	250



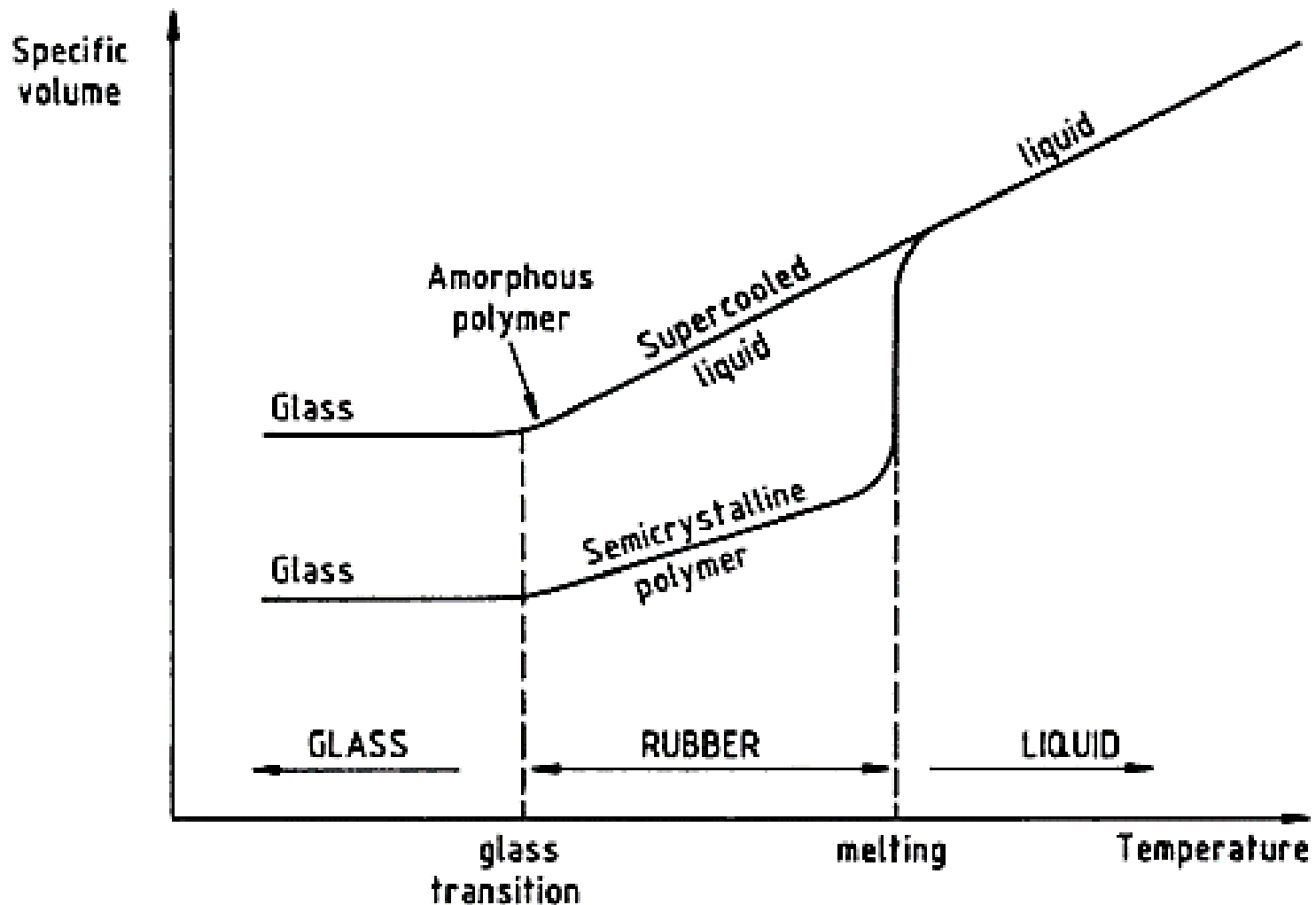


Fig: A schematic diagram showing the variation of specific volume with temperature for an amorphous and a semi-crystalline polymer



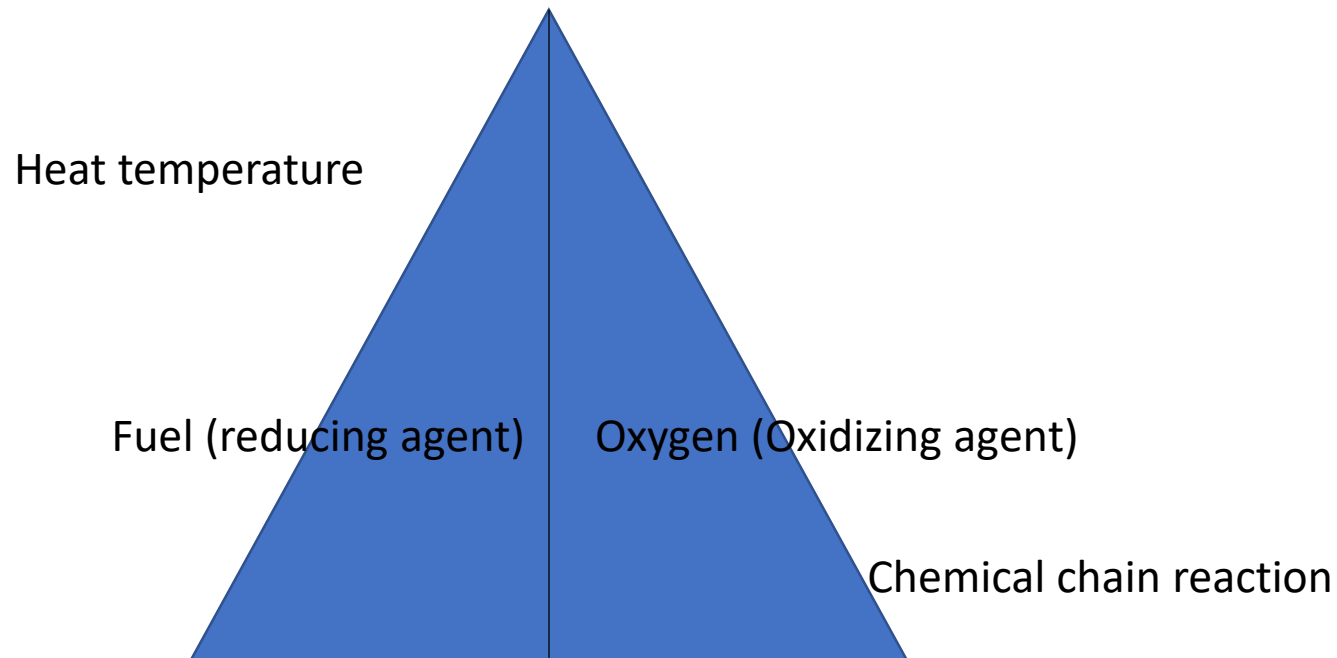
Flammability



- Combustion generally needs three components: flammable material, sufficient thermal energy and enough concentration of oxygen. Stages of combustion:
 - ⑩ Heat absorption and loss of water from fibers;
 - ⑩ Flammable gases formation due to fibers thermal decomposition (pyrolysis);
 - ⑩ Flammable gases ignition (radical reaction between flammable gasses and oxygen in gaseous phase);
 - ⑩ Development heat due to combustion which further support creation of flammable gases.

The flammable gases (products of pyrolysis) only are capable to burn. Polymers containing higher amount of hydrogen bonds (cellulose) are easily flammable. Less flammable are polymers containing aromatic rings or halogen groups (Cl, F).





Polycyclic aromatic Hydrocarbons - Tar And methane

Heat release rate (HRR) = product of mass loss rate per unit of exposed surface area and its actual heat of combustion.

Heat release rate varies with fuel characteristics and vent profiles



Factor influencing the flammability:

● Rigidity: Rigidity \uparrow —Flammability \downarrow

● Crystallinity: Crystallinity \uparrow —Flammability \downarrow

Amorphous \uparrow —Flammability \uparrow

● Bonding force: Covalent bond, Hydrogen bond—Flammability \uparrow

Cl bond—Flammability \downarrow

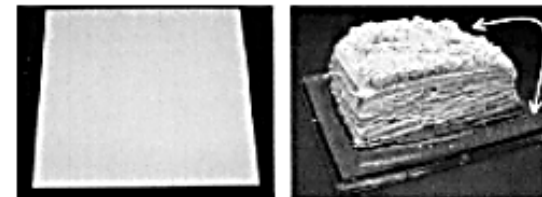
While selecting and designing the flame protective clothing;

1. Burning behavior of textile fibers
2. Influence of fabric structure and garment shape on the burning behavior
3. Selection of non-toxic, smoke free flame retardant additive.
4. Intensity of the ignition source
5. Oxygen supply

Complex textile combustion process – Heating, decomposition leading to gasification (fuel generation), ignition and flame propagation.



- ⑩ Reduction of flammable gases creation;
- ⑩ Restriction of fibers decomposition by increasing of their temperature resistance;
- ⑩ Generation of non flammable gases at fiber decomposition (blocking contacts with atmospheric oxygen) ;
- ⑩ Dilution of flammable gases by nonflammable ones;
- ⑩ Support of fibers dripping during melting (fiber is separated from combustion zone);
- ⑩ Reduction of thermal energy (endothermic decomposition) by using of non flammable materials;
- Creation of thick insulating porous (carbon) layer on the fiber surface (intumescence).



Limiting Oxygen Index

Flammability is often expressed by **limiting oxygen index** which corresponds to the amount of oxygen (percent) in mixture with nitrogen necessary to combustion.

Inflammable fibers have $LOI=26$ and higher



fiber	LOI [%]	T_m or T_R
Nomex	30	400
teflon	95	327
wool	24 – 26	–
cotton	17 – 19	–
polypropylene	19 – 20	164 – 170
nylon	20 – 22	256
polyester	20 – 22	258
acrylic	20	decompose
viscose	17 – 19	–

Fiber degradation

Processes during degradation:

- depolymerization (D)
- random chain scission (P)

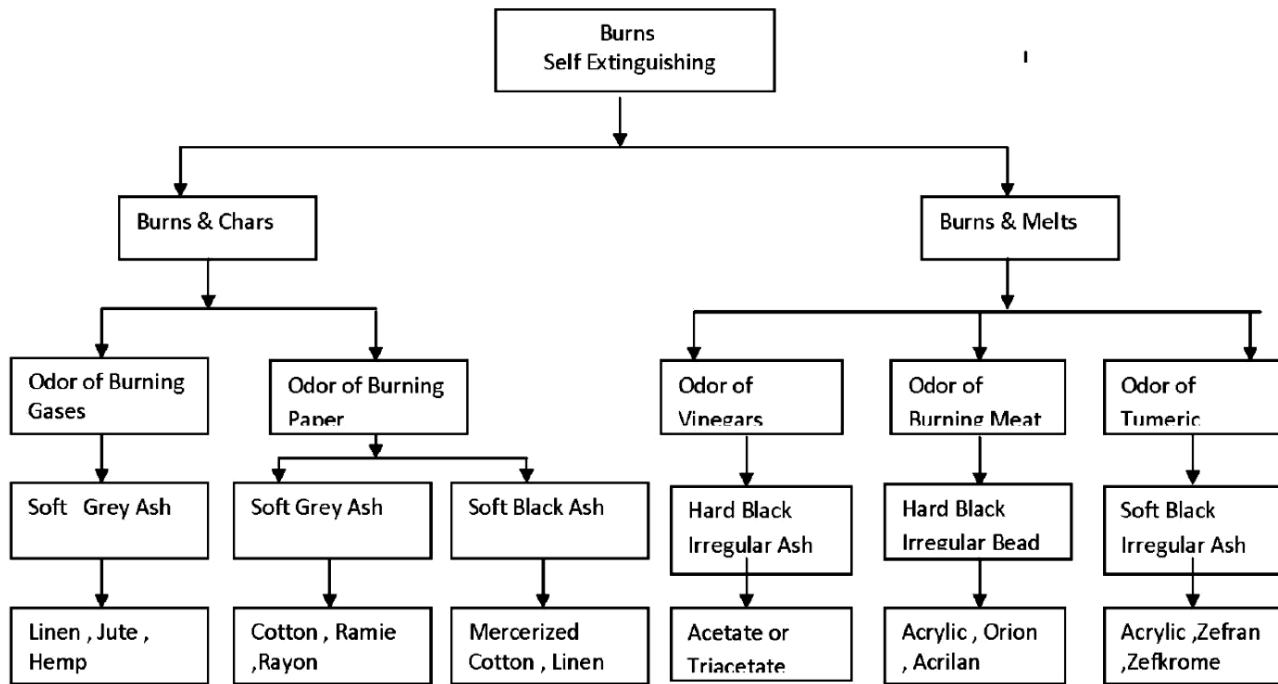
Thermal degradation main process is radical depolymerization,

Photodegradation is dependent on the light intensity and wavelength. Photon energy at wavelengths 400–300 nm is 300–390 kJ/mol. (energy of C-C bonds is 420 kJ/mol). First step is scission of primary bonds in backbone chains and depolymerisation.

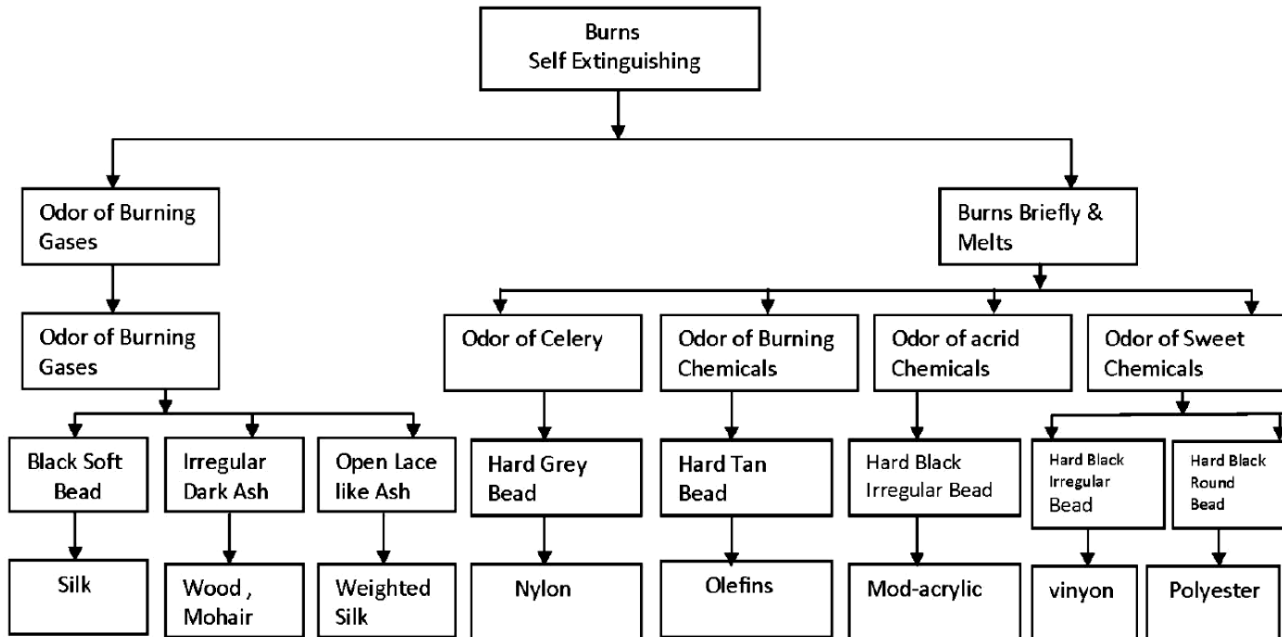
Hydrolytic degradation is caused by action of water or aggressive liquids. Basic process is chain scission.



Oxidation degradation of PP



Burning Behavior of Textile Fibers



Factors affecting the flammability;

- Ease of ignition
- Rate of burning and
- heat release rate

Factors that influence the thermal protection level;

- Melting and shrinking
- Characteristics of synthetic fibers fabrics, and emission of
- smoke and toxic gases during burning.

Selection and designing the flame protective clothing;

- Burning behaviour of textile fibres.
- Influence of fabric structure and garment shape on the burning behaviour.
- Selection of non-toxic, smoke free flame-retardant additive.
- Intensity of the ignition source.
- Oxygen supply.



Material/Fabric Name	Flame Properties	Smoke Properties	Ash/Residue	Smell and Misc
NATURALS	As a general rule they ignite easily with a steady glowing flame	Most have minimal smoke	Usually leaves a soft ash that can be blown or wiped away, if any	Paper, wood or leaves smell.
Cotton	Ignites easily, continues to burn when removed from flame. Usually a sputtering flame.	Little white to grey smoke.	Soft white or grey ash that blows away, the weave in the ash can still be seen on personal tests.	The smell, burning paper or wood. Cotton burns rather slow. Has a glow after flame is out
Hemp	Very similar to cotton.	White to grey smoke	Grey to white ash	The smell of burning paper or wood
Linen	Very similar to cotton, a little harder to ignite and slower to burn.	Same as Cotton	Same as Cotton, may be more brittle at the base of the ash on the fabric edge.	Appearance will differ from cotton,. Same smell.
Silk	Ignites quickly, burns easy, and slower the thicker it is.	Very minimal smoke to light.	Leaves a beaded or gritty dark grey or black ash.	Smells like burning hair but sometime too faint. Harder to extinguish.
RAYON (1/2 natural and synthetic)	Burns slower than cotton. Steady flame, minimal dark grey to black smoke	Tends to have a darker smoke than cotton, but can vary	Soft ash that can be blown away. Is slightly more brittle than Cotton ash and may be gritty.	Paper or wood like smell. Tends to have more ash left and is not as clean of a burn as Cotton. Has a bright glow before flame burns out.
SYNTHETICS	Tend to retreat from flames and melts	Usually dark and thick smoke	Hard, brittle, lumpy ashes, or melted beads	Harsh acidic smells or little to no smell. Usually blended making hard to identify
Acetate	Melts and burns with flame. Will retreat from flame, burns quick.	Sometimes dark grey to black smoke.	Hard dark brittle bead. Can drip while burning be careful.	Vinegary or treated wood smell.
Acrylic	Retreats from flame. Burns rapidly, melts. It will burn if flame is on it long enough. Sputtering flame	Varies	Hard brittle irregular Ash/beading.	Harsh acidic smell.
Nylon	Melts then burns, will retreat from flame. Burns slowly	White smoke	Hard grey, smoky or brown bead.	Vegetable or plant like smell. If ash is burned, smells like plastic.
Polyester	Melts and burns at the same time, retreats from flame.	Black smoke	Hard brittle cream or brown bead. Can turn black if burned excessively.	Sweet or acidic smell. Drips while burning. The drippings are sometimes on fire.
Spandex	Melts, does not retreat from flame		Black or dark ash	An acidic or rubber smell like a hot pencil eraser

Flammable Properties of Fibres

