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"SCHOOL ON POLYMER PHYSICS"

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"THE ROLE OF ADDITIVES IN POLYMERS (Thermoplastics)"

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The Role of additives in Polymers (thermoplastics)

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1. Classification of additives.

Generic	Specific
(i) Processing Additives	Processing Stabilisers Lubricants < Internal / External Processing Aids.
(ii) Mechanical Properties Modifiers	Plasticisers Reinforcing fillers Impact modifiers.
(iii) Surface Properties Modifiers	Antistatic agents Slip and Anti-blocking additives Anti-wear agents Adhesion promoters
(iv) Optical Properties Modifiers	Pigments and Dyes Nucleating agents
(v) Anti-ageing additives	Anti-oxidants U.V. Stabilisers
(vi) Others	Blowing agents Fire retardants

2. Reactions leading to Degradation of Polymer properties during processing.

A. Olefinic Polymers:

$$\left.\begin{array}{l} \underset{\text{(Polymer defect site)}}{RH} \xrightarrow{\text{heat}} R\cdot \;+\; H\cdot \\ \qquad\qquad\qquad\qquad\qquad \downarrow +O_2 \\ \qquad\qquad\qquad\quad ROO\cdot \;+\; \cdot OH \end{array}\right\} \text{Initiation}$$

$$\left.\begin{array}{l} ROO\cdot + RH\,(\text{polymer}) \longrightarrow ROOH + R\cdot \\ ROOH \longrightarrow RO\cdot + \cdot OH \\ \left.\begin{array}{l} RO\cdot \\ \cdot OH \end{array}\right\} + RH\,(\text{polymer}) \longrightarrow \begin{array}{l} ROH + R\cdot \\ R\cdot + H_2O \end{array} \end{array}\right\} \text{Propagation}$$

$$\left.\begin{array}{lll} R\cdot + R\cdot & \longrightarrow & R-R \\ R\cdot + ROO\cdot & \longrightarrow & ROOR \\ ROO\cdot + ROO\cdot & \longrightarrow & ROOR + O_2 \end{array}\right\} \text{Termination}$$

B. Vinyl Polymers

$$\left.\underset{\text{(Polymer defect site)}}{H-R-X} \xrightarrow{\text{heat}} HR\cdot + \cdot X \right\} \text{Initiation}$$

$$\left.\begin{array}{lll} HR\cdot + X\cdot & \longrightarrow & HX + R(=) \\ R(=) & \longrightarrow & R(=)(=) + HX \end{array}\right\} \text{Propagation}$$

$$\left.\begin{array}{lll} R\cdot + R\cdot & \longrightarrow & R-R \\ X\cdot + R\cdot & \longrightarrow & RX \end{array}\right\} \text{Termination}$$

3. Stabilisation against processing degradation

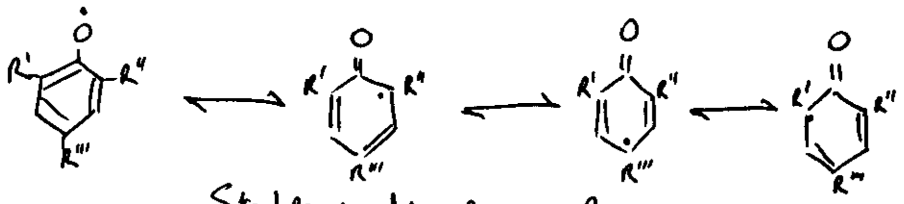
Degradation reactions cannot be prevented but can be slowed down considerably; for this reason the process is known as "Arrestive Stabilisation).

A. Stabilisation of olefinic polymers

(i) Primary Stabilisers : Antioxidants

$$\sim\sim R\cdot + HA\,(\text{Stabiliser}) \longrightarrow RH + \underset{(\text{inactive radical})}{A\cdot}$$

where HA = Hindered Phenols and Aromatic amines



Stable radicals – Resonance.

Examples of phenolic antioxidants are given in table 1.

(ii) Secondary Stabilisers : Peroxide decomposers

$$\sim\sim ROOH \xrightarrow[\text{Agent}]{\text{Reducing}} \sim\sim ROH + (XO)$$

Typical reducing agents are thio and phosphite compounds and are shown in table 2.

(iii) Chelating agents : Metal deactivators.

Complexing agents are often used to minimise the catalytic effects of metal ions in the propagation step of the degradation reactions.
Metal ion impurities may be present as catalyst residues from the polymerisation process or at the interface of polymer/metal components, such as electrical switchgear and cables.

Typical metal deactivators are oxamides and bis-salicylene diamines

B. Stabilisation of Vinyl Polymers.

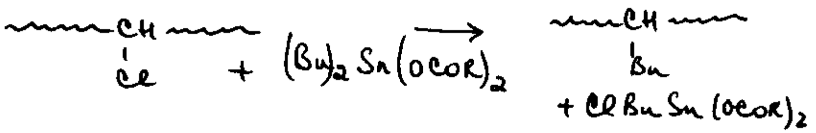
This can be achieved by any of the following mechanisms:

(i) Absorb and neutralise HX, e.g. HCl from PVC or acetic acid from vinyl acetate copolymers
e.g. lead based compounds, weak basic soaps and bases.

(ii) Prevent oxidation reactions and quench free radicals e.g. organotin compounds and conventional antioxidants.

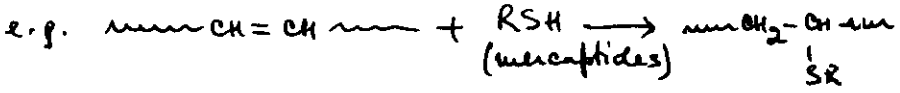
(iii) Displace active, labile substituent groups with more stable substituents

e.g.



$$\sim\sim\underset{Cl}{\overset{|}{CH}}\sim\sim + (Bu)_2Sn(OCOR)_2 \longrightarrow \sim\sim\underset{Bu}{\overset{|}{CH}}\sim\sim + ClBuSn(OCOR)_2$$

(iv) Disrupt conjugation in the polymer chains,



$$\text{e.g.}\ \sim\sim CH{=}CH\sim\sim + \underset{\text{(mercaptides)}}{RSH} \longrightarrow \sim\sim CH_2{-}\underset{\underset{SR}{|}}{CH}\sim\sim$$

Typical stabilisers used for stabilisation of vinyl polymers are shown in table 3.

A special feature of stabilisers is that when used in combinations they can produce synergism, i.e. an effect greater than the expected contribution resulting from the sum of the effects of each individual components. (see figs 1 and 2.

4. Processing Stabilisers.

A. External lubricants : Very low compatibility

(i) Interparticle lubrication : Feeding
(ii) Melt / metal surface lubrication : Flow.

Boundary lubrication : Soaps, e.g. stearates.

Hydrodynamic lubrication: Waxes, Silicone oils

B. Internal lubricants : Low compatibility

Mostly for PVC (e.g. Stearic acid).
Reduce the melt viscosity through "very efficient high temperature plasticisation.

C. Processing aids : High compatibility

Restricted to PVC ; mostly very high M.W. polymethylmethacrylate.

They increase the fusion rate of particles during processing, mostly by immobilising their rotation.

5. Plasticisation by means of additives

Plasticisation is a term used to describe the reduction in glass transition temperature of the base polymer, as shown in figs. 3 and 4

With sufficient amount of plasticiser it is possible to bring a rigid polymer, such as PVC from its glassy state ($T_g = 80°C$) to a rubbery state ($T_g = -20°C$).

Criterion for compatibility

$$\Delta G^M = \Delta H^M - T\,\Delta S^M$$

Normally the increase in entropy for polymers is very small, hence the decisive parameter is ΔH.

the most favourable conditions are for ΔH to be negative, i.e. strong intermolecular attractions (H-bonds) so that ΔG becomes negative.

The minimum requirement is for ΔH = 0, i.e. molecular interactions are approximately the same as for individual components.

Accordingly the solubility parameters for the polymer and plasticiser have to be of the same order of magnitude, i.e.

$$\Delta H = V\left(\delta_1 - \delta_2\right)^2 \phi_1 \phi_2 = 0$$

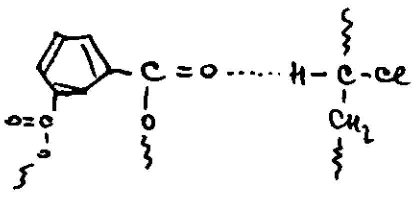
where
ϕ_1 = volume fraction of plasticiser
ϕ_2 = volume fraction of polymer

δ_1 = solubility parameter of plasticiser
δ_2 = " " of polymer
V = Total volume.

ΔH is zero, therefore, only if $\delta_1 = \delta_2$ or if either ϕ_1 or ϕ_2 tend to zero.

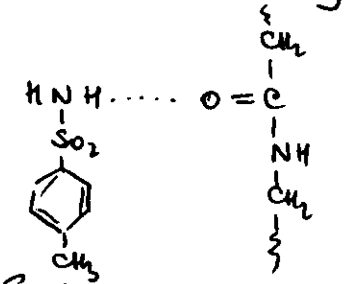
Typical strong interactions between plasticiser and polymer molecules leading to compatibility

(a) Esters for PVC



Phthalates

(b) Amines for polyamides



Sulphonamides.

Classification of plasticisers according to compatibility

1)	Primary Plasticisers	– Totally compatible i.e. at all concentrations
2)	Secondary Plasticisers	– Partially compatible i.e. up to 10-30%
3)	Extenders	– Very low compatibility i.e. about 2-5%

Examples of Primary Plasticisers for Various Polymers.

Polymers		Plasticisers
Polyamides	→	N-ethyl p. toluene sulphonamide
Cellulose acetate	→	Tricresyl phosphate
Polyvinyl chloride	→	Dioctyl phthalate
Polystyrene	→	Triphenyl ethane
Polyethylene	→	Hydrocarbon waxes

Other examples of plasticisers are shown in table 4

Plasticisation Efficiency and Antiplasticisation Phenomena

From fig. 3 it can be seen that the interaction of polymers and plasticisers result in a large reduction in Tg and a substantial depression of β relaxations. The latter causes a concomitant increase in modulus and Yield strength (see also fig 5) over the same temperature range. Such a phenomenon is known as "Antiplasticisation".

It is absolutely clear that Plasticisation and Antiplasticisation are inversely related:

The stronger the polymer/plasticiser interaction the greater the depression of β relaxations and, in turn, the smaller the reduction in Tg. In this respect, therefore, secondary plasticisers are more efficient than primary plasticisers.

The two hypotheses that can be put forward to explain the greater plasticisation efficiency of secondary plasticisers are:

a) More efficient dipole screening, and

b) Greater tendency to phase separate upon approaching the glass transition temperature.

Plasticisation efficiency, however, has also been related to the coefficient of thermal expansion of the plasticiser.

A very simplistic interpretation of the effects of plasticisers on free volumes produces the following expression for the Tg of the plasticised polymer:

$$T_{g(p)} = \frac{\phi_1 \alpha_1 T_{g_1} + \phi_2 \alpha_2 T_{g_2}}{\phi_1 \alpha_1 + \phi_2 \alpha_2}$$

where α = coefficient of thermal expansion
ϕ = volumetric fraction
1,2 = refer to plasticiser and polymer respectively.

6. Reinforcement:

A term used to denote the increase in modulus and strength of polymers by means of inorganic fibres and fillers.
This takes place at all temperatures and without affecting the glass transition temperature of the polymer.
An example is shown below:

Polymer	Tensile strength (MPa)	Modulus (GPa)
Nylon 66	70	2.5
Glass fibres (short) Reinforced Nylon 66	180	8.0

Criterion for Modulus and Strength Enhancement

Upper bounds:

$$E_c = \phi_f E_f + (1-\phi_f) E_m$$

and

$$\hat{\sigma}_c = \phi_f \hat{\sigma}_f + (1-\phi_f)$$

Isometric deformations of fibres and matrix
e.g. Unidirectional continuous fibres – Stress in the direction of fibres.

Lower bounds:

$$\frac{1}{E_c} = \frac{\phi_f}{E_f} + \frac{(1-\phi_f)}{E_m}$$

and

$$\hat{\sigma}_c = (1-\phi_f)\sigma'_m .$$

Isobaric conditions, i.e. fibres (or filler) and matrix carry equal levels of stress,
e.g. Poorly bonded spherical particles (~zero adhesion)

The graphical representation of these bounds is shown in figs. 6 and 7.

Effects of fibre length on modulus and strength

Halpin-Tsai equation:

$$\frac{E_c}{E_m} = \frac{1+\xi\eta\phi_f}{1-\eta\phi_f} \; ; \text{ where } \eta = \frac{E_f/E_m - 1}{E_f/E_m + \xi} \; ; \; \xi = 2(l/d)$$

Concept of Critical fibre length

The critical fibre length, lc, is the minimum length of fibres in a unidirectional composite that carries the maximum stress and, therefore, making the composite to fail by a fibre fracture initiated processes. When the length of of the fibres is less than, lc, the fibres will not reach the maximum (failure stress) and the composite will fail in the matrix, leaving the fibres unbroken.

a) For $l > l_c$:

$$\hat{\sigma}_c = \phi_f \hat{\sigma}_f \left(1 - \frac{l_c}{2l}\right) + (1-\phi_f)\sigma'_m$$

b) For $l < l_c$

$$\hat{\sigma}_c = 2\phi_f \frac{l}{d} \tau_{m/f} + (1-\phi_f)\sigma'_m .$$

where $\hat{\sigma}_f$ = strength of fibres.
$\hat{\sigma}'_m$ = failure stress for the matrix
$\tau_{m/f}$ = interfacial shear strength

Effects of fibre orientation.

$$\frac{E^{\parallel}}{E_{\theta}} = \cos^4\theta + \frac{E^{\parallel}}{E_{\perp}}\sin^4\theta + \left[\frac{E^{\parallel}}{G_{12}} + 2\nu_{12}\right]\cos^2\theta\,\sin^2\theta$$

where θ = angle between fibre direction and applied stress.

E_θ = modulus at angle θ
$E^{\parallel}$ = modulus in the parallel direction
$E_{\perp}$ = modulus in the transverse direction
ν_{12} = Poisson ratio in the fibres plane
G_{12} = Shear modulus in the fibre plane

$$\frac{1}{|\hat{\sigma}_c|^2_{\theta}} = \frac{\cos^4\theta}{|\hat{\sigma}_c^{\parallel}|^2} + \frac{\sin^2\theta\cdot\cos^2\theta}{|\hat{\tau}_{m/f}|^2} + \frac{\sin^4\theta}{|\hat{\sigma}_c^{\perp}|^2}$$

where $\hat{\sigma}_c$ = strength of composite at angle θ
$\hat{\sigma}_c^{\parallel}$ = strength in the longitudinal direction
$\hat{\sigma}_c^{\perp}$ = strength in the transverse direction
$\hat{\tau}_{m/f}$ = interfacial shear strength.

The graphical representation of these equations is shown in figs 8 and 9.

To obtain the modulus and strength of composites where the fibres are organised at random in the plane one can use averaging procedures utilising the above equations

Particulate filler composites

There are basically two approaches in the theories of particulate filler composites:

(a) Halpin-Tsai approach (Modified by Nielson & Lewis)

$$\frac{M_c}{M_m} = \frac{1+\xi\eta\phi_f}{1-\eta\psi\phi_f}\,,\quad \text{where: } M = \text{Shear modulus}$$

$$\xi = \frac{7-5\nu_m}{8-10\nu_m} \quad\text{and}\quad \psi\phi_f = 1-\exp\left[\frac{-\phi_f}{1-\phi_f/\phi^*}\right] \ldots\ldots (22)$$

or $\psi \doteq 1 + \left[(1-\phi^*)/\phi^{*2}\right]\phi_f$ $\qquad$ ϕ^* = maximum packing fraction.
ϕ_f = actual volumetric fraction.

(b) Polynomial approach; (Einstein approach)

$$G_c/G_m = 1 + a\phi_f + b\phi_f^2 \ldots\ldots\ldots\ldots \quad (23)$$

where a and b are empirical coefficients, which depends on the G_f/G_m ratio, adhesion, particle size etc i.e. $a = 2.5$; $b = 14.1$ for rubbery composites.

Alternative equations are also given for rubbery systems, e.g. (Eilers equation)

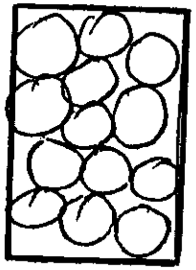
$$G_c/G_m = \left[1 + 1.25\,\phi_f/(1-\phi_f/\phi^*)\right]^2 \ldots\ldots\ldots (24)$$

[illegible]

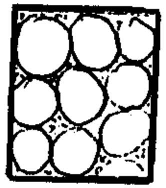
Filler packing Efficiency

It is often important to be able to incorporate into a polymer composition the maximum amount of filler with the minimum reduction in toughness and/or lowest possible increase in melt viscosity. Alternatively particulate fillers are often added to glass reinforced plastics (e.g. BMC, SMC etc) to minimise the resin content i.e. to reduce cost and to reduce mould shrinkage.

It has been found experimentally that packing can be improved by adding fillers of different particle sizes. This is illustrated below, showing how the bulk volume can be reduced when large spherical particles are replaced by small ones, and viceversa.

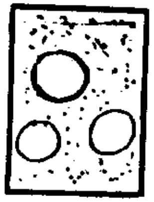


1.0 large
0.0 small
occupied volume = 62.5%



0.72 large
0.28 small
O.V. = 85.0%

0.0 large
1.0 small
O.V. = 62.5%

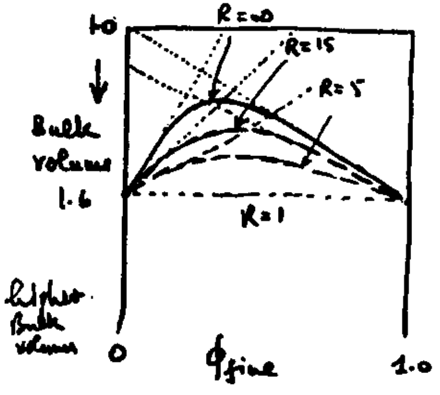


0.33 large
0.67 small
O.V. = 72.0%

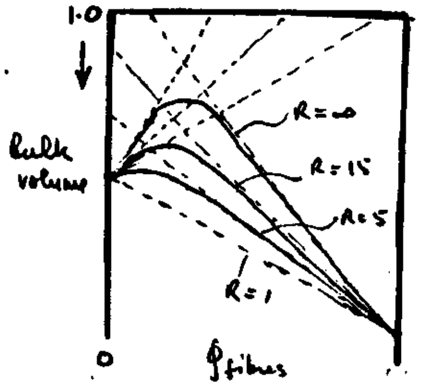
The packing efficiency is dependent on the following:

(a) Diameter ratio of large to small particles (R)

(b) Particle diameter to fibre diameter ratio (R) and length/diameter ratio of the fibres. (L/D)



Replacing large sphere with smallspheres at different R values

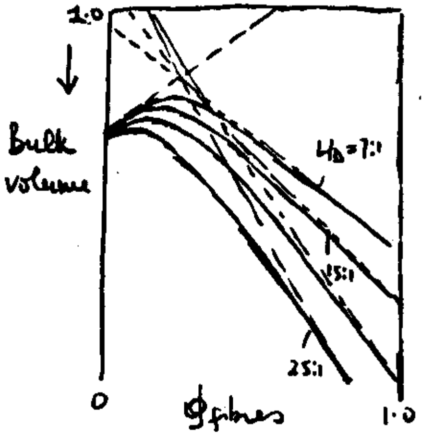


Replacing fibres with spheres at different R values and constant L/D ratio

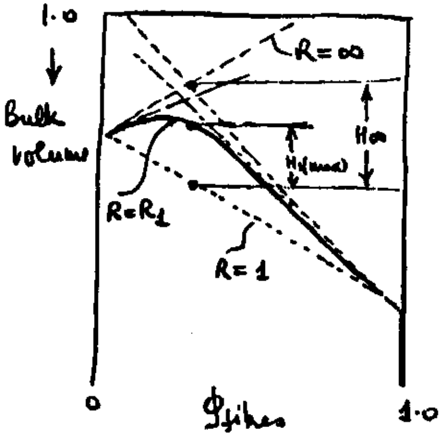
- From the graphs in fig 11 we notice (a) the greater efficiency of packing when large particles predominate (i.e. replace large ones with small spheres) (as shown in previous diagram

(b) The much larger bulk volumes obtained with fibres (i.e. they pack much less efficiently than particles

(c) When R = 1 there is no change in bulk volume for the case of spheres, because there has been no changes in dimensions.

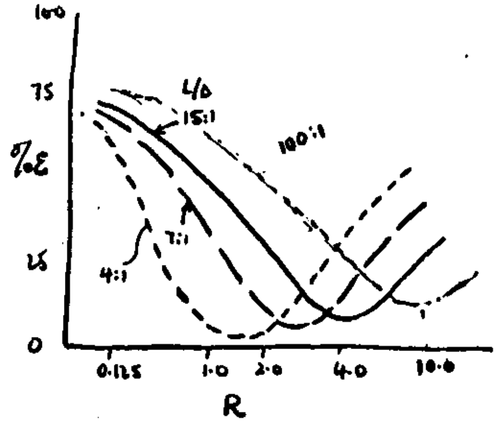


Packing of particles and fibres at constant R and varying L/D.

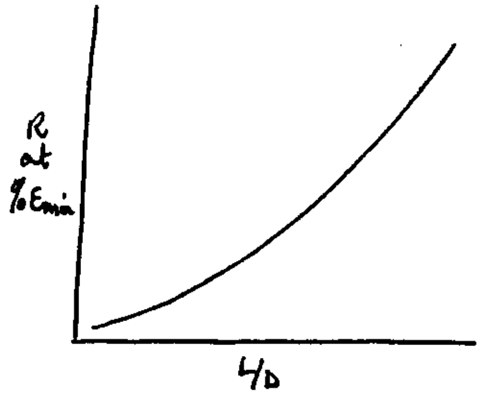


Defining packing efficiency:

$$\%E = \frac{H_1(\max)}{H_\infty} \times 100$$



Packing efficiency as function of sphere/fibre diameter ratio (with L/D as a parameter)



Sphere to fibre diameter ratio minimum efficiency as function of fibre L/D

7. Blowing agents and Cellular Products

A) Physical blowing : Gas dissolved under pressure in melt.

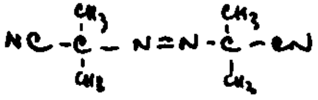
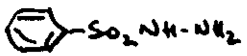
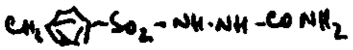
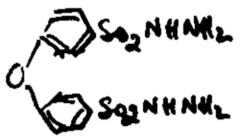
a) Gas injected at head of extruder, (N_2)

b) Low boiling liquids dissolved in polymer e.g. pentane, Freons etc.

B) Chemical blowing : Gas produced from solid additives that will decompose at a specific temperature.

- Nucleation facilitated by products of decomposit

Examples of Chemical blowing agents:

	Chemical nature :	Decomposit
Azo dicarbonamide	$NH_2CON{=}NCONH_2$	160 - 200°C
Azo bis dibutyro nitrile	 $NC-\overset{CH_3}{\underset{CH_3}{C}}-N{=}N-\overset{CH_3}{\underset{CH_3}{C}}-CN$	90 - 115°C
Benzene sulphonyl hydrazine		95-100°C
p Toluene Sulphonyl Semicarbazide		210 - 230°
p.p'-oxybis (benzene sulphonyl hydrazide)		140-160°
Zinc Cpds. (Genitron AF100)	- (Ammonia-free)	230 - 250°

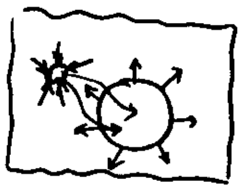
Cell Nucleation:

Henry's Law : $[G]_T = P \cdot S_T$

where $[G]_T$ = conc. of gas dissolved at temp. T
S_T = solubility coefficient at temp. T
P = Pressure (external)

∴ Reduce Pressure to reach saturation and phase separation i.e. gas will form a bubble

Cell Growth:



$$\overset{\text{Internal Pressure}}{\overset{\downarrow}{P}}\,dV = \gamma\,dA$$

Work of Expansion = increase in total surface energy

$V = \frac{4}{3}\pi r^3$; $A = 4\pi r^2$

$dV = 4\pi r^2 dr$; $dA = 8\pi r\,dr$

$$\therefore\ P = \frac{2\gamma}{r}.$$

Pressure inversely proportional to radius i.e. small bubbles are subject to higher internal pressure – hence transport of gas from small to large bubbles.

Cell stabilisation

The size of the cell at a given pressure is determined by surface tension γ; i.e. $Pr = 2\gamma$

∴ Increase γ – by reducing temperature (thermoplastics) or by cross linking (thermosets) – increase the pressure that the cell can tolerate at given size r.

∴ Cell stops growing when $\frac{dP}{dt} = \frac{2}{r}\frac{d\gamma}{dt}$

8. U.V. induced degradation.

The energy spectrum of the solar energy relative to the bond strength of chemical groupings to be found in polymer chains is shown in fig. 13

From this diagram the apparent weakness to UV degradation of polymers such as polyamides, polydienes, polyesters, etc. is clearly revealed.
It is expected, on the other hand, that polymers such as polyolefins, polystyrene, polyvinyl chloride etc would offer considerable resistance to UV induced degradation.
In practice the picture is quite different: polymers such as polymethylmethacrylate and aromatic polyesters, containing very large amounts of UV absorbing groups (C=O chromophores) have been found to exhibit the highest resistance to UV degradation. On the other hand, polypropylene that contains no apparent chromophores is among the least resistant polymers.
There are various explanations that have been put forward to account for such apparent anomalies and that are helpful, at the same time, to provide a rational basis for the UV stabilisation of polymers by means of additives.

Quantum Yield

It is not sufficient for the polymer to absorb UV energy in order to bring about bond cleavage. The absorbed energy can be re-emitted through photoluminescence i.e. fluorescence or phosphorescence via spin inversion through a triplet state. (Fig 13) The % energy which brings about bond rupture is known as the "quantum yield" of the degradation process.

Typical quantum yields are shown below:

$C-H = 5 \times 10^{-2}$ $C-Cl = 10^{-1}$
$C-C = 3 \times 10^{-2}$ $O-O \simeq 1$
$C-C{=}O = 1 \times 10^{-1}$

Impurities as chromophores.

Chromophoric impurities are introduced during synthesis, processing or storage. Typical chromophoric impurities are hydroperoxide groups, peroxides, carbonyl groups, catalyst residues, conjugated unsaturation etc. Consequently polymers that in their pure state are very resistant to UV degradation, such as polyolefins, acquire considerable vulnerability through impurities.

Of these peroxides are particularly harmful as they will readily decompose (100% yield) into radicals upon absorption of UV light.

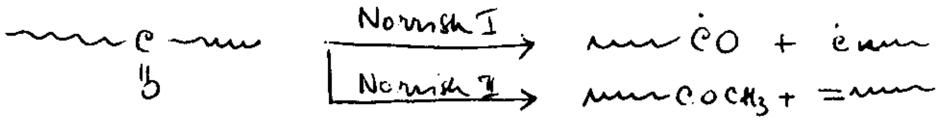
Typical reaction mechanisms of photodegradation

$R-R \text{ (defect)} \xrightarrow{h\nu} R-R^* \longrightarrow 2R\cdot$ } Initiation

$R\cdot + O_2 \longrightarrow ROO\cdot$
$ROO\cdot + R'H \longrightarrow R'\cdot + ROOH \rightarrow RO\cdot + OH\cdot$ } Propagation

$2R\cdot \longrightarrow R-R$
$2RO\cdot \longrightarrow ROOR$
$2ROO\cdot \longrightarrow ROH + RCO + O_2$
} Termination

In addition to these reactions there can be direct degradation occurring from decomposition of carbonyl groups, i.e.



$$\sim\!\!\sim C(=O) \sim\!\!\sim \xrightarrow{\text{Norrish I}} \sim\!\!\sim \dot{C}O + \dot{C}\sim\!\!\sim \qquad \xrightarrow{\text{Norrish II}} \sim\!\!\sim COCH_3 + {=}\!\sim\!\!\sim$$

Furthermore the presence of metal ions will accelerate the decomposition of hydroperoxides by a 'redox' mechanism, i.e.

$ROOH + Me^{n+} \longrightarrow RO\cdot + OH^- + Me^{(n+1)+}$
$ROOH + Me^{(n+1)+} \longrightarrow ROO\cdot + H^+ + Me^{n+}$

Approach to UV stabilisation

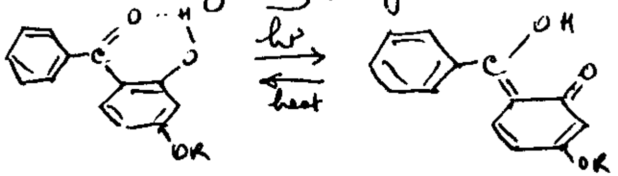
Photostabilisation by means of additives can be brought about in a number of ways. These can be summarised as follows:

(i) UV absorption

Protection against UV degradation can be obviously achieved by introducing additives that will readily absorb UV light hence reducing the number of photons absorbed by the polymer chromophores.

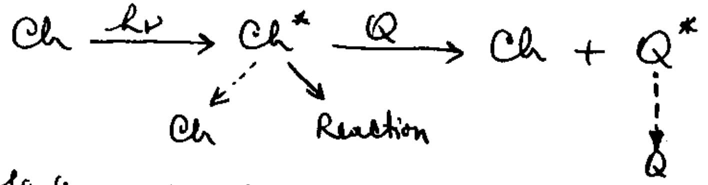
Typical additives that will act in this manner are:
(a) Carbon black, Iron oxide and other pigments
(b) Compatible organic compounds, such as hydroxybenzophenone and hydroxy phenyl benzotriazole

e.g.



(ii) Deactivation of excited species

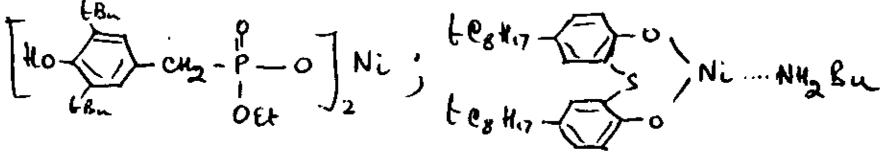
Following absorption of a photon, a chromophore (Ch) may revert to the ground state by some photophysical processes or it may react, but it can also be made to transfer its excess electronic energy to a quenching additive (Q), i.e.



If the rate of energy transfer to the quencher can compete with reaction, decomposition, etc., by Ch* and if Q* can dissipate the excess energy, then the system is stabilised. Energy transfer can occur efficiently only if the energy level of the quencher is below that of the ground state of the chromophore.

Typical excited state quenchers are Nickel chelates, amines, Carbon black and possibly also benzotriazoles.

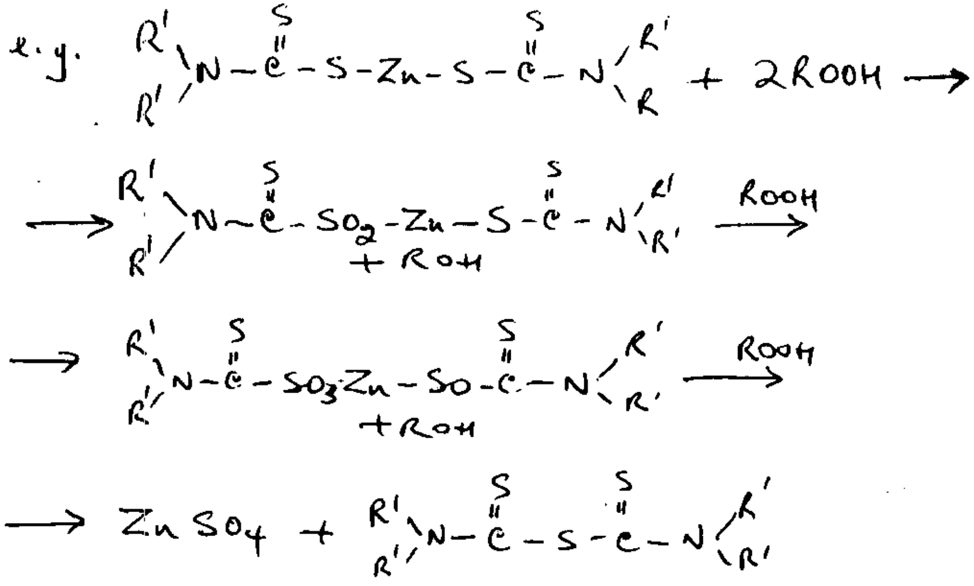
e.g.



(iii) Hydroperoxide decomposers.

These are additives which can catalyse the decomposition of hydroperoxides and convert them into non-active species. Typical compounds are metal dialkyl-dithiocarbamates and di-thiophosphates.

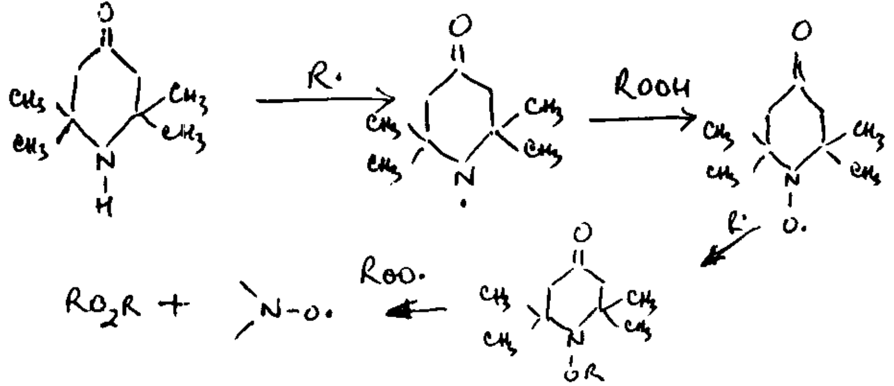
e.g.



(iv) Radical scavengers.

Although conventional phenolic and aromatic amine antioxidants are excellent quenchers of free radicals they are lost or destroyed during UV irradiation and, therefore, cannot be used for UV stabilisation purpose.

The more common types of radical scavengers used for UV stabilisation are hindered amines derived from piperidine, e.g.



9. Fire retardancy by means of additives

Consider the mechanism of flame propagation in fig. 14. From this it can be inferred that intrinsically some polymers are more resistant than others to ignition and flame propagation. The relationship between polymer structure and Ignition resistance is shown in table. and between polymer structure and char formation is shown in fig. . Accordingly these diagrams suggest various routes to develop fire retardant polymer compositions:

(i) Retardation of pyrolysis by antioxidants:

This method is not very effective because antioxidants and auxiliary stabilisers will be easily lost by vaporisation.

(ii) Char formation to provide a thermal barrier

Aromatic compounds (e.g. PPS) which will readily form Polynuclear rings have found limited applicability as additives.

Char formation is more widely utilised in Intumescent coatings, e.g.

Polyhydric alcohol + blowing agent + dehydrating agent

$$R(OH)_n + \text{Acid} \longrightarrow \underset{\substack{\downarrow \\ \text{Char}}}{RO} + \underset{\substack{\downarrow \\ H_2O \text{ gas}}}{\text{Acid}(H_2O)_n}$$

(iii) Ignition inhibitors

- Dilution of combustible gases
- Slow down oxygen diffusion in the ignition zone.

e.g. a) Mixtures of halogenated compounds + Antimony oxide $\xrightarrow{\text{heat}}$ SbOCl↑ + higher oxychlorides (dense fumes)

b) Aluminium trihydrate, Magnesium hydroxide, Zinc borate etc.

$$X(OH)_n \xrightarrow{\text{heat}} XO + n\,H_2O\uparrow$$

c) Melamine and derivatives

$$M^+X^- \xrightarrow{\text{heat}} \text{Sublimation products}\uparrow$$

(iv) Flame extinguishing additives

a) Mixtures of halogenated compounds and Sb_2O_3 or Mo_2O_3.
Free radicals formed from the decomposition of these products will react with the free radicals formed from the pyrolysis of the polymer, reducing the reaction rates in the gas phase and with it the amount of heat generated by combustion. This will in turn reduce the rate of pyrolysis until the amounts of pyrolysed gases produced are insufficient to cause ignition and support the flame.

i.e. $X\bullet + RO\cdot \longrightarrow ROX$ termination

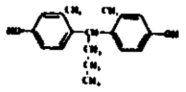
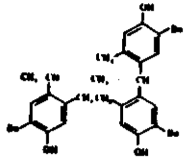
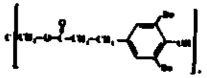
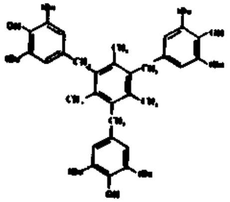
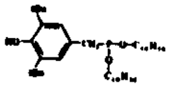
(v) Smoke Suppressants

These have the ability of catalysing the oxidation of carbonaceous matter in the smoke.

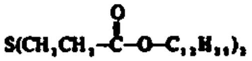
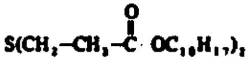
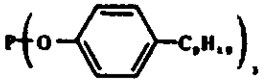
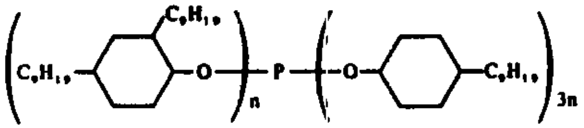
Typical additives are finely divided Mo_2O_3, $Al_2O_3(3H_2O)$, MgO etc. These become highly activated by the heat in the flame to become efficient catalysts for completing the oxidation reactions and reduce smoke formation.

Table 1

Typical antioxidants available commercially
(Total levels of addition: approximately 0·2–0·75 p.h.p.)

Chemical name	Structure	Trade name and supplier	Comments
4,4'butylidene (6-tert-butyl m. cresol)		Santowhite Powder (Monsanto)	–
1,1,3-tris (2 methyl-4-hydroxy-5-tert-butylphenyl) butane		Topanol CA (I.C.I.)	Good ageing and processing stabilizer. Can be synergized with DLTD or DSTDP
tetra tris methylene-3-(3',5'-di-ter-butyl-4'-hydroxy phenyl) propionate methane		Irganox 10 10 (CIBA-Geigy)	–
2,4,6-tris (2-6 di-tibutyl-4-hydroxybenzyl)-1,3,5-trimethyl benzene		Ionox 330 (Shell)	Excellent processing stabilizer. Widely used in cables formulations. Dipoles perfectly balanced, hence little effect on dielectric losses.
Di(*n*-octadecyl)-3,5-di-t-butyl-4-hydroxy benzyl phosphate		Irganox 1093 (CIBA-Geigy)	Good processing stabilizer.

Typical secondary stabilizers available commercially
(Total level of addition: approximately 0·1—0·5 p.h.p.)

Chemical name	Structure	Trade name and supplier
Dilaurylthio-dipropionate	 $S(CH_2CH_2-\overset{O}{\overset{\Vert}{C}}-O-C_{12}H_{25})_2$	Plastanox LTDP (American Cyanamid) and DLTDP (Robinson Bros.)
Distearylthio-dipropionate	 $S(CH_2-CH_2-\overset{O}{\overset{\Vert}{C}}\cdot OC_{18}H_{37})_2$	Plastanox STDP (American Cyanamid)
Tris(nonylphenyl) phosphite		Santowhite TNPP
Tris (mixed mono- and dinoylphenyl phosphite)		Polygard (Uniroyal)

For a more comprehensive guide for the selection of stabilizers consult *Modern Plastics Encyclopaedia* (McGraw-Hill).

Table 3

Typical stabilizers for vinylchloride polymers
(Total level of addition: approximately 0·5–2·0 p.h.p.)

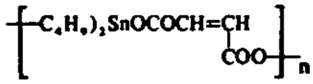
Chemical name	Structure	Trade name and supplier	Comments
Lead stabilizers			
Basic lead carbonate	$PbO \cdot PbCO_3$	White lead (Associated Lead Manufacturers Ltd.)	Low cost and efficient. Toxic
Tribasic lead sulphate	$3PbO \cdot PbSO_4 \cdot H_2O$	TBLS (As above)	Low cost and efficient. Used in cable formulations.
Dibasic lead phosphite	$2PbO \cdot PbHPO_3 \cdot ½H_2O$	DPLP (As above)	Good heat stabilizer, offers synergism in ageing stabilization and chelation towards metal impurities.
Mixed cadmium barium zinc stabilizers			
Coprecipitated cadmium/barium laurates	$Cd(OCOC_{11}H_{23})_2$ $Ba(OCOC_{11}H_{23})_2$	Mellite 101 (Allbright & Wilson (Mfg) Ltd.)	Susceptible to sulphide staining.
Barium/cadmium/zinc complexes	–	Nuostabes V1277 (Durham Raw Materials Ltd.)	
Organo-tin stabilizers			
Dibutyltin maleates	 $\left[(C_4H_9)_2SnOCOCH{=}CH\text{–}COO\right]_n$	Mellite 135 (Allbright & Wilson (Mfg) Ltd.)	Good high temperature stabilizer.
Dibutyltin, bis(lauryl) mercaptides	$(C_4H_9)_2Sn(SC_{12}H_{25})_2$	Mark A (Angus Chemicals)	Excellent for clear clear applications.

Table 4

Examples of commercial plasticizers for plastics materials

Plasticizer	Polymer	Plasticizer type
Di-octyl phthalate (DOP)	Polyvinyl chloride and copolymers	General purpose, primary plasticizer
Tricresyl phosphate (TCP)	Polyvinyl chloride and copolymers	Flame retardant, primary plasticizer
Tricresyl phosphate (TCP)	Cellulose nitrate	Flame retardant, primary plasticizer
Tricresyl phosphate (TCP)	Cellulose acetate	Flame retardant, primary plasticizer
Di-octyl adipate (DOA)	Polyvinyl chloride, cellulose acetate butyrate	Low temperature plasticizer
Di-octyl sebacate (DOS)	Polyvinyl chloride, cellulose acetate butyrate	Secondary plasticizer
Adipic acid polyesters (MW = 1500–3000)	Polyvinyl chloride	Non-migratory secondary plasticizer
Sebacic acid polyesters (MW = 1500–3000)	Polyvinyl chloride	Non-migratory secondary plasticizer
Chlorinated paraffins (%Cl = 40–70) (MW = 600–1000)	Most polymers	Flame retardant, plasticizer extenders
Bi- and terphenyls (also hydrogenated)	Aromatic polyesters	Various
N-ethyl o,p.toluene sulphonamide	Polyamides	General purpose primary plasticizer
Sulphonamide-formaldehyde resins	Polyamides	Non-migratory secondary plasticizers

Table 5

Fibres and particulate fillers for polymer reinforcement.

A.) Fibres

i) Continuous fibres	Density (Kg/m³)	Tensile Strength (MPa)	Tensile Modulus (GPa)
Glass E type	2.50	2400	72
Glass S "	2.44	2800	86
Carbon	1.38	1700	140
Graphite	1.38	1700	250
Boron	2.52	3400	400
Aramid	1.44	3660	127
UHMWPE	0.95	2600	119

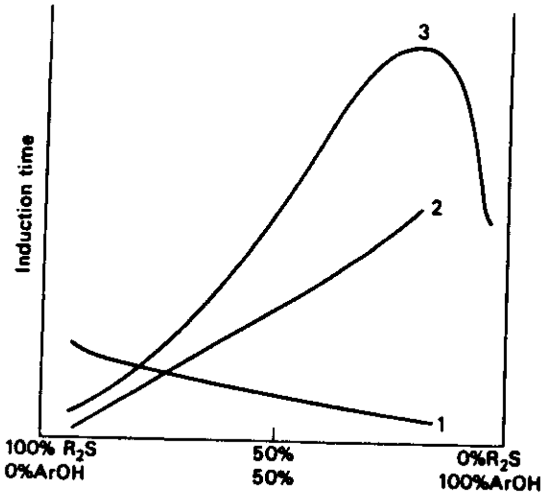
ii) Short fibres

Silicon Carbide	3.12	11000	840
Al_2O_3	3.88	19000	410
Silicon Nitride	3.2	5000	400
Asbestos (Chrysotile)	2.5	2800	150
Carbon (chopped)	1.4		
Glass (Milled & chopped)	2.5		

B) Particulate fillers

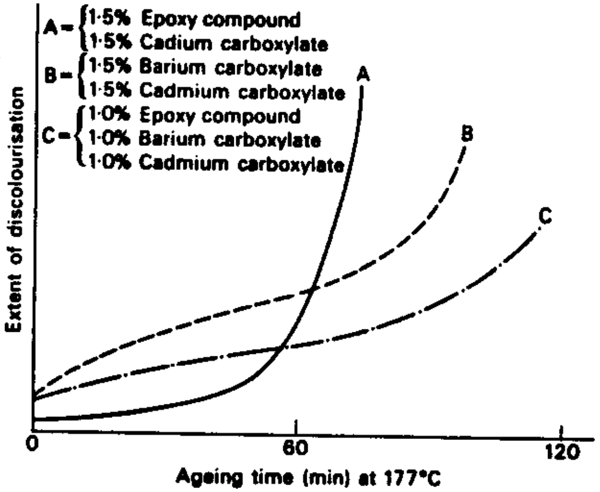
Mica flakes	–
Glass flakes and microspheres	–
Talc	–
China Clay	–
Calcium carbonate	–
Silica flour	–
Chalk	–
[illegible] Barytes	–

Fig 1

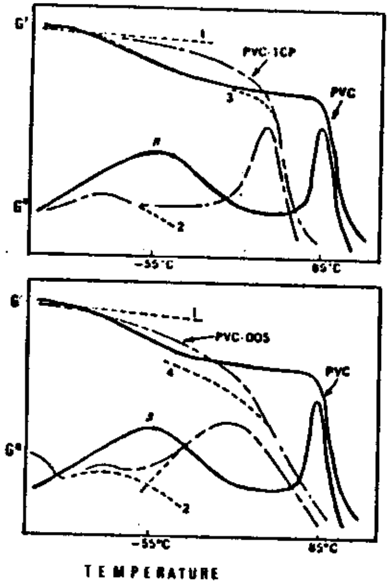


Synergistic effects between primary and secondary stabilizers. Dependence on the induction period in the oxidation of polypropylene on the molecular fraction of di-decyl sulphide and 2,6-di-tert-octyl cresol. Total stabilizer concentration = 0·2 mol/kg at 200°C and oxygen pressure of 300 mm Hg. (After Neiman, M. B., *Ageing and Stabilization of Polymers*, Consultants Bureau (N.Y.), 1965, p. 30.)

Fig 2

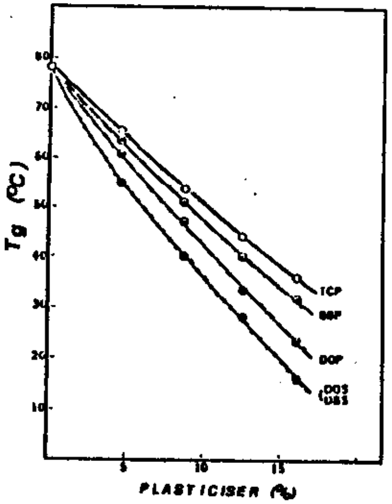


Synergistic effects in PVC stabilization. (After Chevassus, F. and de Broutelles, R., *The Stabilization of Polyvinyl Chloride*, Edward Arnold, 1963.)



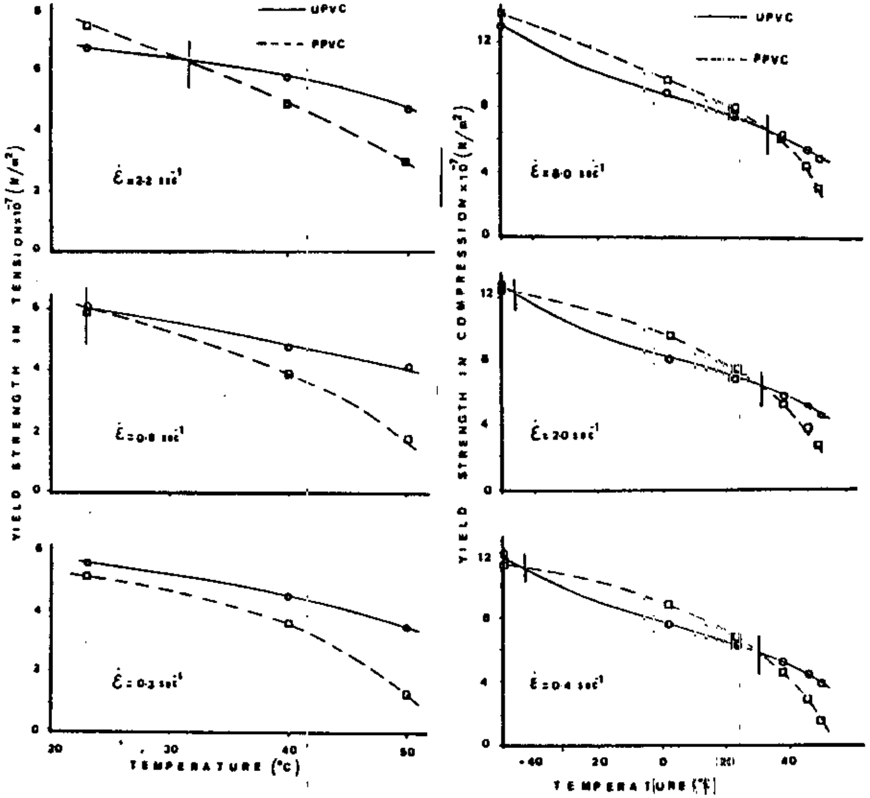
3

Figure Dynamic mechanical spectra of plasticised PVC



4

Figure Effects of types of plasticisation efficiency



Effects of strain rate on Yield Strength.

Fig. 5

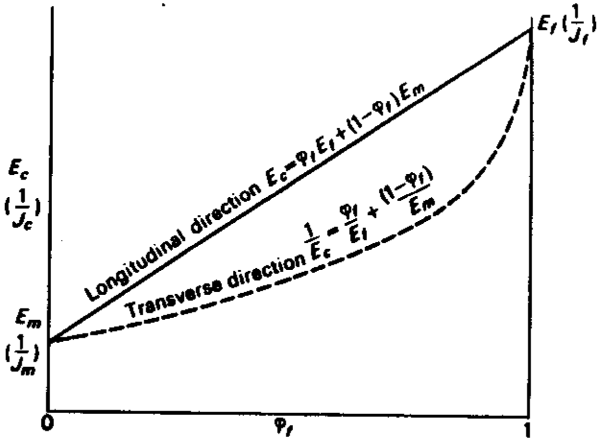


fig 6

Idealized behaviour of continuous unidirectional composites in the longitudinal and transverse direction.

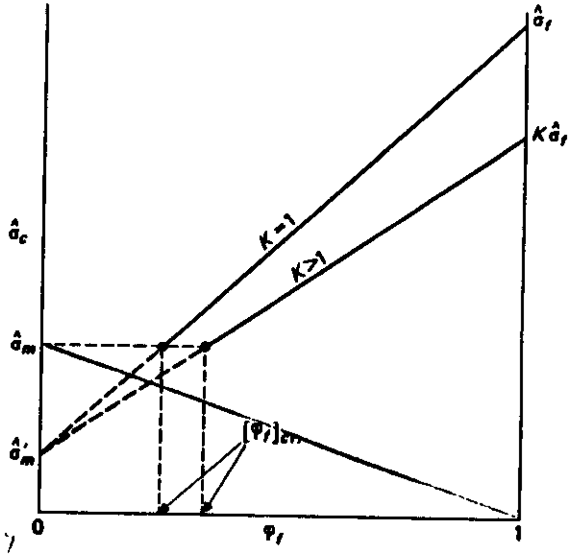
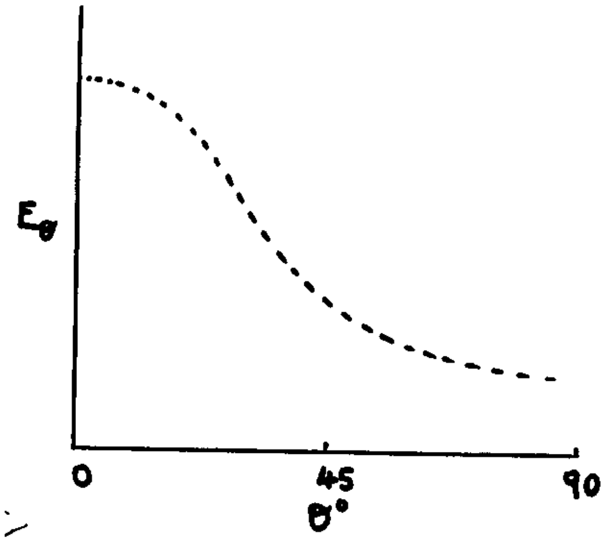


fig 7

Critical volumetric fractions in unidirectional composites.

Fig 3 [illegible] fibre orientation angle



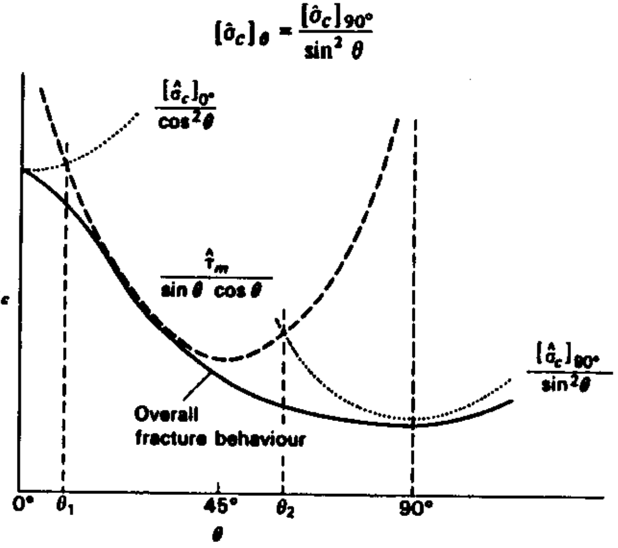


Fig 4

Strength variations of unidirectional composites as a function of the fibre orientation angle.

Table 5

Fibres and particulate fillers for polymer reinforcement.

A.) Fibres

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Glass (Milled & chopped)	2.5		

B) Particulate fillers

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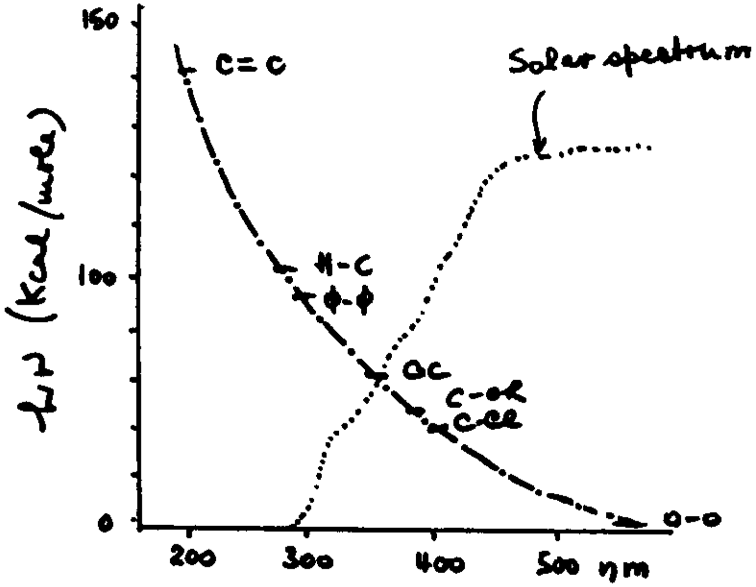
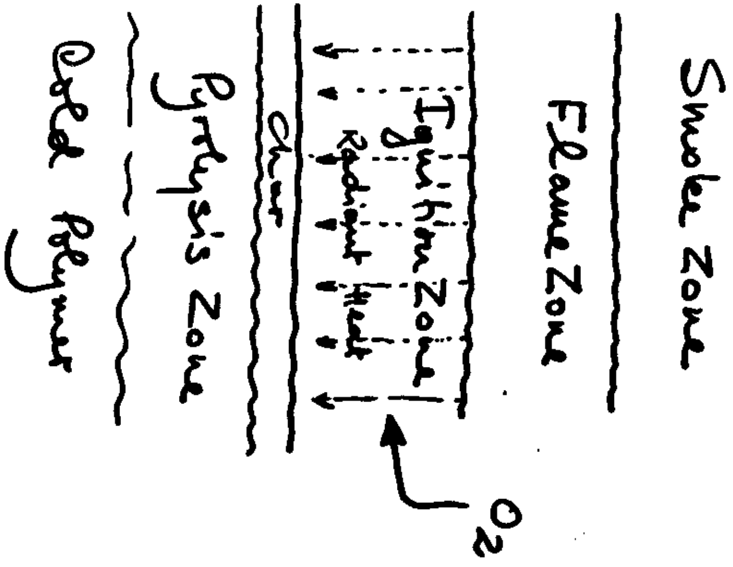
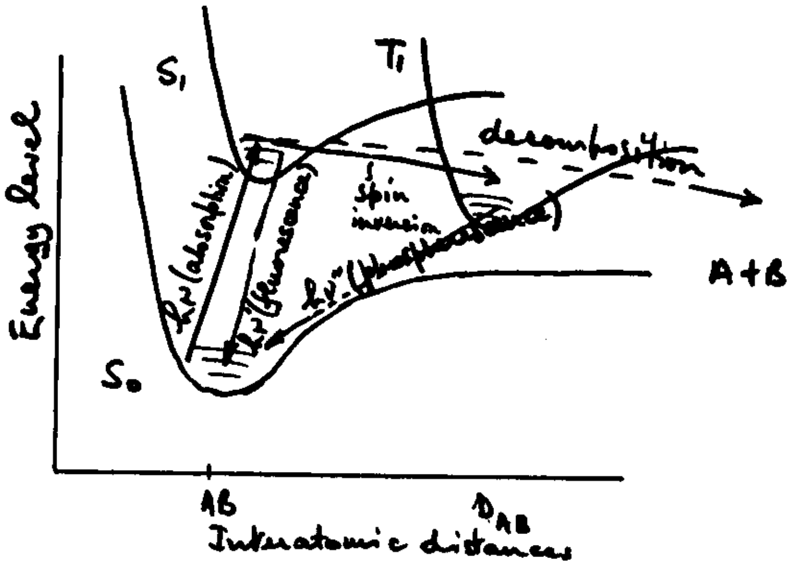
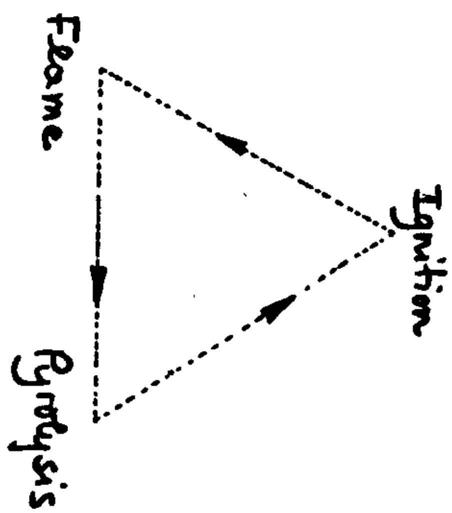
Glass flakes and microspheres	–
Talc	–
China Clay	–
Calcium carbonate	–
Silica flour	–
Chalk	–
Barytes	–

fig 13


hν (Kcal/mole)
150
100
0
C=C
H-C
ϕ-ϕ
OC
C-OR
C-Cl
O-O
Solar spectrum
200
300
400
500 ηm


Smoke Zone
Flame Zone
Ignition Zone
Radiant Heat
Char
Pyrolysis Zone
Cold Polymer
O_2


Energy level
S_1
T_1
S_0
decomposition
spin inversion
hν (absorption)
hν' (fluorescence)
hν'' (phosphorescence)
A+B
AB
D_{AB}
Interatomic distances


Flame
Ignition
Pyrolysis