Technical Brief

UV Protection of Coated Line Pipe

Background

Fusion bonded epoxy (FBE) is a one part powdered epoxy coating that is sprayed onto the hot metal substrate where it melts, flows and cures to give a corrosion resistant coating. The first line pipe coated with FBE was placed into service in 1960¹. Since that time, FBE coatings have become the most commonly used coating for new pipeline construction in North America. FBE coatings are formulated to meet both the requirements of the applicator who will apply the coating and the performance requirements of the end user (pipeline owner).

The primary raw materials used to formulate FBE coatings include epoxy resins, curing agents (hardeners), catalysts, pigments and fillers. Other additives may be used to control the flow characteristics, improve adhesion performance and provide other useful benefits. While there are several types of epoxy resins commercially available, those based on diglycidyl ether of bisphenol A (DGEBA) or novolac chemistry are the two epoxy resin types most frequently used in FBE coatings. While these epoxy resins can be used to make polymers with a wide range of properties and are very versatile in many ways, they are aromatic and thus have poor ultraviolet (UV) light resistance limiting their use in exterior applications.

UV Exposure – Chalking

Due to the presence of the aromatic group, epoxy resins generally absorb at about 300 nm and will degrade in the presence of UV light and humidity via photoinitiated freeradical degradation. This polymer degradation is known as chalking and results in the formation of a loose powdery residue on the pigmented coating surface. The residue on the polymer surface protects against further degradation unless it is removed. Removal of this protective barrier (either by natural or mechanical means) exposes a fresh surface which is then subject to further UV exposure and degradation.

Numerous studies have been conducted to investigate the UV degradation of epoxy resins²⁻⁵. One study investigated several possible weak links in amine cured epoxy systems and reported that the presence of the aromatic bisphenol moiety is primarily responsible for the absorption of UV light⁶. Modification of the polymer backbone by changing the chemistry (use of alternate diglycidyl ethers such as diglycidyl ether of bisphenol F and/or varying the curing agent) can have some impact on the degree chalking but does not eliminate the phenomena. In other words, all FBE pipeline coatings based on aromatic epoxy resins will chalk but there may be some difference in the degree of chalking due to slight differences in the chemistry of the various formulations.

Efforts have been made to improve the UV stability of epoxy products; however, to date commercial success of epoxy resins with improved weatherability has been limited ⁷⁻⁹. These resins are much higher in price and end users have other ways to limit UV exposure as will be discussed later in this paper.



In addition to the susceptibility of specific FBE formulations to UV attack, the degree of chalking also depends on direct exposure to UV, the intensity and duration of the UV radiation, and the availability of water on the coating surface¹. A pipe stored above ground experiences the most chalking on the top (12 o'clock position), less on the sides (3 and 9 o'clock positions) and little or none on the bottom (6 o'clock position). Since the degree of chalking is dependant on the intensity and duration of the UV radiation and the presence of moisture, it is not surprising that variations in the degree of chalking observed in the field appear to be geographic-location specific.

Effects of Chalking on Coating Performance

The chalking process is polymer degradation and thus thickness loss is an obvious concern. Thickness loss is caused by alternate chalking and removal of this loose surface material by wind, rain, tidal splash or blowing particulate. The rate of thickness loss depends on the rate of removal of the protective laver as well as the factors that determine the degree of chalking reviewed in the previous section. Field experience suggests that there is considerable variance in the rate of thickness loss which tends to relate to location/geography. The chalking process takes some time to get started. One study reported a thickness reduction in the 12 o'clock position of about 20 µm (3/4 mil) after approximately a year of storage in northern US and southern Canada¹⁰. Historical observation suggests that measurable thickness loss typically begins within 9 to 18 months¹. Once started, the typical rate of loss is in the range of 10 to 40 µm (0.375 to 1.5 mil) per year.

As long as thickness has not been substantially reduced, weathering appears to have only minimal effects on the performance of FBE coatings. One published study of pipe coated in the US and installed in the Middle East showed no significant reduction in either flexibility or short-term cathodic disbondment tests (65°C, 3% NaCl, and 48 hour duration) after 3 years in a stockpile¹¹. The Cetiner study, which evaluated pipe that had been stored for approximately one year, showed no measurable reduction in performance in either the 48-hour cathodic disbondment test or hot water adhesion tests. There was however a measurable reduction in flexibility as measured by the CSA FBE flexibility test method at -30°C¹². Based on this work, Cetiner and coworkers recommended that pipe stored for longer than one year should be protected from UV radiation.

Again, it is important to keep in mind that the rate of chalking/thickness loss can vary considerably and is dependant on the susceptibility of the specific FBE formulation to UV attack, the intensity and duration of the UV exposure, the availability of moisture, as well as the rate at which the protective chalk layer is removed.

Common Industry Solutions

Many different methods have been used throughout the industry to protect coated pipe from UV radiation. As a preventative measure, many applicators apply additional coating thickness at the time the FBE coating is applied in order to compensate for any thickness loss that may occur during the time between when the pipe is coated and when the pipe is actually installed. The typical procedure in most cases is to provide a barrier between the sun and the coated pipe. The barrier could include any of the following:

- 1. Covering pipe stock piles with tarps.
- Applying white wash to the UV exposed upper layer of the stock pile.
- 3. Applying an overcoat of an aliphatic polyurethane to the entire coated surface
- Applying an overcoat of polyester powder coating. (Separate spray booths are required due to the incompatibility of epoxy and polyester systems)

Selection of the barrier is dependant on the length of time the UV exposure is expected. In the short term, a water permeable paint such as latex is sufficient. For longer term storage or permanent above ground usage, selection of the barrier coating and surface preparation are crucial. Prior to use, any UV-barrier coating should be evaluated for their ability to adhere to the FBE coating. Any residual chalking must be removed before application of a UV-barrier coating. The long-term adhesion performance of the UV-barrier coating can be improved by roughening the FBE coating surface with sandpaper or a light abrasive blast. For storage over two years; a weldable primer should be applied to the cutback area. This helps prevent corrosion in the cutback area and undercreep of the FBE coating.

References

¹Alan J. Kehr, "Fusion Bonded Epoxy (FBE): A Foundation for Pipeline Corrosion Protection", NACE International Publication, 2003.

² P. G. Kelleher, B. D. Gesner, J. Appl. Polym. Sci., 13 (1969) 9–15.

- ³B. D. Gesner, P. G. Kelleher, J. Appl. Polym. Sci., 13 (1969) 2183–2191.
- ⁴A. Rivaton, L. Moreau, J.-L. Gardette, Polym. Degrad. Stab. 58 (1997) 321–332.
- ⁵A. Rivaton, L. Moreau, J.-L. Gardette, Polym. Degrad. Stab. 58 (1997) 333–339.
- ⁶V. C. Malshe, G. Waghoo, Prog. Org. Coat. 51 (2004) 267–272.
- ⁷H. Q. Pham, M. J. Marks, "Epoxy Resins" Ullmann's Encyclopedia of Industrial Chemistry
- ⁸V. C. Malshe, G. Waghoo, Prog. Org. Coat. 51 (2004) 172–180.
- ⁹V. C. Malshe, G. Waghoo, Prog. Org. Coat. 56 (2006) 131–134.
- ¹⁰ M. Cetiner, P. Singh, J. Abes, Oil Gas J. 99 (2001) 58–60.
- ¹¹ Surfcote Bulletin, "Case History of Fusion Bonded Coated Pipe Shipped to Middle East" Houston, TX Winter 1979/80.
- ¹² CSA Z245.20-98, "External Fusion Bonded Epoxy Coating for Steel Pipe," (Etobicoke, Ontario, Canada: Canadian Standards Association, April 1998).

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------ Forwarded message ------From: **Flammia, Dwight** <dwight.flammia@vdh.virginia.gov> Date: Tue, Apr 30, 2019 at 7:52 AM Subject: Fwd: Re: Installation of UV Degraded FBE Pipe To: Parham Jaberi <parham.jaberi@vdh.virginia.gov>

here is a 2 of 2 email correspondences with 3M This email was forwarded to many other at VDH. I believe this to be the extent of my email communication with 3M. I spoke to Andrew Morabu from 3M and nothing more was provided. We spoke during the same period the emails were sent.

Dwight Flammia, Ph.D. State Public Health Toxicologist Virginia Department of Health 101 North 14th Street Room 1540 Richmond, VA 23219

Phone 804 864-8127 Fax 804 864-8131

------ Forwarded message ------From: **Andrew Morabu** <amorabu@mmm.com> Date: Mon, Oct 29, 2018 at 10:17 AM Subject: RE: Re: Installation of UV Degraded FBE Pipe To: Flammia, Dwight <dwight.flammia@vdh.virginia.gov>

Hi Dwight,

We have not done any testing looking at the degradants in the environment and we do not know the exact compounds formed by UV degradation or microbe activity. This was based on professional judgement based on knowledge of the chemistry. Perhaps the attached references may be helpful.

Thanks,

Andrew.



Andrew K. Morabu | Sr Product Responsibility Liaison
3M Electrical Markets Division | Regulatory Affairs and Product Stewardship
3M Austin Center, 6801 River Place Blvd., Bldg. 145-4N-15 | Austin, TX 78726-9000
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From: Flammia, Dwight [mailto:dwight.flammia@vdh.virginia.gov]
Sent: Friday, October 26, 2018 3:03 PM
To: Andrew Morabu <amorabu@mmm.com>
Subject: [EXTERNAL] Re: Installation of UV Degraded FBE Pipe

I am looking at a letter dated September 19, 2018 titled <u>Material Declaration on 3M EMD Products sold</u> <u>in the USA</u>. Any additional insight into specific compounds that the chalking produces. The paper lists carboxylic acids, amines, and aromatics.

I am trying to perform a risk assessment and knowing the exact compounds formed by UV degradation and even microbe activity would be helpful.

If there are any risk assessments that look at the epoxy coating or its degradates in the environment I would appreciate looking at them.

Dwight Flammia, Ph.D.

State Public Health Toxicologist

Virginia Department of Health

101 North 14th Street Room 1540

Richmond, VA 23219

3M Electrical Markets Division

3M Austin Center 6801 River Place Blvd. Austin, TX 78726-9000



September 19, 2018

Material Declaration on 3M EMD Products sold in the USA¹

Dear Valued 3M Customer,

This letter is in response to your request regarding soil leaching and UV degradation of 3M[™] Scotchkote[™] Fusion Bonded Epoxy Coatings and 3M[™] Scotchkote[™] Liquid Epoxy Coatings. These products are for industrial use only and not for consumer use. The customer will need to verify the product suitability for the desired application.

These products are composed predominantly of polymeric materials and inorganic compounds. If the products are applied as per 3M application guidelines AND fully cured upon application, they are expected to resist degradation and have negligible water solubility under normal environmental conditions. Unreacted components are expected to remain physically entrained within the coating which may limit leaching of product components from the cured coating. As leaching studies have not been performed on these products, soil leachability from these products is unknown.

At the core, surface photolysis is the breaking up of a polymer by light of the proper frequency to make radicals. The radicals interact with atmospheric oxygen and/or limited water to form ever smaller fragments of the polymer and ultimately, small molecules. One key there is "at the surface". The reactions are only at the surface, maybe 1-3 mm deep. If the small fragments are removed, photo-degradation keeps going and the pitting gets deeper, which is why the 3M technical guidance recommends not to remove the chalking.

In the case of chalking, the resulting molecules will be aldehydes (which react with water to make carboxylic acids), amides (which further degrade into amines and carboxylic acids), various aromatics similar in structure to either xylene, substituted phenols, bisphenol A, aniline, methylated anilines and water. Overall, the process is similar to but faster and with fewer degradation products than what is anticipated to happen when compared to biodegradation. (Biodegradation would make the same materials plus a number of others.)

None of the photo-degradation products are anticipated to bio-concentrate although a few will be toxic to aquatic species. The vast majority of the photo-degradation products will be persistent to readily degradable although there will be some larger fragments which could be very persistent. If the top of the pipe is covered with chalking and is buried shallow, the microbes will take care of the photo-degradation products. If the pipe is buried deep, the anaerobes will take care of the hydrocarbon portions although some low molecular weight acids and di-acids will be free to travel throughout the matrix in which the pipe is buried. The low molecular weight acids and diacids are not toxic and would be readily degradable if they weren't buried so deep.

Overall, the environmental impact is minimal.

Please contact your 3M representative for additional information. Declaration electronically signed:

Andrew Morabu

Product Responsibility Liaison 3M Electrical Markets Division

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On Tue, Oct 9, 2018 at 3:10 PM Andrew Morabu amorabu@mmm.com> wrote:

Hi Dwight,

Please take a look at the attached paper. Please let me know if you have further questions and I can put you in touch with our technical experts.

Thanks,

Andrew.

id:image005.png@01D45FD9.DBCAF400

Andrew K. Morabu | Senior Product Responsibility Liaison
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Photo-oxidation of epoxy resins cured by non-aromatic amines 1981_polyme....pdf 435K

polymer photodegradation - mechanisms and experimental methods Chapter 4....pdf 5118K

Knapp, Allen <allen.knapp@vdh.virginia.gov> To: Maryanne Wollman <maryanne.wollman@vdh.virginia.gov> Tue, Apr 30, 2019 at 4:56 PM

I was not the author but this may be responsive to Mr. Limpert's request.

Allen.

-----Forwarded message ------From: Flammia, Dwight <dwight.flammia@vdh.virginia.gov> Date: Tue, Oct 9, 2018 at 3:30 PM Subject: Fwd: Installation of UV Degraded FBE Pipe To: Allen Knapp <allen.knapp@vdh.virginia.gov>, Roadcap, Dwayne <dwayne.roadcap@vdh.virginia. gov>

Dwight Flammia, Ph.D. State Public Health Toxicologist Virginia Department of Health 101 North 14th Street Room 1540 Richmond, VA 23219

Phone 804 864-8127 Fax 804 864-8131

------ Forwarded message ------From: **Andrew Morabu** <amorabu@mmm.com> Date: Tue, Oct 9, 2018 at 3:10 PM Subject: Installation of UV Degraded FBE Pipe To: dwight.flammia@vdh.virginia.gov <dwight.flammia@vdh.virginia.gov>

Hi Dwight,

Please take a look at the attached paper. Please let me know if you have further questions and I can put you in touch with our technical experts.

Thanks,

Andrew.



[Quoted text hidden]

--Allen Knapp, Director Office of Environmental Health Services Virginia Department of Health (804) 864-7456 (804) 337-2562 (c)

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PHOTO-OXIDATION OF EPOXY RESINS CURED BY NON-AROMATIC AMINES

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Departement Materiaux, ENSAM, 151 Bd de l'Hôpital, 75640, Paris 13, France

ABSTRACT

The photo-oxidation of epoxy resins based on bisphenol A and cured by non-aromatic amines: diethylene triamine, aminoethyl piperazine and isophorone diamine results in carbonyl and amide formation, decrease of glass transition temperature, and the appearance of a new endotherm at $70-80^{\circ}$ C in the DSC traces. The carbonyl and, essentially the amide yield depend strongly on the hardener structure and concentration. The mechanisms of formation of these groups are discussed.

INTRODUCTION

Although epoxy based composites are often used in conditions involving direct exposure to sunlight, the photochemical ageing of these materials has received little attention in comparison to thermal or hydrolytic ageing.¹

Conventional methods are used to characterise the change in optical (yellowing), electrical² or mechanical^{2,3} properties during natural or artificial ageing. The changes in the macromolecular skeleton due to photo-oxidation, can lead to surface stresses, possibly responsible for microcrazing as observed by electron microscopy.⁴ The simultaneous use of methods such as FTIR spectroscopy, ESCA thermogravimetry, laser pyrolysis and dynamic mechanical measurements for the study of natural and artificial ageing of an epoxy novolacbased composite leads to the following observations:^{5,6} (1) The thermal stability decreases during UV exposure. Here the presence of water has a strong accelerating effect. (2) The ageing results in a decrease in the glass transition

Polymer Photochemistry 0144-2880/81/0001-0069/\$2.50 © Applied Science Publishers Ltd, England, 1981 Printed in Northern Ireland temperature and erosion of superficial layers. (3) Thermal oxidation during the cure treatments has a significant photosensitising effect, the photostability is improved by the use of antioxidants. (4) Resins based on bisphenol A are more stable than epoxy novolacs. In the case of diglycidyl ether of bisphenol A (DGEBA) systems, some mechanistic data on photodegradation and photo-oxidation can be derived from the results obtained with phenoxy resins, which contain the bisphenol and glyceryl structures.⁷ The aim of our work is to study the photo-oxidation kinetics and mechanisms of epoxy resins and, if possible, to establish the structure-properties relationship in this area. The present paper is devoted to the study of non-aromatic amine hardeners including diethylene triamine, aminoethyl piperazine and isophorone diamine in DGEBA systems.

EXPERIMENTAL

The polymers were prepared from a diglycidyl ether of bisphenol A (DGEBA) which had an epoxy index of $5 \cdot 30$ M/kg. The samples were denoted by a code consisting of the abbreviation used for the hardener: DETA for diethylene triamine, AEP for aminoethyl piperazine and IPD for isophorone diamine. All products were Ciba Geigy industrial grades. Two sets of samples were studied. In the first, the amine concentration was close to the stoichiometric value; in the second, we studied the influence of hardener concentration for the DGEBA-DETA system. The code indicates the DETA concentration in per cent of the stoichiometric value.

Films, 24 μ m thick, were cast on a clean mercury surface from a solution of the two components in benzene (Prolabo analytical grade). After 2 h at 120°C, the solvent was evaporated off (controlled at 675 cm⁻¹ in the IR spectrum) and a hard transparent film was obtained.

For IR quantitative measurements (Perkin-Elmer 580), we used the peak at 1885 cm^{-1} as the internal standard.

Absorbance at 1885 cm⁻¹ per thickness unit = 26 ± 6 cm⁻¹. We verified that the extinction coefficient of this band is independent of hardener structure and ageing time. The extinction coefficient of hydroxyl groups has been calculated from the data obtained with the DETA 50 sample, assuming a 100% conversion of the amine-epoxide reaction and taking into account the contribution of DGEBA (calculated value: [OH]=0.34M/kg). The result, $\varepsilon_{OH}=$ 44 kg M⁻¹ cm⁻¹, agrees reasonably well with the literature data and allows an estimation of the conversion factor for the other samples. The initial characteristics of the films are summarised in Table 1. DSC measurements (for three samples) were taken before and after exposure.

For photo-oxidation studies, we used a reactor equipped with a fluorescent

TABLE 1 INITIAL DATA										
Sample	Hardener (M/kg)	NH hardener (м/kg)	Thermal treatment (h) at 120°C	А _{он}	A _{co}	A _{con} <	Tg (K)			
DGEBA	0	0	0		0	0				
IPD	1.36	5.42	2	12.9	0.17	0	405			
IPD (T)	1.36	5.42	5	14.5	0·36	0				
AEP	1.29	5.16	2	7.7	0.53	0	383			
AEP (T)	1.29	5.16	5	9.0	0.20	0.7				
DETA	1.06	5.30	2	9.4	0.18	0	373			
DETA (T)	1.06	5.30	5	10.4	0.27	0·9				
DETA 50	0.53	2.65	8	5.1	0.25	0				
DETA 75	0.80	3.98	2	7.3	0.23	0				
DETA 100	1.06	5.30	2	9.4	0.18	0				
DETA 125	1.33	6.63	2	9.9	0.31	0				
<u></u>	A		1. :							

Note: $A_i = \frac{\text{Absorbance of peak } i}{\text{Absorbance of 1885 cm}^{-1} \text{ peak}}$

lamp: Osram L 20 W 70 emitting between 300 and 450 nm. The overall light intensity at the sample level is 24×10^{14} photons cm⁻² s⁻¹ (ferrioxalate actinometry). In the first experiment, the samples were exposed for 189 h at 27°C, we calculated the mean rates: r_{CO} and r_{CON} , and determined graphically the initial rates of carbonyl r_{iCO} and amide r_{iCON} formation from the kinetic curves of the 1725 and 1660 cm⁻¹ peak growth. In the second experiment, the samples were exposed for 70 h at 60°C and we only determined initial rates. Despite the relative inaccuracy of these last values, the activation energies were estimated.

RESULTS

1. Photo-oxidation of DGEBA at 27°C (capillary film on CaF_2 plate)

We observed an essentially carbonyl formation (maximum absorbance at 1735 cm⁻¹). A small peak appears also at 1670 cm⁻¹, which could be attributed to conjugated oxidation products of the bisphenol moiety. The hydroxyl absorbance increases only after a long induction period (500 h).

2. Influence of the hardener structure (27°C exposure)

We observed changes in the IR spectrum in three distinct regions: the hydroxyl region (3400 cm^{-1}) , the carbonyl region $(1725-1735 \text{ cm}^{-1})$ and the amide



Fig. 1. A (carbonyl) versus exposure time at 27°C: ○, IPD; ●, IPD (T); ■, DETA; □, DETA (T); ▲, AEP; △, AEP (T)



Fig. 2. A (amide) versus exposure time at 27°C, same symbols as in Fig. 1.

region $(1650-1660 \text{ cm}^{-1})$. The kinetic curves of carbonyl and amide growth are given in Figs 1 and 2, respectively.

The mean rates of normalised absorbance variation are given in Table 2. The behaviour of the three systems can be summarised as follows: (1) IPD has the higher carbonyl yield and the lower amide yield (2) AEP shows exactly the opposite behaviour, and DETA is intermediary.

TABLE 2
MEAN RATES OF CARBONYL AND AMIDE GROWTH. INFLUENCE OF HARDENER STRUCTURE AND THERMAL
TREATMENT

Samples	[OH] ₀ (M/kg)	[а CH ₂] ₀ (м/kg)	$r_{\rm CO}^{a}$ (×10 ⁻³ h ⁻¹)	$r_{\rm CON} \lesssim^{a}$ (×10 ⁻³ h ⁻¹)	ρ _{CON} < ^b	T _g ^c (K)
IPD IPD (T)	7.56	6·80 6·80	3·7 5·3	3·2 4·2	0·47 0·62	388
DETA DETA (T)	5·51	9∙54 9∙54	2·1 3·7	7·4 8·5	0·77 0·89	363
AEP AEP (T)	4·51	15·48 15·48	1.0 1.6	16∙4 16∙4	1∙06 1∙06	371

Note:

^a $r_i = \frac{1}{A_{1885 \text{ cm}^{-1}}} \frac{\Delta A_j}{\Delta t} 10^3 \text{ h}^{-1}$, where A_j = absorbance of peak *j*. ^b $\rho_{\text{CON}} \leq \frac{r_{\text{CON}} \leq}{[\alpha \text{ CH}_2]_0}$ ^c After 189 h exposure.

The amide groups were derived from an oxidative attack of the methylene groups:



Assuming a 100% conversion of the amine-epoxide reaction, we have calculated the initial α methylene concentration and the amide yield during photooxidation: ρ_{CON} = rate of amide growth per initial α methylenic unit. The higher yield is found in AEP samples, the lower in IPD samples, DETA being intermediary (Table 2).

DSC data shows that there is a slight decrease in T_g but, essentially, it shows the appearance of a new endothermic peak near the 70°C point (Fig. 3 and Table 2).

3. Influence of thermal treatment

Thermal treatment at 120°C in air results in a thermo-oxidation: carbonyl groups appear in IPD and DETA samples, whereas amide groups appear in



Fig. 3. DSC curves for DETA 100 before (above) and after (below) UV exposure. ∇ , glass transition and Ψ , new endotherm.



Fig. 4. A (carbonyl) versus exposure time at 27°C for the DETA systems. ●, DETA 50; □, DETA 75; ○, DETA 100; ▲, DETA 125.



Fig. 5. A (amide) versus exposure time at 27°C for the DETA systems, same symbols as in Fig. 3.

DETA and AEP samples (Table 1). This thermal oxidation has a slight but noticeable sensitising effect on subsequent photochemical ageing (Table 2)

4. Influence of hardener concentration (DETA)

At 27°C, the mean rate of carbonyl growth is higher for DETA 50 than for DGEBA but it decreases when the hardener concentration is increased. On the contrary, the amide growth increases regularly with the DETA concentration whereas the yield ρ_{CON} remains in the 0.6-0.8 range (Figs 4 and 5). The

INFLUENCE OF HARDENER CONCENTRATION (DETA)												
Sample	[OH] _о (м/kg)	τ°	[αCH ₂] ₀ (м/kg)	r _{i€0} (27°C)	r _{ico} (60°C)	E _{act} (kJ/M)	ricon (27°C)	r _{icon} (60°C)	E _{act} (kJ/M)	r _{co} (27°C)	r _{con} (27°C)	ρ _{con} (27°C)
DGEBA	0·34 ^b	0	0		_		-			2.2	0.ec	
DETA 50	2.99	0.50	4.77	_		—				4·2	4.1	0.76
DETA 75	4·28	0.74	7.16	3.03	17.9	45	4.72	30	47	2.6	4.5	0.63
DETA 100	5.51	0.98	9.54	2.11	13.6	47	4.94	22.9	39	2.2	7.4	0.77
DETA 125	5.80	excess	11.93	0·2ª	10.0	98	7.86	28.6	33	2.4	7.8	0.65
Sample DGEBA DETA 50 DETA 75 DETA 100 DETA 125	[OH] ₀ (m/kg) 0·34 ^b 2·99 4·28 5·51 5·80	τ ^a 0 0.50 0.74 0.98 excess	[αCH ₂] ₀ (M/kg) 0 4·77 7·16 9·54 11·93	r_{iCO} (27°C) 3.03 2.11 0.2^{d}	^r ico (60°C) — 17·9 13·6 10·0	E _{act} (kJ/M) 45 47 98	ricon (27°C) - 4·72 4·94 7·86	ricon (60°C) 30 22.9 28.6	E _{act} (kJ/M) 47 39 33	r _{CO} (27°C) 2·2 4·2 2·6 2·2 2·4	rcon (27°C) 0.6° 4.1 4.5 7.4 7.8	ρ _{cx} (27

TABLE 3

Note:

^{*a*} $\tau = ([OH] \text{ measured} - [OH]_{DEGEBA})/5.30$

^b Calculated from epoxide index.

^c Weak band appearing at $1670 \,\mathrm{cm^{-1}}$ which can contribute to the amide absorption in crosslinked samples.

^d Strong data scattering.

initial rates r_{iCO} and r_{iCON} have been measured at 27°C and 60°C. The estimated activation energies seem to increase for CO groups and decrease for

CON groups with the DETA content (Table 3).

5. Influence of temperature on initial rates for the three hardeners

The results are summarised in Table 4. A strong difference appears in the estimated activation energies between IPD and the two other samples for carbonyl growth, and between AEP and the two other samples for amide growth.

TABLE 4 INITIAL RATES OF CARBONYL AND AMIDE GROWTH AT 27 AND 60° C									
Sample	r _{ico}	r _{ic∞}	Е _{асt}	r _{icon} ≲	r _{icon} <	E _{act}			
	(27°C)	(60°C)	(kJ/м)	(27℃)	(60°C)	(kJ/M)			
IPD	5·35	10	16	2.82	5·71	18			
DETA	2·11	13·6	47	9.52	22·90	22			
AEP	1·20	8·6	49	23.80	28·6	5			

DISCUSSION

1. Influence of hardener structure (Scheme 1)



Scheme 1. Structural units of (a) DGEBA (epoxy resin) and (b) the hardeners DETA, AEP and IPD. Note: the arrows indicate the carbon atoms able to give a carbonyl or a carboxyl group after photo-oxidation.

On carbonyl growth: The results suggest that a majority of the carbonyl groups derive from secondary hydroxyl groups. As a matter of fact, r_{CO} increases with the initial OH concentration (Table 2). The difference in carbonyl yield between pure DGEBA and the sample crosslinked with 50% of DETA (Table 3) could also be explained by the presence of hydroxyl groups due to the amine-epoxide reaction in the latter.

Many ways exist for carbonyl formation from secondary hydroxyl groups (Scheme 2). The hydroperoxidation of secondary alcohols has been shown in low molecular compounds such as isopropanol. The hydroperoxide can easily be hydrolysed to give the corresponding ketone, and hydrogen peroxide.⁸

Whereas DETA and AEP do not possess any groups able to be transformed into carbonyl groups (all lead to amide or other structures), each IPD molecule



Scheme 2. Formation of carbonyl groups from secondary hydroxyl groups.



Fig. 6. $\sqrt{r_{CON}}$ versus initial concentration in α methylenes. **I**, DETA; O, IPD; Δ , AEP.

supplies three methylenes and one tertiary —CH unit, which could give a carbonyl. It should be noted that methylenes give, as an intermediary state, a secondary peroxyl radical which could be involved in a cross termination reaction (Scheme 2).

On amide growth: The rate of amide growth is, without any doubt, linked to the initial concentration of available α methylenes since the following order is found for r_{CON} : AEP (12 α CH₂ per structural unit) > DETA (9 α CH₂)>IPD (5 α CH₂). The amide yields per initial α CH₂ seems to indicate a noticeable difference in the reactivities of hardeners, but since the initial concentrations in α CH₂ are different, the comparison of these values is not necessarily valid. In fact, we observed a linear correlation between the square root of r_{CON} and [α CH₂], (Fig. 6). This result is consistent with a second order process relative to [α CH₂], with a rate constant independent of hardener structure.

2. Influence of thermal pretreatments

We used hardeners having relatively high reactivities so that the curing is practically finished after 2 h at 120°C. Therefore, we essentially studied the effects of thermal oxidation and found results which agree with the literature data:⁵ The thermal oxidation has a photosensitising effect. However, a previous

study on similar systems hardened at lower temperatures showed that the curing has a noticeable stabilising effect.⁹ A thermal pretreatment can, therefore, have contradictory influences on photostability; positive before the complete reaction between hardener and resin, and negative when oxidation predominates over crosslinking.

3. Influence of hardener concentration (DETA)

As previously hypothesised, for low hardener concentrations, the increase of $r_{\rm CO}$ with [DETA] could correspond to the increase in secondary hydroxyl group concentration. For high hardener concentrations, the lowering of molecular mobility (which inhibits intermolecular propagation) and the steric hindrances, are responsible for the rate decrease, as previously observed for incompletely cured samples.⁹ We can expect a maximum of $r_{\rm CO}$ for a sample having its glass transition near the temperature of UV exposure.

The kinetics of amide formation have the following characteristics:

- (1) The rate r_{CON} increases with the concentration of available [α CH₂]. The reaction is slightly inhibited by the lowering of molecular mobility (Fig. 6), but to a lesser extent than the carbonyl formation.
- (2) The apparent activation energy decreases with the DETA content.
- (3) The kinetics are second order relative to $[\alpha CH_2]$.

These data are consistent with a mechanism involving an intramolecular propagation step (Scheme 3) and perhaps a catalytic effect of the tertiary amine structures.¹⁰ They could also explain the low value of the activation energy for the amide growth in AEP samples, and its decrease with the hardener concentration in the DETA system.



Scheme 3. Oxidation of α methylene groups: intramolecular propagation.

4. DSC data

The decrease in T_{g} shows the predominance of skeleton breaking reactions over crosslinking. The peak at $\approx 70^{\circ}$ C is probably due to decomposition, or rearrangement, of a structure, resulting from the photo-oxidation. The study of this phenomenon is in progress in the laboratory.

REFERENCES

- 1. MORGAN, R. J. and O'NEAL, J., Polym. Plast. Technol. Eng., 10 (1) (1978) 49.
- 2. MENGES, G. and HESSELT, F., Kunststoffe, 58 (7) (1968) 5 and 509.
- 3. WURLINGER, A., Kunststoffe, 57 (1) (1967) 56.
- 4. BLAGA, A. and YAMASAKI, R. S., J. Mater. Sci., 11 (1976) 1513.
- 5. GEORGE, G. A., SACHER, R. E. and SPROUSE, J. F., J. Appl. Polym. Sci., 8 (1977) 2241.
- 6. GEORGE, G. A., SACHER, R. E. and SPROUSE, J. F., Int. conf. on weathering and degradation of polymers, Plastics and Rubber Institute, London, 1976, Preprint D4.
- 7. RANBY, B. and RABEK, J. F., Photodegradation, photo-oxidation and photostabilization of polymers, J. Wiley & Sons, New York, 1975, pp. 217-33.
- SCHENK, G. O., Ber., 96 (1963) 509.
 ZAGHLOUL, F. and VERDU, J., Unpublished results.
- 10. SVERN, D., Organic peroxides Vol. 2, J. Wiley & Sons, New York, 1975, pp. 74-7.

Photodegradation and photo-oxidative degradation of heterochain polymers

4.1 POLYETHERS

4.1.1 Polyoxymethylene

The polyoxymethylene (4.1) contains only C—C and C—O bonds and is therefore not expected to absorb light of wavelength longer than 190–220 nm. However, this polymer is not resistant to light and photo-oxidative degradation [826, 1026, 1597].

The photodegradation occurs with scission of main chain bonds:

$$-CH_2 - O - CH_2 - O - \xrightarrow{h\nu} - CH_2 - O' + CH_2 - O -$$
(4.1)
(4.1)

and/or abstraction of hydrogen from the main chain:

$$-CH_2 - O - \xrightarrow{h\nu} - \dot{C}H - O - + H^{\bullet}(RH)$$
(4.2)

A subsequent reaction is the formation of formaldehyde by a depolymerization (unzipping) reaction:

$$-CH_2 - O - CH_2 - O' \rightarrow -C - O' + CH_2 O$$

$$(4.3)$$

The photolysis of formaldehyde proceeds to radical and nonradical products, depending upon the wavelength of light:

$$H\dot{C}O + H^* \longrightarrow 2H^* + CO$$
(4.4)
CH₂O \xrightarrow{hv}

(4.5)

UV irradiation of polyoxymethylene in the presence of air (oxygen) leads

СО + Н

J. F. Rabek, *Polymer Photodegradation* © Chapman & Hall 1995 to the formation of hydroperoxides:

$$-CH_{2}^{\cdot}+O_{2} \longrightarrow -CH_{2}^{-}O-O^{\cdot} \qquad (4.6)$$

$$-CH_{2}^{-}O-O^{\cdot}+-CH_{2}^{-}O \longrightarrow -CH_{2}^{-}OOH + -\dot{C}H - O - \qquad (4.7)$$

$$\dot{O}$$

$$-\dot{C}H - O - +O_{2} \longrightarrow -CH - O - \qquad (4.8)$$

$$\dot{O}$$

$$-\dot{C}H - O - + -CH_{2}^{-}O - \longrightarrow -CH - O - + -\dot{C}H - O - \qquad (4.9)$$
Photodecomposition of hydroperoxide (OOH) groups subsequently gives end-hydroxyl (OH) and end-formyl(aldehyde) (-C < 0 + H) chains:

$$-CH_2 - OOH \xrightarrow{hv} - CH_2 - O' + OH$$
(4.10)

$$-CH_2-O'+-CH_2-O-\longrightarrow -CH_2-OH+-\dot{C}H-O- (4.11)$$

and

$$\begin{array}{ccc} OOH & O \\ | \\ -CH - O - \xrightarrow{hv} - CH - O - + OH \end{array}$$
(4.12)

$$\overset{O}{\xrightarrow{}}_{H^{-scission}} -CH_2 - C \overset{O}{\xrightarrow{}}_{H^{-scission}} -CH_2 - C \overset{O}{\xrightarrow{}}_{H^{-scission}} + O - CH_2 - (4.13)$$

$$H^{-scission} + O - CH_2 - (4.14)$$

The reaction of the different radicals with one another gives many products: H_2 , H_2O , CO, CO_2 , HCOOH, CH_4 and C_2H_6 have been identified by mass spectrometry [826, 1026]. Some of the radicals, such as $H\dot{C}O-$, $-O-\dot{C}H-O-$ and HOO^{+} , were studied by ESR spectroscopy [676, 1026].

During photodegradation of this polymer, mechanical properties (tensile strength and elongation) and the weight of sample decrease. At the beginning of the degradation, the surface of the film cracks and then the cracks gradually propagate throughout the surface of the film, which finally peels off.

4.1.2 Poly(ethylene oxide) and poly(propylene oxide)

Photo-oxidative degradation of poly(ethylene oxide) (4.2) poly(propylene oxide) (4.3) and poly(tetramethylene oxide) (4.4) and low molecular weight



(a)



(b)



(c)

Fig. 4.1. Photomicrographs (300x) of: (a) poly(ethylene oxide) before irradiation and; (b) and (c) after UV irradiation for 30 and 60 min, respectively [1774].

polyethers (polyglycols) occurs by a very similar mechanism to that of polyoxymethylene (cf. section 4.1.1) [690, 706, 1175].

$$-CH_{2}-CH_{2}-O- -CH_{2}-CH_{2}-CH_{2}-O- -CH_{2}-CH_{2}-O- -CH_{2}-O- -CH$$

Photo-oxidative degradation of poly(ethylene oxide) completely destroys its ability to crystallize in the form of spherulites (Fig. 4.1) [1117, 1774].

Decomposition of the poly(propylene oxide) hydroperoxides into formate groups shows that hydroperoxidation occurs at the secondary carbon atom of the propylene glycol monomeric unit, rather than at the tertiary carbon.

Poly(ethylene oxide) films have been used to monitor solar UV radiation [535]. The basis of this method is that the absorbance of the film at 400 nm increases in proportion to the incident dose of UV radiation below 320 nm.

Photolysis of poly(ethylene oxide) is very much enhanced by ozone and is dependent on pH [1041]. The hydroxide ions formed accelerate the UV irradiated ozonization. Ozone absorption is increased remarkably by UV irradiation in acidic and neutral solutions; however the highest effect on UV degradation has been observed at pH 13.

Photodegradation of poly(ethylene glycol), poly(propylene glycol) and poly(tetramethylene) glycol have also been reported [706, 1870]. Photo-degradation of poly(ethylene glycol adipate) has an effect on the rate of spherulic growth [520].

4.1.3 Poly(2,6-dimethyl-1,4-phenylene oxide)

The photodegradation of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (4.5) has been extensively investigated [84, 416–419, 424–426, 1096, 1117, 1176, 1701, 1712, 1721, 1722, 1846, 1847, 1995, 2008, 2211, 2213]. This polymer shows rapid discoloration after a few weeks or months of outdoor exposure, and also after about a year indoors under a combination of fluorescent and window lighting [1722].

The absorption spectrum of commercial poly(2,6-dimethyl-1,4-phenylene oxide) is shown in Fig. 4.2; it increases during UV irradiation.

Three mechanisms have been proposed for the photo-oxidative degradation of poly(2,6-dimethyl-1,4-phenylene oxide):

1. Photo-oxidation of methyl groups [84, 1176]:



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Fig. 4.2. Ultraviolet absorption spectra of poly(2,6-dimethyl-1,4-phenylene oxide) UV irradiated (at 253.7 nm) in air at different times: 0, 1, 2, 5, 10, 20, 30, 45, 60, 120, 240 min (provided by Dr H. Kaczmarek).



This mechanism has been strongly supported by ESCA spectroscopy measurements [585, 1701].

2. Direct photolytic cleavage of the main chain during which phenoxy (4.6) and (4.9) and phenyl (4.7) and (4.8) radicals are formed [1117, 1712, 1846, 1847, 2144, 2154, 2213]:



3. Electron transfer mechanism: an excited polymer fragment undergoes electron transfer during which a radical cation and radical anion pair is formed. The radical anion rapidly transfers an electron to oxygen to make superoxide (O_2^{-}) . Superoxide and the radical cation recombine to make unstable primary oxidation products which undergo further oxidation to give the final degraded products [1721, 1722].

ESR spectroscopy has proved the formation of phenoxy radicals (4.6); however, no ESR signals have been obtained which could confirm the presence of benzyl radicals [2144, 2154]. Phenoxy radicals are very stable and can exist in air for 30-35 h at room temperature.

The ESCA spectra of poly(2,6-dimethyl-1,4-phenylene oxide) photo-oxidized in oxygen are shown in Fig. 4.3. The increase in the intensity of the O_{1s} band with duration of photo-oxidation is accompanied by the appearance of an envelope of peaks to the high binding energy side of the main C_{1s} peak [585, 1701]. Greater photo-oxidation of the surface can be explained by intensive oxidation of methyl group in poly(2,6-dimethyl-1,4-phenylene oxide).

Both polymer phenyl and/or polymer phenoxy radicals can abstract hydrogen from the methyl groups of the same or neighbouring macromolecule,



Fig. 4.3. ESCA spectra C_{1s} and O_{1s} core levels for poly(2,6-dimethyl-1,4-phenylene oxide) UV irradiated for different intervals of time [1701]. (Reproduced with permission from [1701]; published by John Wiley & Sons, Inc., 1981.)

giving side-group radicals (4.10):





The side-group polymeric radical may react further with oxygen giving polymeric side hydroperoxides (4.12):



Photodecomposition of the polymeric hydroperoxide (4.12) leads to formation of the polymer side oxy radical (4.13):



Polyethers

Radicals formed at the side groups may terminate each other giving crosslinked structures:



The polymeric side-group radical can isomerize to the 2,4-cyclohexane methide radical (4.14), which may participate in the chain scission process with the formation of quinone-methide end groups (4.15), which has an absorption at 340 nm:



Polymer phenyl radicals (4.8) may react with oxygen giving polymeric aromatic hydroperoxides (4.16), which are further photodecomposed into

polymer phenoxy radicals (4.6):



Phenoxy radicals (4.6) can isomerize into more resonance-stabilized cyclohexanedienenonyl radicals (4.17) and (4.18) [1768, 1847]:



The rate of isomerization is of the order of $10^8 1 \text{ mol}^{-1} \text{ s}^{-1}$ [594].

Whilst considering the possibility of formation of cyclohexanedienenonyl radicals (4.17) the following reaction provides the possibility of formation of polymeric hydroperoxide of another type (4.19) [1846]:



Polyethers

The scission of these polymeric peroxides can lead to the formation of polymeric α,β -unsaturated acids (4.20):



Another type of cyclohexanedienenonyl radical (4.21) reacts with oxygen, finally giving a new polymer hydroperoxides (4.22):



The polymer hydroperoxide (4.22) may either aromatize into polymer aromatic hydroperoxide (4.23) and/or homolyse into polymer phenoxy radicals in the semi-quinone form (4.24):



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The last polymer phenoxy radical (4.24) in the presence of oxygen can disproportionate to polymer quinone-methide (4.25) and polymer with phenolic group (4.26):



Recombination of polymer phenyl (4.8) and polymer phenoxy (4.6) radials with each other leads to crosslinking reactions [1096, 1175, 1176, 1847]:



Photo-oxidative degradation of poly(2,6-dimethyl-1,4-phenylene-oxide) is always accompanied by the evolution of CO_2 and H_2 .

The following electron transfer mechanism has been proposed for the

formation of the phenyl endo-peroxide (4.27):



Photodecomposition of these polymeric phenyl endo-peroxides may lead to the formation of different quinoid structures (4.28) and (4.29) and even to the ring-opening reaction (4.45) [1846]:





The above mechanism has been proposed on the basis of sensitization, quenching, radical scavenging and flash photolysis experiments.

The photodegradation of poly(2,6-dimethyl-1,4-phenylene oxide) blends with polystyrene have also been reported [1722, 2129, 2130].

4.1.4 Poly(ether crown)picrate complexes

Poly(ether crown) picrate complexes (4.30) under UV irradiation can liberate 4'-acetobenzo-15-crown-5 or 4'-acetobenzo-18-crown-6 by the following reaction [1967]:



(4.46)




4.2 POLY(o-NITROBENZALDEHYDE ACETAL)

Poly(*ortho*-nitrobenzaldehyde acetal) (4.31) under UV irradiation is photorearranged to polyglycols and *o*-nitrobenzoate ester [1711]:



4.3 EPOXY RESINS

Epoxy resin based on bisphenol-A-epichlorhydrin (4.32) is susceptible to photodegradation when exposed to prolonged UV radiation [675, 814, 1174, 1340, 1691, 1698, 2109].

The UV irradiation can initiate the following primary processes:



Table 4.1 Relative volumes of CO and CO_2 evolved from phenoxy polymers during UV irradiation [741]

Exposure conditions	Time of irradiation (h)	Relative CO volume	Relative CO ₂ volume
Vacuum	6	9	1
	24	18	2
	100	80	7
	1000	420	48
Oxygen	24	150	72
	100	360	1500
	1000	1200	6000

(Reproduced with permission from [741]; published by John Wiley & Sons, Inc., 1969.)

2. Side group abstractions:





3. Hydroxyl group reactions:

$$\overset{O}{\xrightarrow{}} O \\ -O-CH_2-CH-CH_2- \longrightarrow O-CH_2-CH + CH_2-$$
(4.61)

$$-O-CH_2-CH \xrightarrow{h\nu} -O-CH_3 + CO$$
(4.62)

Epoxy resins are characterized by a high evolution of carbon monoxide and carbon dioxide when photolysed in vacuum and in an oxygen atmosphere (Table 4.1). A rapid increase in the rate of formation of CO and CO_2 may be due to the following reactions:



 $R-O-COOH \xrightarrow{hv} R+OH+CO_2$ (4.69)

Other volatile products formed during photolysis are hydrogen water, ethane, propane and propylene. It is suggested that propane and propylene are formed by the following reactions [1174]:



$$CH_3 - \dot{C}H - CH_3 + PH \longrightarrow CH_3 - CH_2 - CH_3 + P'$$
 (4.72)

$$CH_3 - \dot{C}H - CH_3 + P' \longrightarrow CH_3 - CH = CH_2 + PH$$
 (4.73)

The formation of acetone indicates a chain scission at the isopropylidenearomatic bond [1174]:







Chain scission reactions are accompanied by crosslinking, during which insoluble gel is formed (Fig. 4.4).

The available weathering data show that the exposure to UV radiation of epoxy resins induces crack formation on exposed surfaces and erosion of superficial layers by atmospheric agents, indicating the existence of an efficient skeleton breaking process [728].

The instability of dyed epoxy resin systems with prolonged exposure to sunlight is an important technological problem. Both the epoxy resin and dyes undergo changes. In particular, epoxy resins suffer extensive chain scission, crosslinking and yellowing [701, 728, 1174] while the dyes (e.g. 2-piperidinoanthraquinone) photofade [51, 53].

4.3.1 Epoxy-acrylate coatings

Epoxy-acrylate cured coatings based on an epoxy-diacrylate oligomer derived from the glycidyl ether of bisphenol-A (cf. Table 4.2) and of tripropyleneglycol

Table 4.2 Components of epoxy-amine resin network



Aminoethyl piperazine

Isophorone diamine

 $\begin{array}{c} CH_2 - CH_2 \\ NH_2 - (CH_2)_2 - N \\ CH_2 - CH_2 \\ CH_3 - - C$

Boron trifluoride-monoethyl amine complex

Aromatic amines:



217-220, 701, 779

728

where: $X = -CH_2 - , -O_-, -SO_2,$ $R = H, CH_3, -CH(CH_3)_2$



Fig. 4.4. Kinetics of gel formation during UV irradiation of poly(2,6-dimethyl-1,4-phenylene oxide) in air and in vacuum for different intervals of time.

diacrylate are four orders of magnitude more resistant towards UV irradiation than linear polymers of similar chemical structure, either acrylates or bis-phenolic epoxy polymers. This high light stability can be the result of the high crosslink density, which causes chain scission to have a less damaging effect on the physical properties (because of the numerous remaining connecting chains) and prevents, through the restricted segmental mobility that favours cage radical recombination, the development of the degradative chain reactions [565].

Similar conclusions may be drawn from the photo-oxidative degradation of cured acrylated epoxy and urethane resin films [109].

The hardness of coatings based on bisphenol-A-epichlorhydrin containing reactive acrylate diluents such as β -carbonyl ethylacrylate or isobornylacrylate initially increases with time on exposure to UV radiation and then decreases [675].

4.3.2 Epoxy-amine coatings

Epoxy-amine cured coatings based on di-, tri- and tetra-functional epoxydes and aliphatic or aromatic amines (Table 4.2) undergo complicated photoreactions when exposed to UV radiation.

At least four kinds of chromophores can contribute to the colour development during photo-oxidation of epoxy resins [216, 218–220]:

1. Products resulting from the oxidation of the phenoxy part. The most

probable mechanism involves an oxidative attack on the glycidyl part:



The occurrence of a photo-Fries rearrangement is well established in polycarbonates (cf. section 4.5), which contain very similar structures.

2. Products resulting from the oxidation of the amine part, independent of diamine structure:



3. Oxidation products depending on the hardener structure. For example, diamino diphenyl methane (4.33) undergoes the strongest yellowing of all amines, and produces an unknown chromophore absorbing at 615 nm, according to the mechanism:



The sequence of oxidation processes can lead to highly conjugated structures (4.34):



and probably also to their photoproducts (4.35), which derive from photo-Fries rearrangements:



4. The methylene bridge is able to undergo chemical transformation, leading to highly conjugated structures:



Skeleton breaking in the epoxy-amine network during photo-oxidation is assisted by internal stresses, which are induced by shrinkage in the glassy state network, and is dependent on the crosslinking density. The backbone scission in constrained network segments favours stress relaxation. Similar 'oxidative stress relaxation' has also been observed in the case of polypropylene [1733], though in this case the rate of oxidative chain scission is enhanced in presence of mechanical stresses [1820]. The network degradation of epoxyamine resins in the glassy state can also be affected by stress on the skeleton [220].

4.4 PHENOLIC RESINS

Analytical and kinetic studies of photo-oxidation in the solid state of phenolic resins (phenol-formaldehyde polycondensates) (4.36) show that photoreaction involves two processes [1845]:

1. Photolysis of the phenolic groups leads to the formation of quinone methide structures:



2. Photo-oxidation of dimethylene ether linkages causes the formation of hydroperoxy groups, which are further converted into ester and formate

groups:



4.5 POLYCARBONATES

Polycarbonates based on bisphenol-A (4.37) exposed to UV radiation (or to sunlight for several years) become yellow and show evidence of deep degradation processes; main chain scission and gel formation [1, 130, 133, 225, 459, 463–465, 537–539, 638–640, 673, 741, 882, 884, 888, 889, 1008, 1027, 1028, 1321, 1453, 1507, 1523, 1528, 1633, 1742, 1844, 1848–1850, 2121, 2219].



UV irradiation of bisphenol-A polycarbonate causes the formation of yellow coloured products [463, 538, 1742]. The extent of this photoyellowing is dependent on the wavelength of the light used and at shorter wavelengths (<314 nm), it can be greater than in the presence of oxygen [1742].

The UV/VIS spectra of bisphenol-A polycarbonate (λ_{max} at 264 nm) before and after UV irradiation are shown in Figure 4.5. After UV irradiation, two new absorption bands appear at 320 and 355 nm, which are attributed to



Fig. 4.5. Absorption spectra of bisphenol-A polycarbonate: (a) nonirradiated and (b) UV irradiated for 60 min [900]. (Reproduced with permission from [900]; published by John Wiley & Sons, Inc., 1970.)

polyphenylsalicylate (4.38) and polydihydroxybenzophenone (4.39) structures formed by the photo-Fries rearrangement [133, 638, 884, 1321, 1523, 1633].



The photo-Fries products are themselves easily photo-oxidized, making it difficult to find evidence of the photo-Fries pathway [1848, 1849].

The yellowing of bisphenol-A polycarbonate need not only be the result of the formation of the *ortho*-dihydroxybenzophenone structure (4.39) [884, 1633] but can also be a result of the formation of cyclodienone-type structures (4.43, 4.44 and 4.45), which arise from phenoxy radicals (4.40) (cf. reactions 4.100-4.103) or from the photo-oxidation of bisphenol-A units (cf. section 2.14) [638, 639].

The yellowing of bisphenol-A polycarbonate can also be a result of photooxidation of the phenyl ring [463–465, 638, 639]. ESCA studies of resin photooxidized under both sunlight (> 300 nm) [465] and UV radiation (280 nm) [463, 1528] show a decrease of the π - π shakeup ESCA satellite, indicating the loss of aromatic groups. Quantitative FTIR analyses of laser induced polycarbonate photodegradation [2219] indicate a depletion of main chain aromatic groups and suggest an increase in ring substitution. Oxygen uptake experiments [638] indicate the absorption of up 12 mol of O₂ per monomer unit and the evolution of 4.6–7.7 mol of CO + CO₂ per monomer unit during the photo-oxidation of thin polymer films using different light sources. These values cannot be explained by side-chain oxidation and carbonate group hydrolysis alone and indicate that ring oxidation is also occurring.

Both outdoor and artificial weathering experiments of side-chain free polycarbonate made from bis(3-hydroxyphenyl)ether demonstrated that it photoyellowed approximately three times faster than the bisphenol-A polycarbonate [640]. This indicates that, in the case of polycarbonate made from bis(3-hydroxyphenyl)ether, ring oxidation is the source of photoyellowing and suggests that ring oxidation probably plays an important role in the photoyellowing of bisphenol-A polycarbonate. Gas chromatography-high resolution mass spectrometry has confirmed the presence of small amounts of photo-Fries and ring oxidation products along with large amounts of side-chain oxidation products [639]. The degradation process is caused by main chain scission [1, 884, 1028, 2121]:



during which carbon monoxide and carbon dioxide are formed (Table 4.3):

$$-\bigcirc -\bigcirc -\bigcirc -\bigcirc -\bigcirc -\bigcirc + \operatorname{CO} \qquad (4.98)$$

Main chain scission may also occur in the bisphenol-A units (cf. section 2.14).

The phenoxy radicals (4.40) may isomerize to the 2,4-cyclohexane-dienoyl radical (4.41) [1844].



which can react with phenyl carboxy radicals (4.42), giving different yellow coloured cyclodienone-type compounds:



Exposure conditions	Time of irradiation (h)	Relative CO volume	Relative CO ₂ volume
Vacuum	6	4	11
	24	7	17
	100	22	46
Oxygen	6	22	34
	24	130	90
	100	300	940

Table 4.3 Relative volumes of CO and CO_2 evolved from polycarbonate during UV irradiation [741]

(Reproduced with permission from [741]; published by John Wiley & Sons, Inc., 1969.)

Formation of phenoxy radicals, phenyl radicals and polyenyl-type radicals during UV irradiation of bisphenol-A polycarbonate has been confirmed by ESR spectroscopy [900].

Photodegradation of polycarbonate films exposed outdoors to longer wavelengths can be due to initiation mechanisms caused by the presence of impurities, as well as to the structural defects in the polymer [464, 465, 638, 1507, 1528, 1742, 1848, 1849].

Photodegradation of bisphenol-A-epichlorhydrin [1225], poly(dian carbonates) [1738] and of polycarbonate blends with polypropylene [1282] and poly(methyl methacrylate) has also been described [673, 1645].

4.6 POLYESTERS

4.6.1 Unsaturated polyesters

The photo-oxidation of aliphatic unsaturated polyesters such as poly(1,2-maleate) (4.46) [2188] and poly(propylene-1,2-maleate) (4.47) [1099, 1357, 1474, 1475, 1814] is accompanied by extensive chain scission, crosslinking and yellowing.





Polyesters

Coatings based on mixed unsaturated aromatic polyesters which have benzene nuclei, such as poly(1,2-maleate-propylene-o-phthalate) (4.48), are also susceptible to photo-oxidative degradation [1375, 1814]. On exposure to sunlight, gradual changes take place in their chemical and physical properties, starting at the surface to produce microcracks and chalking.



The photolysis of unsaturated polyesters shows the disappearance of double bonds and partial decomposition of ester carbonyl groups to carbon monoxide and carbon dioxide molecules. This type of polyester contains a distinct conjugated system of double bonds and carbonyl groups (4.49), which absorbs UV radiation and exists in the triplet state (T_1) as a resonance form (4.50):

The resonance form allows the existence of several different intermediate reactive biradicals:

$$\begin{array}{cccc} O & O & O \\ -C & -CH - CH - C & \downarrow & \parallel \\ -C & -CH - CH - C & \leftarrow C & -CH - CH - C \\ & & O \\ & & \downarrow & -C & -CH = CH - C \\ & & \downarrow & \parallel \\ & & \leftarrow & -C & -CH = CH - C \\ \end{array}$$
(4.105)

The spin components of the two excited electrons are neither 'paired' nor 'unpaired'; they are independent and delocalized. The observed rapid crosslinking is interpreted as being due to reactions of the intermediate radicals with a segment of the same or neighbouring macromolecules:





A primary photolytic chain scission occurs by the Norrish Type I reaction, which produces the observed CO and CO_2 :



The Norrish Type II intermolecular rearrangement yields terminal carboxylic groups: **Polyesters**



The photo-oxidative degradation occurs via a free radical mechanism with the formation of polymer peroxy (PO_2) and polymer oxy (PO') radicals and polymeric hydroperoxides (POOH).

During photolysis of mixed unsaturated polyesters containing o-phthalate nuclei, the main chain scission yields polymeric phenyl radicals (4.51):



Oxidation reactions of polymeric phenyl radicals yield the formation of an *o*-hydroxy group:







Under UV irradiation the *ortho*-hydroxyester end-group (4.52) can be isomerized into *o*-diquinone (4.53):



The photodegradation of photocrosslinked unsaturated polyesters has also been reported [1816].

4.6.2 Polylactacide

Polylactacide (4.54) is a saturated aliphatic polyester which is susceptible to photo-degradation [1449]. The main reaction is a chain scission by the Norrish Type I reaction with the formation of CO_2 and H_2O :

4.6.3 Poly(ethylene terephthalate)

Poly(ethylene terephthalate) (4.55) is a thermoplastic material used widely in the form of fibres and films, and as a support material for photographic and magnetic media. Poly(ethylene terephthalate) [82, 170, 354, 433, 438, 546–549, 616, 691, 1040, 1404, 1432, 1463, 1468, 1495, 1648, 1657, 1680, 1681, 1982, 2058, 2060, 2061, 2069, 2176, 2206, 2309. 2336] and its analogue poly(butylene terephthalate) [611, 2079] are thermally stable, but photometal ions play a significant role in the rate of degradation. The latter may be particularly important, since metal derivatives are used as either transesterification or polycondensation catalysts during the manufacture of poly(ethylene terephthalate). Furthermore, during the manufacture and processing of poly(ethylene terephthalate) into film or moulded products, the polymer is subjected to temperatures in the range 200-300 °C, which are sufficient to initiate thermal



Fig. 4.6. Transmission spectrum of poly(ethylene terephthalate) [1404]. (Reproduced with permission from [1404]; published by John Wiley & Sons, Inc., 1967.)

degradation. The presence of moisture and acid or alkaline impurities will affect hydrolysis.

Poly(ethylene terephthalate) (which has high c. 50% crystallinity) forms transparent films, when slowly evaporated in a solution in trifluoroacetic acid (3 g/l). Such film transmits radiation of wavelength > 320 nm, but absorbs strongly near 310 nm, and is opaque to radiation of wavelength 302 nm (Fig. 4.6).

The UV irradiation of poly(ethylene terephthalate) causes random chain scission by:

1. the Norrish Type I mechanism [616, 1432, 2058]:

$$\begin{array}{c} 0 & 0 \\ -C & -O \\$$

2. and alternatively by the Norrish Type II cleavage:



Carbon monoxide and carbon dioxide are produced by the reactions:

$$\begin{array}{c} O & O \\ -C & -C \\ -C & + \\ -C & + \\ -C & -C \\ -C & + \\ -C$$

$$-O-CH_2-CH_2-O-C' \longrightarrow -O-CH_2-CH_2-O' + CO$$
 (4.128)

$$-O-CH_2-CH_2-O-\overset{\parallel}{C} \longrightarrow -O-CH_2-CH_2 + CO_2 \qquad (4.129)$$

The rate of evolution of carbon dioxide is much higher in the presence of air. The quantum yields of CO and CO₂ formation are $\phi_{CO} = 6 \times 10^4$ and $\phi_{CO_2} = 2 \times 10^{-4}$ respectively, and have the same values when a sample is exposed to 253.7 and 313 nm irradiation [1404].

The formation of hydroxy and carboxylic end-groups [548, 1404], which are located mainly at the surface [264] was proved by FTIR-ATR spectroscopy (cf. section 10.17.5):



Hydroxyl groups have also been found to arise as a consequence of substitution reactions in the aromatic ring, resulting in the formation of mono-(4.56) and di-hydroxyterephthalate (4.57) units:

290

Polyesters





$$\begin{array}{c} O & O \\ -C & -C \end{array} \begin{array}{c} O & O \\ -C & -C \end{array} + HO' \longrightarrow -C - C \end{array} \begin{array}{c} O & O \\ -C & -C \end{array}$$
(4.134)



An alternative mechanism for the formation of mono- and di-hydroxyterephthalate groups is by the formation of benzene ring hydroperoxides [2176]:





The presence of these groups has been identified by fluorescence spectroscopy [82, 433, 438, 1404, 1681].

The formation of quinone and di-quinone groups may be responsible for the yellowing:

291



Commercial polyesters containing both unsaturated and aromatic groups in the chain are crosslinked by the addition of styrene, which reacts with some of the chain double bonds.

Chain scission reactions are always accompanied by crosslinking, which causes polymer films to become brittle with crazed surfaces [170, 1495, 2309], whereas fibres lose their tenacity, elongation and elasticity [547, 2206]. The quantum yield of crosslinking is $\phi_c = 5.5 \times 10^{-4}$. The crosslinking occurs by termination of all possible polymeric radicals formed during photo-oxidative degradation of the polymer.

UV irradiation of poly(ethylene terephthalate) membranes decreases their permeability to the gases He, H₂, CO₂, Ar and N₂ by 7–57%, depending on the specific nature of the permeant gas (Fig. 4.7) [1463]. As a result, the permeation selectivity of the membranes increases by up to 117% (Fig. 4.8). These effects are probably the result of crosslinking that takes place in the polymer during the irradiation process and thus reduces the free volume in a membrane.



Fig. 4.7. Effect of UV radiation on the relative permeability coefficient of poly(ethylene terephthalate) membranes at 323 K [1463]. (Reproduced from Mercea, P. et al., Polym. Commun., 28, 31, by permission of the publishers, Butterworth Heinemann Ltd. © 1987.)

UV irradiation causes changes in the electrical properties of poly(ethylene terephthalate) [1040]. Irradiation results in decreases in the relative dielectric constant and dielectric strength, whilst the dielectric loss factor is increased.

Photodegradation of poly(ethylene terephthalate) has also been studied for the archival life of cinematograph films and for environmental degradation [616].

Photodegradation has also been reported for poly(ethylene terephthalateco-4,4'-bis-phenyldicarboxylate) [568]; poly(ethylene terephthalate-co-4,4'bis-sulphonyldibenzoate) [2069]; poly(ethylene-co-dimethyl- γ -ketopimelate);



Fig. 4.8. Effect of UV radiation on the permeation selectivity of poly(ethylene terephthalate) membrane at 323 K [1643]. (Reproduced from Mercea, P. et al., Polym. Commun., 28, 31, by permission of the publishers, Butterworth Heinemann Ltd. © 1987.)

poly(ethylene terephthalate-co-diethyl acetyl succinate) and poly(ethylene terephthalate-co-diethyl butyryl succinate) [42].

4.6.4 Poly(4,4'-diphenylolpropane isophthalate)

The photoyellowing of poly(4,4'-diphenylolpropane isophthalate) (4.58) has been attributed to a photo-Fries rearrangement in a polymer containing o-hydroxybenzophenone as part of the chain structure (4.59) [1391]:



This reaction is accompanied by photocleavage of the main chain.

4.6.5 Poly(ethylene-2,6-naphthalate)

Poly(ethylene-2,6-naphthalate) (4.60) under UV irradiation is photodegraded by a mechanism analogous to that for poly(ethylene terephthalate) (cf. section 4.6.3) [81, 1664].



4.6.6 Poly(fluorenone-isophthalates)

Fluorenone based polyesters such as poly(9,9-bis(4-hydroxyphenyl) fluorene isophthalate) (4.61), poly(9,9-biscresol fluorene isophthalate) and poly(9,9-bis(3,5-dimethyl-4-hydroxyphenyl)fluorene isophthalate) undergo, under UV irradiation, typical photo-Fries rearrangement, during which linear *o*-hydroxybenzophenone moieties can be formed [1346]:



(4.61)



4.6.7 Segmented block poly(ester-co-ethers)

Photolysis of block poly(ester-co-ethers) containing such structures as (4.62) [1022] and (4.63) [1101, 2080, 2081], show the formation of hydroperoxide

groups, mainly in the α -position with respect to the oxygen atom of the elastomeric polyether segments.



Chain scission and crosslinking occur both in argon and in air by similar mechanisms to those described for poly(ethylene terephthalate) (cf. section 4.6.3).

4.7 POLYAMIDES

The photodegradation and photo-oxidative degradation of different polyamides have been the subjects of many publications (Table 4.4) and reviews [1319, 1321, 2065].

4.7.1 Aliphatic polyamides

Aliphatic polyamides do not absorb light above 290 nm and photo-oxidative degradation of these polymers in that region can be initiated by the presence of such impurities as: hydroperoxides, [47, 139] carbonyl groups [1869], α , β -unsaturated carbonyl groups [47, 65, 89, 99, 103] and traces of metal ions [236].

Carbonyl groups, which form in nylons either by photo-oxidation and thermal oxidation or by the interaction of carboxyl end-groups during processing, appear to exist as keto and *N*-acylamide (or imide) groups.

Nylons 6 and 6,6 exhibit a weak absorption at about 290 nm, which is associated with the n, π^* transition of α,β -unsaturated carbonyl groups, because the π electron donation from the nitrogen is more efficient than its withdrawal.

The C—N bond is the weakest in the polyamide molecule (c. 53 kcal mol⁻¹). The major initial step in the photo-oxidation of aliphatic polyamides at

Name	References
Nylon 6	99, 587, 672, 726, 727, 939, 1321, 1395, 1396, 1855, 1856, 2058, 2059, 2205, 2306
Nylon 6 blends with polyethylene	2038, 2039, 2303, 2306
Nylon 6 6	49 65 66 92 99 1840 2065
Polyamide 11 (polyundecanamide)	1321 1855 1856 2001_2003
Polyamide 12 (polydodecanamide)	1321, 1853, 1855, 1856
Poly(amide-co-carbon monoxide)	587
Poly(<i>\varepsilon</i> -caproamide)	1735
Poly(1,1-dimethylethylene sebacamide)	1024
Polyamide-block-polyethers	705-707, 1717
N-substituted aliphatic polyamide	671
Poly(N-chloroamide)	174, 879
Modified polyamides with aromatic groups:	1061
	SO ₃ Cu
-CH=CH- SO ₃ Na SO ₃ Na	
Poly(1.3-nhenylene isonhthalamide)	260 271 278 2122
Poly(1,-phenylene terentthalamide)	371
Poly(truxillic amide):	348, 349. 1506
	-
Polyamides with coumarine dimer component:	919
<u> </u>	

 Table 4.4
 Photodegradation of polyamides – references



254 nm is direct photoscission, which is independent of the length of the carbon chain [18, 587, 659, 943, 1508, 2058, 2059]:

$$-CH_{2}-NH-CO-CH_{2}-\overset{hv}{\longrightarrow}-CH_{2}-NH^{*}+CO-CH_{2}-(4.144)$$
$$-CH_{2}-NH^{*}+-CH_{2}-NH-CO-CH_{2}-\overset{}{\longrightarrow}$$
$$-CH_{2}-NH_{2}+-CH-NH-CO-CH_{2}-(4.145)$$
$$-CH_{2}-CO^{*}+-CH_{2}-NH-CO-CH_{2}-\overset{}{\longrightarrow}$$
$$-CH_{2}-C\overset{O}{\underset{H}{\leftarrow}}+-CH-NH-CO-CH_{2}-(4.146)$$

$$-CH_{2}-C \swarrow H \xrightarrow{h\nu} -CH_{2}-COOH$$
(4.147)

 $-CH_{2}-CO^{\bullet} \longrightarrow -CH_{2}^{\bullet}+CO \qquad (4.148)$

The main groups formed are amines, aldehydes and carboxylic acids.

At wavelengths longer than 300 nm photo-oxidation occurs through the formation of hydroperoxy groups and their photolysis to imide groups (-CO-NH-CO-) [1321, 1853, 1856]:

$$-CH_{2}-CH_{2}-NH-CO-CH_{2}+R' \longrightarrow$$
$$-CH_{2}-CH-NH-CO-CH_{2}-+RH \quad (4.149)$$

$$-CH_{2}-CH_{2}-CH_{2}-CH_{2}-HH_{2}-CH_{2}$$

Imide groups are very photolabile, especially to 254 nm irradiation, and are completely hydrolysed by traces of water formed *in situ*:

$$-CH_{2}-CO-NH-CO-CH_{2}-\xrightarrow{hv}$$

$$-CH_{2}-CO-NH-CO^{*}+CH_{2}-(4.153)$$

$$-CH_{2}-CO-NH-CO-CH_{2}-H_{2}O\longrightarrow$$

$$-CH_{2}-CO-NH_{2}+HO-CO-CH_{2}-(4.154)$$

Imide groups formed in polyamide 6 (polyhexanamide) hydrolyse faster than in polyamide 11 (polyundecanamide) and polyamide 12 (polydodecanamide). The role of water in the photo-oxidation of aliphatic amides is limited to a reaction with the imide groups [1321].

Hydroperoxy groups in polyamides can also be decomposed to polymer oxy radicals, which then abstract hydrogen from the same or neighbouring macromolecules and produce hydroxyl groups [47, 1853, 1856]:

$$-CH_{2}-CH--NH--CO--CH_{2}-\xrightarrow{hv}$$

$$OOH$$

$$-CH_{2}--CH--NH--CO--CH_{2}-+HO' (4.155)$$

$$OH$$

$$-CH_{2}--CH--NH--CO--CH_{2}-+PH \longrightarrow$$

$$OH$$

$$-CH_{2}--CH--NH--CO--CH_{2}-+P' (4.156)$$

$$OH$$

$$-CH_{2}--CH--NH--CO--CH_{2}-\xrightarrow{\rho \text{scission}}$$

$$OH$$

$$-CH_{2}+H \rightarrow CO--CH_{2}-(4.157)$$

The concentration of hydroperoxide groups formed depends on the type of polyamide, e.g. it is higher in polyamide 12 (polydodecanamide) (18 mmol kg⁻¹) than in polyamide 6 (polyhexanamide) or polyamide 11 (polyundecanamide) (2–4 mmol kg⁻¹) [1321].

Hydrogen bonding is also believed to play a role in photodegradation [587]. The following mechanism has been proposed to explain the stability of peptide bonds subjected to light:

299



The absorption band at 1620 cm^{-1} may indicate the formation of double bonds such as $-CH=CH_2$ and/or -CH=N-. The $-CH=CH_2$ bond can be formed by the following reactions [587]:

300



$$O$$

$$-CH_2-C-NH-CH_2-CH_2-\xrightarrow{hv}$$

$$-CH_2-CO-NH_2+CH_2=CH-$$
(4.167)

$$\begin{array}{cccc} & O & O \\ & \parallel & \parallel & \parallel \\ & -CH_2 - C - NH - C - CH_2 - \xrightarrow{hv} \\ & -CH_2 - CO - NH - CO - CH_3 + CH_2 = CH - \\ & O \\ & -CH_2 - \stackrel{\parallel}{C} - CH_2 - \xrightarrow{hv} - CH_2 - CO - CH_3 + CH_2 = CH - \\ \end{array}$$
(4.168)

There may also be interaction between keto and amide groups, which results in destabilization leading to photodegradation, by the following mechanism [587]:



Hydrogen, methane and carbon monoxide are the predominant gases formed during the photolysis of nylons [587, 2058].

The mechanism of photo-oxidative degradation of polyamides has also been investigated using low molecular weight compounds such as N-hexyl-hexanamide; 1,6-hexamethylenebis(hexanamide); N,N'-bis(hexyl)adipamide; N-alkylamides; and N-acylamides [587, 1221, 1348, 1683, 1880, 1959].

Ozone accelerates the photodegradation of polyacrylamide in water solution [726, 727]. Photo-oxidative degradation of polyamides causes a decrease of their mechanical properties [1395, 1396, 2305].

4.7.2 Poly(1,3-phenylene isophthalamide)

Poly(1,3-phenylene isophthalamide) (polyaramide (4.64) deteriorates rapidly on exposure to terrestrial sunlight. Fibres made from this polymer suffer loss of breaking strength and become yellow [369–371, 378, 2131, 2132].

During UV irradiation of poly(1,3-phenylene isophthalamide) in vacuum, a chain scission of the amide link yields two radicals (4.65) and (4.66), which can either recombine directly or eliminate carbon monoxide [368–371, 1105]:



This scission reaction is accompanied by a photo-Fries rearrangement which occurs by [378]:

1. A free radical mechanism:



2. A cyclic transition state:



No photo-Fries product was detected after UV irradiation in air. The crosslinking reaction occurs only in the absence of oxygen. The photo-oxidation reaction of poly(1,3-phenylene isophthalamide) is accompanied by a rapid chain scission [369]:



The formation of nitroso (-NO), nitro ($-NO_2$) and carboxylic (-COOH) groups has been confirmed by IR spectroscopy.

4.7.3 Photoreversible depolymerization of poly(hexamethylene-α-truxillamide)

Polyamides derived from the condensation of cinnamic acid photodimers with aliphatic diamines such as poly(hexamethylene- α -truxillamide) (4.67) are highly photodegradable, photochromic materials.

This polyamide exhibits a reverse degradation-polymerization reaction [2088]. Under UV irradiation at 224 nm, the polyamide is degraded and characteristic *trans*-cinnamide absorption is observed. This *trans*-cinnamide absorption disappears following exposure to light of wavelength 304 nm (Fig. 4.9), and poly(hexamethylene- α -truxillamide) is reformed (Fig. 4.10). The observed reverse reaction can be explained by the following mechanism:



Such a reaction occurs only in the polymer matrix. When the photodissociation of α -truxillamide moieties occurs in the polymer matrix, the geometry of α -truxillamide is inherited by the resulting cinnamide groups and, hence, two separate cinnamide groups facing each other may retain conformation in the polymer matrix. Such pairs of cinnamide groups can easily dimerize into the original polymer.

The addition of strong acid to a solution of the above materials induces a large increase in the rate of photolysis [119, 347–349]. The mechanism of the


Fig. 4.9. Change in the ultraviolet absorption spectrum of poly(hexamethylene- α -truxillamide) during UV irradiation at 224 nm [2088]. (Reproduced with permission from [2088]; published by John Wiley & Sons, Inc., 1971.)



Fig. 4.10. Change in ultraviolet absorption spectrum of photodepolymerized poly(hexamethylene- α -truxillamide) during irradiation by light of wavelength 304 nm [2088]. (Reproduced with permission from [2088]; published by John Wiley & Sons, Inc., 1971.)

acid catalysis can be explained in terms of acid-base equilibria of the ground and excited states involved in the photolysis.

Amides are very weak bases in the ground state, but become much stronger bases in the first excited singlet state (S_1) . Therefore, protonation of the amide group by means of strong acids occurs more efficiently when the sample is irradiated by UV radiation.

In the case of polyamides containing truxillic units, protonation of the amide group weakens the cyclobutane ring and a strong catalytic effect on the photocleavage is observed [1506].

4.8 POLYIMIDES

4.8.1 Aliphatic polyimide

Under UV irradiation poly(dimethylacrylimide) (4.68) decomposes by elimination of isocyanic acid (HNCO), which results in main chain scission with the formation of olefin and ketene end-groups, as shown below [947]:

$$CH_{2} \xrightarrow{CH_{2}} CH_{3}$$

$$CH_{2} \xrightarrow{CH_{2}} CH_{3}$$

$$CH_{2} \xrightarrow{CH_{2}} CH_{3}$$

$$H^{\nu} \xrightarrow{-CH_{2} - C} = CH_{2} + O = C = C - + HCNO$$

$$H$$

$$(4.178)$$

$$(4.68)$$

Microcapsules prepared by a coupling reaction of disuccinimido-4,4'azobis(4-cyano-valerate) with L-lysine and/or polyallylamine show a lightresponsive release of an inner content, succinylated bovine serum albumin, to the outer bulk phase [1207].

4.8.2 Aromatic polyimides

Aromatic polyimides have excellent thermal stability, but rather poor long term photostability. Under both UV and VIS (350–500 nm) irradiation, they undergo a colour change from light yellow-brown to dark purple [120, 1105, 1501].

The following aromatic polyimides have been studied in detail:

1. Based on pyromellitic dianhydride and 4,4'-oxydianiline [140, 998]:



(4.69)

2. Based on 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 4,4'-oxydianiline [140, 1035]:



3. Based on perfluorinated dianhydride and 4,4'-oxydianiline [140, 993–995, 998]:



4. Based on perfluorinated dianhydride and 4,4'-methylene dianiline [994]:



Pyromellitic-dianhydride based polyamide is the most photostable of the above group (4.69). The photolytic decomposition in air of polyimide films based on a dianhydride and a diarylamine with hexafluoroisopropylidene 6F bridging groups (4.71 and 4.72) is extremely rapid, leading to efficient chain cleavage and subsequent photo-oxidative decomposition. On the basis on the photo-oxidation of several model compounds and IR difference spectroscopy, it has been shown that the photodecomposition process occurs via decomposition of the arylimide linkage [996, 998]:



The electron withdrawing/donating substituents and solvent polarity greatly alter the efficiency of the photolysis process [996]. The great differences in the photostability of polyimides can be explained by the formation of the charge-transfer (CT) complexes. In particular polyimides with hexafluoro-isopropylidene groups (4.71 and 4.72) form weaker complexes than other polyimides (4.69 and 4.70) and photodegrade quite rapidly upon exposure to UV radiation. The presence of oxygen is essential to the photolytic degradation process, which ultimately results in the oxidative ablation of thin polyimide films [995].

4.9 POLYBENZOXAZOLES

Polybenzoxazoles (4.73) are thermally stable polymers, whose possible use under space conditions as a transparent coating aboard spacecraft is restricted by their photodegradability [577].



This photodegradability, which results in a loss of optical properties (strong yellow coloration) is due to structural features of benzoxazoles as well to the presence of residual impurities from their synthesis (ketones, esters and amides).

4.10 POLYURETHANES

4.10.1 Aliphatic polyurethanes

The photodegradation of aliphatic polyurethanes with structure (4.74) is postulated to be similar to that of polyamides (cf. section 4.7.1) [1637, 2105, 2106].

Random chain scission occurs by the Norrish Type I reaction:



Photo-oxidative degradation is initiated by the abstraction of hydrogen from the methylene (--CH₂---) groups, then followed by the formation of a polymer peroxy (PO₂) radical and polymer hydroperoxide (POOH), the formation of a polymer oxy (PO') radical and its β -scission, and the formation of a hydroxyl group (POH):





The termination reaction of different (P^{\bullet} , PO^{\bullet} and PO_{2}^{\bullet}) radicals with each other causes crosslinking.

Polyurethanes based on dimethylglyoxime-hexamethylene diisocyanate (4.75) are rapidly degraded when exposed to UV radiation [987].

$$-O-N=R-N-O-C-NH-R'-NH-C-O-$$

$$(4.75)$$

The random chain scission occurs by photocleavage of the weak N—O bond $(53 \text{ kcal mol}^{-1})$. The photolysis mechanism has been studied using a low molecular weight model compound, i.e. benzophenone oxime-diphenyl urethane (4.76).



The photo-oxidative degradation of polyurethane-acrylate cured networks occurs mainly by the Norrish Type I photocleavage of the excited carbonyl groups from both carbamate and acrylate groups, which leads to main chain scission and the formation of imines, formates, amines and hydroperoxides [567].

4.10.2 Aromatic polyurethanes

The photodegradation mechanism of aromatic polyurethanes is generally much more complex than aliphatic polyurethanes, and the products obtained are difficult to separate and identify [12, 204, 567, 680–682, 689, 997, 999, 1003–1007, 1262, 1317, 1567. 1637, 1652, 1836–1838, 1901, 1902, 2105].

Polyurethanes with aromatic diisocyanates are more unstable with respect to light than those with aliphatic diisocyanates [1837, 1901, 1902, 2098]. The stability of the different polyurethanes follows the order:

diphenylmethane-4,4'-diisocyanate (4.77) < toluene-2,4-diisocyanate (4.78) < hexamethylene-diisocyanate (4.79):



(4.77)





The UV/VIS absorption spectra of the polyurethane based on diphenylmethane-4,4'-diisocyanate (4.77) is shown in Figure 4.11. Absorption peaks observed in the range 235–250 nm in aromatic urethane are due to (π, π^*) transition of the intramolecular charge-transfer complex of the urethane, and broad absorption peaks in the 280–290 nm region are due to the π, π^* transition of the lowest excited state of the aromatic nucleus in the urethane group.

The absorption spectra of polyurethane change during photoirradiation (Fig. 4.11). An absorption peak at 246 nm (due to intramolecular charge-



Fig. 4.11. Change in ultraviolet absorption spectra of polyurethane in tetrahydrofuran (THF) at different times of UV irradiation (min) [1652]. (Reproduced with permission from [1652]; published by Elsevier Science Publishers Ltd, 1971.)

transfer) decays and an isobestic point is observed at approximately 230 nm. This change is a result of photo-Fries rearrangement of the phenyl group [204, 680–682, 1003, 1004, 1736].



Yellow coloration can also be a result of the formation of monoquinone imide (4.80) and/or diquinone imide (4.81) [76, 567, 680-682, 1566-1568, 1898, 1900]:











It has been reported that the photo-Fries reaction occurs during irradiation with wavelengths < 340 nm, whereas formation of quinone structures takes place with wavelengths > 340 nm [680–682].

The random chain scission of aromatic polyurethanes occurs from the excited singlet state S_1 (π , π^*) [1652]; however, the triplet state T_1 (π , π^*) may also be involved [1643]. The excited singlet state (S_1) has an energy value of 98.6 kcal mol⁻¹ (fluorescence lifetime = 3.2 ns), whereas the triplet state (T_1) has an energy value of 76.7 kcal mol⁻¹ (phosphorescence lifetime = 2.9 s) [1652].

The random chain scission occurs mainly by the Norrish Type I reaction:



The main gaseous products are carbon monoxide (21%) and carbon dioxide (49%), though several other products are also formed (Table 4.5) [1644, 2098].

Photo-oxidative degradation of aromatic polyurethanes occurs in a very similar manner to that of aliphatic polyamides (cf. section 4.7.1).

Products Polotivo	CO ₂	СО	CH4	C_3H_8	C ₃ H ₁₀	HCN	others
yield (%)	49.9	21.0	12.6	2.9	8.7	0.4	5.4

 Table 4.5
 Gaseous photodecomposition of products of polyurethane [1644]

(Reproduced with permission from [1644]; published by John Wiley & Sons, Inc., 1975.)

Photodegradation of polyurethanes has also been studied using several low molecular weight model compounds such as *N*-ethyl carbamide, ethylphenyl carbamide, *N*-phenyl-substituted carbamino-acids and esters, and *N*-phenylcarbamide [204, 226, 997, 1644, 1905, 2133].

Laser flash photolysis of model compounds of diphenylmethane-4,4'diisocyanate based polyurethane low molecular weight model compounds, such as mono- and bis-carbamates, exhibits the formation of diarylmethyl radicals which readily react with oxygen. The formed polymer peroxy (PO₂) radicals abstract hydrogen and yield polymer hydroperoxides (POOH) [1000, 1001, 1003, 1006, 1007].

On the other hand, the photodegradation of segmented polyurethanes based on methylene 4,4'-diphenyldiisocyanate (MDI) is dependent on the physical structure of the polymer. Such segmented polyurethanes are formed from poly(ethylene oxide) (PEO) or poly(tetramethylene oxide) (PTMO) with various polyether polyols, which are chain extended with 1,4-butanediol (BDO) [680–682, 1006, 1321].



As the hard segment content of the polyurethane is increased, the photodegradation efficiency is lowered. In particular, the extent of photolytic decomposition is inversely dependent on the degree of hydrogen bonding in the aryl carbamate groups in the polyurethane backbone. The restrictive mobility imposed by hydrogen bonding is a critical factor which must be considered in the photochemistry of polyurethanes [1006].

The extent of degradation upon photolysis of polyurethanes decreases with increasing polymer stiffness and crystallinity [1004]. The extent of photodegradation is accelerated above the glass transition temperature (T_g) , indicating the role of chain flexibility and/or oxygen diffusion in the decomposition process [997].

The photodegradation of polyurethane elastomeric adhesives and its polyblends with poly(vinyl chloride), poly(vinyl alcohol), poly(vinyl acetate) and poly(vinyl acetate-co-vinyl chloride) [652], and rubbers based on poly-(diene urethanes) and poly(ether urethanes) has also been reported [1062].

Crosslinked polyurethane-acrylate elastomers are remarkably resistant to UV degradation [566].

4.10.3 Polyurethane coatings

Polymer coatings based on acrylic urethane and acrylic melamine products show, under UV irradiation, the formation of carbonyl groups followed by strong crosslink scission reactions [186–190, 731, 733, 734, 1478]. The rates of these processes are dependent upon polymer and crosslinker composition, the presence of additives and exposure conditions. For a given coating system, the rate of carbonyl growth correlates well with the rate of crosslink scission and both can be used as relative measures of the photodegradation. For most coatings, the rate of chemical change is almost constant after a brief exposure period. Photo-oxidation of coatings involve both free radical and non free radical processes.

It has been found that the photoinitiation rates of acrylic urethane and acrylic melamine coatings depend primarily upon the nature and concentration of chromophores that are incorporated into the acrylic copolymer during polymerization [731, 732]. The primary chromophores for conventional polymerization (peroxide and hydroperoxide initiators in ketone solvents) are ketonic end-groups [359, 735].

The rate of photo-oxidation in both urethane and melamine crosslinked coatings was found to be linear with hydroperoxide concentration [190, 1478]. In urethane coatings, the photo-oxidation rate reaches zero with zero hydroperoxide concentration whilst in melamine coatings there is a residual photo-oxidation rate at zero hydroperoxide concentration. This residual photo-oxidation appears to be related to melamine photochemistry.

4.11 POLYSULPHIDES

Poly(methylene disulphide), poly(methylene tetrasulphide), poly(ethylene disulphide) and poly(ethylene tetrasulphide) are photodegraded under UV irradiation with the formation of carbon monosulphide (CS), carbon disulphide (CS₂) and hydrogen sulphide (HS) according to the mechanism [1047, 1971]:

$$-SS-CH_2CHS \xrightarrow{h\nu} -SS-CH_3 + CS \qquad (4.202)$$

$$-SS-CHS - \xrightarrow{hv} -SSH + CS$$
(4.203)

$$-SS-CHS \xrightarrow{hv} -SH + CS_2 \tag{4.204}$$

The photolysis of the poly(methylene polysulphides) yields about 100 times more carbon disulphide than the poly(ethylene polysulphides) [1047].

The quantum yield of chain cleavage (ϕ_s) = 0.16–0.21 for poly(propylene disulphide), 0.19 for poly(propylene sulphoxide) and 0.05–0.09 for poly(propylene sulphide) [1971].

4.12 POLYSULPHONES AND POLYETHERSULPHONES

The photodegradation and photo-oxidative degradation of polysulphones (4.82) [4, 534, 536, 543, 585, 740, 741, 779, 1266, 1531–1533, 1701, 1745] and polyethersulphones (4.83) [4, 79, 1265, 1266] have been the subject of intensive studies. Both these polymers shows strong absorption in the range 250-300 nm (Fig. 4.12). During UV irradiation, chain scission, crosslinking and extensive yellowing occur. The development of this discoloration, shown in Figure 4.13, is probably due to the formation of a conjugated π -electron system. At the same time, samples become brittle, with decreased strength and elongation at break.



Photolysis of polysulphone (4.84) prepared from the polycondensation of bisphenols (e.g. 2,2-bis-(4-hydroxyphenyl)propane) with 4,4'-dichlorodiphenyl-sulphone occurs by the following mechanism [4, 79, 740]:







Fig. 4.12. Ultraviolet absorption spectra of: (a) polysulphone and (b) polyethersulphone. (Reprinted with permission from [1266], Pergamon Press Ltd, Oxford, England.)

UV irradiation in vacuum or in air (oxygen) yields a number of gaseous products (Table 4.6).

Sulphur dioxide undoubtedly arises after scission at the carbon sulphur linkage:

$$\xrightarrow{O}_{B} \cdot \xrightarrow{hv} \xrightarrow{V} \cdot + SO_{2}$$
 (4.209)



Fig. 4.13. Changes of ultraviolet absorption spectra of poly(ether sulphone) film $(100 \,\mu\text{m})$ during UV irradiation in air [79]. (Reproduced with permission from [79]; published by John Wiley & Sons, Inc., 1977.)

	Composition, vol %		
Constituents	Photolysed in vacuum	Photolysed in oxygen-enriched air	
Hydrogen	22.9	0.03	
Water	ND	ND	
Methane	1.9	0.14	
Ethane	Trace	ND	
Benzene	0.1	Trace	
Carbon monoxide	41.9	9.6	
Carbon dioxide	25.9	32.2	
Nitrogen	2.0	57.4	
Oxygen	2.3	0.02	
Carbonyl sulphide	2.6	0.01	
Sulphur dioxide	0.5	0.001	
Carbon disulphide	ND	Trace	

Table 4.6Gaseous products formed during 500 h UVirradiation of polysulphone [740]

ND = not detected

(Reproduced with permission from [740]; published by John Wiley & Sons, Inc., 1968.)

Carbonyl sulphide (COS) and carbon disulphide (CS₂) can be formed by the interaction of carbon monoxide and sulphur dioxide:

$$CO + SO_2 \longrightarrow COS + O_2$$
 (4.210)

$$6CO + 2SO_2 \longrightarrow CS_2 + 5CO_2 \tag{4.211}$$

Sulphur dioxide may decompose polymeric hydroperoxide groups (POOH) to polymeric peroxides (POOP) and/or polymeric esters of sulphuric acid (POSO₂OH):

$$POOH + SO_2 \longrightarrow POSO_2OH$$
 (4.212)

$$2\text{POSO}_2\text{OH} \longrightarrow \text{POSO}_2\text{OP} + \text{H}_2\text{SO}_4 \qquad (4.213)$$

$$POOH + POSO_2OP \longrightarrow POOP + POSO_2OH$$
 (4.214)

$$POOH + POSO_2OH \longrightarrow POOP + H_2SO_4$$
(4.215)

During the photolysis of polysulphones, oligomeric sulphonic acids may also form (4.85):



The polymeric sulphonyl radicals (PSO₂) formed by C—S bond cleavage can react with oxygen to give polymeric sulphonyl peroxy radicals (PSO₂OO'):

$$PSO_2 + O_2 \longrightarrow PSO_2OO^*$$
(4.216)

Reaction of polymeric sulphonyl peroxy radicals (PSO_2OO°) with polymer (PH) leads to the formation of polymeric sulphonyl hydroperoxides (PSO₂OOH):

$$PSO_2OO' + PH \longrightarrow PSO_2OOH + P'$$
(4.217)

Decomposition of this hydroperoxide yields polymeric sulphonic acid (PSO₂OH):

$$PSO_2OOH \xrightarrow{hv} PSO_2O' + OH'$$
(4.218)

$$PSO_2O' + PH \longrightarrow PSO_2OH + P'$$
 (4.219)

ESCA spectra of polysulphones (4.84) photo-oxidized in oxygen are shown in Figure 4.14. The increase in the intensity of the O_{1s} band with duration of photo-oxidation is accompanied by the appearance of an envelope of peaks to the high binding energy side of the main C_{1s} peak, and in the S_{2p} region. Oxygen doubly bonded to sulphur has a significantly lower binding energy than an acyl oxygen. This is consistent with the binding energy of 532.7 eV for the low binding energy component of polysulphone, which contains a contribution from the oxygens of the sulphoxide groups. For polysulphone, the doublet $(S_{2p3/2}$ and $S_{2p1/2})$ in the S_{2p} regions at 168.0 and 169.3 eV is due to sulphur, as it is in the unreacted polymer. The appearance



Fig. 4.14. ESCA spectra C_{1s} and O_{1s} core levels for polysulphone films UV irradiated in an oxygen atmosphere for varying periods of time [1701]. (Reproduced with permission from [1701]; published by John Wiley & Sons, Inc., 1981.)

of high binding energy components is indicative of the presence of more highly oxidized sulphur [1701].

Photolysis of polysulphones and polyethersulphones is accompanied by simultaneous chain scission and crosslinking, which proceed below and above T_g , but crosslinking is predominant above 170° C. The ratios of chain scission to crosslinking rates were found to be 4.5 for polysulphone and 6.0 for polyethersulphone in the early stage of photodegradation [1266]. Quantum yields of chain scission (ϕ_s) and crosslinking (ϕ_c) were found to be of the order of 1×10^{-4} for both polysulphones and polyethersulphones, and they are not greatly affected by the irradiation atmosphere or irradiation intensity [1265].

The rapid development of yellow coloration of polysulphone films has been used to monitor solar UV irradiation [534, 536, 543, 1745]. The basis of the method is that the absorbance of the film at 330 nm (Fig. 4.13) increases proportionally with the incident dose of UV radiation, below 320 nm.

4.13 POLYTHIOPHENES

Poly(3-alkylthiophenes) (4.86) and π -electron conjugated polymers exhibit high electrical conductivity in the oxidized state and fast third-order nonlinear optical activity in the neutral state. The presence of the alkyl side-chain both enhances solubility in common organic solvents and decreases the glass transition temperature.

Poly(3-alkylthiophene) undergoes chain scission in organic solvents when irradiated with UV/VIS light [958, 959]. Absorption of a photon and intersystem crossing results in the formation of an excited triplet state, which subsequently sensitizes (by energy transfer) the formation of singlet oxygen $({}^{1}O_{2})$. Singlet oxygen can attack the thienyl ring bonds at four positions. However, the predominant mechanism must involve ${}^{1}O_{2}$ addition at the 2-position of a 3-hexylthienyl unit in order to form a hydroperoxide, which upon photolysis leads to chain scission. Photolysis of the O—O bond yields the corresponding alkoxy and hydroxyl radicals. Chain scission then proceeds as a result of α -cleavage of the polymer alkyloxy radical (4.87):



Quantum yields of chain scission are dependent on the presence or absence of oxygen, the nature of the solvent and the wavelength of the incident light. Concurrent with photo chain scission is a photochemical 1,4-Diels-Alder addition of singlet oxygen:



Disruption of the π -system will lead to a diminished state of conjugation and consequently, a reduction in electronic conductivity and nonlinear optical activity.

4.14 PHOSPHAZENES

The main chain of poly(organophosphazenes) (4.88) consists of -P=Nbonds, which are very stable towards UV irradiation. However, photodegradation of phosphazenes occurs by photolysis of side-groups:

$$\begin{array}{c} R & R \\ -N = P - \xrightarrow{+h\nu} - N = P + R^{*} \\ | \\ R \\ (4.88) & (4.89) \end{array}$$

$$(4.225)$$

Reactions which appear during photodegradation are discoloration, changes in physical properties, formation of volatile products and in some cases, chain scission and crosslinking.

In the absence of oxygen, the phosphazene radicals (4.89) crosslink with each other:

Phosphazene radicals react easily with oxygen giving phosphazene hydroperoxides:



The chain scission reaction may occur by thermal and/or photodecomposition of the hydroperoxide (OOH) group [785]:



Free radicals (4.90) may also participate both in chain scission (4.231) and/or crosslinking (4.232 and 4.233) reactions:





or



However, the cleavage of -P-R or R-H bonds in a side groups in poly(organophosphazenes) is not a common photochemical behaviour. They occur in the case of phosphazenes having structures:

OR $-N = P - P - Where R = C_2H_5, CH_2CF_3, C_6H_5 [951, 1621, 1910]$ $R = C_{10}H_7 [785]$ $R = -C_6H_5 - CH(CH_3)_2 [781, 782, 1490]$

$$NH-R = N = P - where R = C_6 H_4 CH_3 [278, 786]$$

$$NH-R$$

In the case of poly[bis(4-benzoylphenoxy)phosphazene] (4.91), which contains the benzophenone chromophoric group, the photocrosslinking

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reaction occurs by the formation of pinacol structures (4.92) [783, 787]:



However, this reaction is also followed by a chain scission process. Both crosslinking and chain scission reactions can be inhibited by an energy transfer process between benzophenone groups and free or attached phosphazene naphthalene groups [784, 1489].

4.15 POLYSILICONES

The photodegradation and photo-oxidative degradation of different polysilicones include two main groups: polysilanes (section 4.15.1) and polysiloxanes (section 4.15.2).

4.15.1 Polysilanes

Polysilanes (4.93) are polymers which are rapidly photodegraded by UV irradiation, both in the solid state [172, 173, 898, 1392, 1393, 1486, 2099,

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2134, 2135, 2335] and in solutions [898, 1155, 1447, 1448, 1476, 1477, 2135, 2217].



Polysilanes have an intense absorption in the UV to near-UV region owing to the σ -delocalization along the linear Si—Si polymer backbone (Fig. 4.15). The photodegradation of polysilanes occurs by the random chain scission of the Si—Si bond with formation of very reactive silyl (4.94) radicals [1050]:



Fig. 4.15. Absorption spectra of: (a) poly(cyclohexylmethylsilane) and (b) poly-(phenylmethylsilane)-1 in tetrahydrofuran (THF). (Reprinted with permission from [2217]. Copyright (1992) American Chemical Society.)

$$R_{1} \qquad R_{1} \qquad H_{1} \qquad (4.237)$$

$$R_{1} \qquad H_{1} \qquad H_{2} \qquad H_{2} \qquad (4.237)$$

$$R_{2} \qquad R_{2} \qquad R_{2}$$

The quantum yield for the chain scission of poly(methylphenylsilane) in solution is $\phi = 0.97$, whereas in a thin film, $\phi = 0.17$ [2135]. The lower quantum yield of chain scission in a film, in comparison to that in solution, can be explained by the cage effect (in the solid), which hinders free motion and favours recombination of reactive sites so formed.

Polysilanes (e.g. poly(methylphenylsilane) and poly(methylpropylsilane)) (4.93), under UV irradiation in the presence of oxygen, are oxidized to polysiloxanes (e.g. poly(methylphenylsiloxane) (4.95) according to the mechanism [172]:



IR spectroscopy (Fig. 4.16) indicates changes in the absorption of silane (Si-Si) bonds at 800–700 cm⁻¹ and the formation of a new band at 1050 cm⁻¹, attributed to the siloxane (Si-O) bond. ESCA spectroscopy, especially, has the advantage of separating silane (Si-Si) bonds from siloxane (Si-O) bonds (Fig. 4.17). The Si_{2p} core level signal observed at 100.4 eV (Si-Si bonds) before irradiation, disappears after UV irradiation and a new signal at 102.9 eV (Si-O bonds) appears [172].



Fig. 4.16. IR spectra of: (a) poly(methylphenylsilane) before UV irradiation and (b) after photo-oxidation [172]. (Reproduced with permission from [172]; published by John Wiley & Sons, Inc., 1987.)



Binding energy

Fig. 4.17. ESCA spectra of O_{1s} core level of poly(methylphenylsilane): (a) original polymer; (b) after 1 min and (c) 5 min UV irradiation [172]. (Reproduced with permission from [172]; published by John Wiley & Sons, Inc., 1987.)

Silane copolymers which contain dimethysilane units (4.96) are rapidly photodegraded under UV irradiation [173, 2330]. When the copolymers were irradiated in an argon atmosphere some crosslinking took place with simultaneous chain scission. Copolymers with aryl groups attached to silicon undergo more photocrosslinking in argon than those without aryl substituents:



Photodegradable aramids based on 1,2-bis(*p*-aminophenyl)tetramethyldisilane and various aromatic diacid chlorides (4.97) have been investigated [1682].



Photolysis of poly(1,4-bis(dimethylsilyl)benzene) (4.98), [1050, 1552] poly(1,4-bis(dimethylsilyl)naphthalene (4.99) [1311], poly(2,5-bis(dimethylsilyl)furan) (4.100) [986] and poly(2,5-bis(dimethylsilyl)thiophene) [1021] in benzene-methanol solution results in a rapid degradation of these polymers, according to the mechanism:



Poly(o-(trimethylsilyl)-phenylacetylene) is highly stable against photodegradation in film and in organic solvents; however rapid degradation occurs in chlorinated solvents such CHCl₃ or CCl₄, via the formation of chargetransfer complexes between the polymer and solvents [1562].

Photodegradation of polysilanes has been used for the production of photoresists [172, 2335].

4.15.2 Polysiloxanes

UV irradiation causes rapid degradation of polysiloxanes, but its extent depends on the type of side-group substituents [333, 569, 1485, 1987, 2267].

The main reaction in the case of polydimethylsiloxane (4.101) is photocleavage of side methyl groups and the formation of very reactive silyl radicals (4.102) [569, 1402]:

which can abstract hydrogen from the methyl group and participate in crosslinking:



The silyl (4.103) radical may also react with oxygen, giving a polysilylperoxy radical which abstracts hydrogen from a methyl group, and gives polysilyl hydroperoxides:

$$\begin{array}{c}
\dot{O}\\
\\
O\\
\\
\dot{O}\\
\\
O\\
\\
O\\
\\
O\\
\\
CH_{3}\\
CH_{3}\\
(4.103)
\end{array}$$

$$(4.247)$$



The photocleavage of polysilylhydroperoxides yields polysilyoxy radicals

(4.104) which abstract hydrogen giving polysilanols (4.105):



In the presence of oxygen, the methylene side radical $(-CH_2)$ is also simultaneously oxidized [569]:





Poly(dimethylsiloxane) oils with a high content of silicon hydride, (-Si-H) groups located inside the chain (4.106) and/or at the end of the chain (4.107) are much more unstable towards UV irradiation than the corresponding poly(dimethylsiloxanes) [1053].



Silicon hydride groups (—Si—H) react easily with free radicals (R' or ROO') producing very reactive silyl radicals (—Si'), which react with oxygen, finally producing polysilyl hydroperoxides (4.108):

$$\xrightarrow{|}_{\text{Si}} H \xrightarrow{+R'(ROO')} \xrightarrow{|}_{\text{Si}} + RH(ROOH)$$
(4.258)

$$\xrightarrow{|} O_{2} \xrightarrow{|} O_{2} \xrightarrow{|} OO^{*} \xrightarrow{+PH} \xrightarrow{|} OOH + P^{*}$$

$$(4.259)$$

$$(4.108)$$

Polysilyl hydroperoxides (4.108) are thermally stable up to 65°C and are easily

decomposed, by UV irradiation, to form polymersilyloxy (4.109) radicals:

$$- \stackrel{|}{\underset{|}{\text{Si}}} - \text{OOH} \xrightarrow{hv} - \stackrel{|}{\underset{|}{\text{Si}}} - \text{O'} + \text{OH}$$
(4.260)
(4.109)

Polymersilyloxy radicals can abstract hydrogen from silicone hydride groups (-Si-H) producing polysilanols (4.110) and polysilyl radicals (4.111):

Polysilanols can further participate in condensation reactions:

$$2 \xrightarrow{|} OH \xrightarrow{|} Si \xrightarrow{|} O \xrightarrow{|} H_2O \qquad (4.262)$$

$$- \underbrace{Si}_{i} - OH + - \underbrace{Si}_{i} - H \longrightarrow - \underbrace{Si}_{i} - O - \underbrace{Si}_{i} - H_{2} \qquad (4.263)$$

Increasing viscosity and finally gel formation have been attributed to the formation of tridimensional polysiloxanes:

$$\begin{array}{c} CH_{3} & CH_{3} \\ | & \\ -O - Si - O - \frac{h_{\nu}}{+O_{2}} - O - Si - O - \\ | & \\ H & O \\ | & \\ \end{array}$$
(4.264)

or a polycondensation reaction between end Si-H and Si-OH groups.

Poly(dimethylsiloxane) oils containing vinyl groups inside the chain (4.112) and/or at the end of the chain (4.113) undergo rapid degradation according to the mechanism [1052]:





UV irradiation of poly(methylphenylsiloxane) (4.114) [1986], poly(hexylmethylsilane) (4.115) and poly(cyclohexylmethylsilane) (4.116) [579] causes chain scission and crosslinking processes. In the case of poly(methylphenylsiloxane) (4.114) very small amounts of different gaseous products with low quantum yields ($\phi_{H_2} = 2.6 \times 10^{-5}$, $\phi_{CH_4} = 0.63 \times 10^{-5}$, $\phi_{C_2H_6} = 0.12 \times 10^{-5}$ and $\phi_{C_2H_2} = 0.06 \times 10^{-5}$) are formed [1986].



Polysiloxanes with phenyldisilanyl groups (4.117) are photocleaved under UV irradiation, with the formation of very reactive silyl radicals (4.118) which can easily abstract hydrogen from methyl groups [1051, 1551]:



The polymeric radicals (4.118) and (4.119) effectively form crosslinked structures.

Photodegradation of poly(pentamethyldisylyl)styrene sulphone (4.120) occurs with the evolution of SO₂ and depolymerization reactions [2218]:





The different polymer endalkyl radicals thus formed terminate each other, giving strongly crosslinked structures.

4.16 POLYELECTROLYTE SOLUTIONS

It has been reported that the viscosities of aqueous solutions of a number of polyelectrolytes, such as sodium salts of poly(acrylic acid), carboxymethyl cellulose and copolymer of maleic and vinyl acetate, decrease rapidly when they are UV irradiated, due to chain scission reactions [1049].

4.16.1 Zwitterionic polymers

Water soluble zwitterionic polymers (4.121) and (4.122) that contain reactive thiosulphate groups, undergo sulphur-sulphur cleavage, under UV irradiation and lose their water sensitivity [1002].

$$\begin{array}{cccc} OH & OH & OH & OH \\ H_2 \overset{+}{N} - \begin{pmatrix} CH_2 CHRCHCH_2 \overset{+}{N}H \\ - \end{pmatrix}_m CH_2 CHRCHCH_2 \overset{+}{N}H_2 \\ CH_2 CH_2 SO_3^- & CH_2 CH_2 SO_3^- & CH_2 CH_2 SO_3^- \\ & (4.121) \end{array}$$



where:



4.17 POLYPYRROLE – SEMICONDUCTING POLYMER

Polypyrrole (4.123), a semiconducting polymer, is rather stable towards UV irradiation, which can even increase its conductivity. However, the stability of polypyrroles against UV irradiation depends on the type of dopant present in the polymer [1520]. Tetrafluoroborate doped polypyrrole (4.124), when exposed to UV radiation, shows a rapid deterioration of electrical conductivity, with a conductivity loss ratio of 0.62 after exposure for 90 h. During the irradiation, polypyrrole tetrafluoroborate undergoes a dedoping reaction, whereby tetrafluoroborate ions decompose to fluoride ions and volatile boron trifluoride gas.



Polypyrroles doped with perchlorate or with *p*-toluenesulphonate show high resistance to exposure to UV radiation for up to 90h.

4.18 NATURAL POLYMERS

4.18.1 Wood

Wood, textiles and paper consist of lignocellulose, which is a polymer blend of cellulose and lignin. Lignocellulosic products are more or less rapidly photodegraded on exposure to sunlight or outdoor conditions, i.e. weathering.

Wood, a lignocellulosic polymer composite, contains a fibrous structure of cellulose, hemicellulose, and a three-dimensional network of lignin and several extractives (Table 4.7). Figure 4.18 shows the chemical components of a typical softwood cell wall [650].

	Percentage composition		
	Softwood (coniferous)	Hardwood (deciduous)	
Cellulose	43	43	
Hemicellulose	~ 28	~ 38	
Lignin	23-33	16-25	
Extractives	5-8	2-4	
Ash	~1	~1	





Fig. 4.18. Chemical components in a typical softwood cell wall (values are given as percentages) [650]. (Reprinted with permission from [650]. Copyright (1990) American Chemical Society.)

Wood is an excellent absorber of UV radiation, terrestrial sunlight and visible light, which can initiate photochemical reactions. However, UV radiation is unable to penetrate into wood by more than 75 μ m, and visible light can penetrate to only 200 μ m. Under exposure to UV radiation, rapid discoloration of the wood surface occurs, accompanied by the loss of gloss, roughening and checking. Photo-oxidative degradation of wood occurs mainly at the surface; however, products of photochemical reactions may attack the underlying layers [650, 981, 985].

Quinoid structures which are present in the lignin structure are largely responsible for the absorption of light by wood (cf. section 4.18.4).

Under UV irradiation, the lignin content decreases, with a continuous increase of acidity and carbonyl group concentrations. Carbon monoxide,
carbon dioxide, hydrogen, water, methanol, formaldehyde, organic acids, vanillin and siringaldehyde are the major low molecular weight products. Chemical changes also take place in the polysaccharide portions of wood. The chemical changes in cellulose and lignin cause loss of mechanical properties and discoloration [981].

4.18.2 Paper

Yellowing of paper under UV irradiation is a result of photo-oxidation of hemicellulose, which includes xylan and glucomanan [773, 981, 1859]. A seven-line ESR spectrum has been recorded during UV irradiation of xylan [968]. The photolytic chain scission of hemicellulose may occur either at the end of the molecule or in the middle of the chain. Hemicellulose can yield monosaccharides after photoirradiation, followed by transformation into coloured materials.

4.18.3 Cellulose

Cellulose is a polysaccharide built of β -D(+)-glucose units (4.123) joined in linear chains, which forms fibrous structures.

Polymers based on cellulose includes native cellulose (wood and cotton), regenerated cellulose (viscous rayon) and cellophane. There are many cellulose derivatives such as cellulose acetate, cellulose carboxymethylate, hydroxyethyl cellulose, methyl cellulose and ethyl cellulose.

Theoretically, pure cellulose should not have an absorption spectrum. A typical cellulose absorption spectrum is shown in Figure 4.19. The absorption



Fig. 4.19. Ultraviolet absorption spectra of cellulose film: (----) before and (\cdots) after 2h UV irradiation. (Reproduced with permission from [981]; published by Chapman and Hall, 1981.)

band at 260 nm has been attributed to the presence of internal chromophoric groups such as acetal or glycosidic linkage. The prolonged tail absorption up to 400 nm can result from the presence of external chromophoric groups such as carbonyl, carboxylic and/or hydroperoxide, which were formed during chemical oxidation and mechanical degradation of wood [968, 1323]. It is almost impossible to isolate cellulose in its pure form.

Photodegradation and photo-oxidation of cellulose have been reviewed in detail elsewhere [191, 604, 650, 981, 1499, 1719].

Photodegradation of cellulose does not occur in vacuum at wavelengths longer than 340 nm [968]. However, in the presence of oxygen, photo-oxidative degradation occurs by solar irradiation [603, 977, 978]. Cellulose is rapidly photodegraded, both in vacuum and in air, during UV irradiation with wavelengths below 340 nm.

ESR spectroscopy of free radicals formed in UV irradiated cellulose has been the subject of many publications [192, 968, 969, 971, 973–976, 980, 981, 1466, 1467, 1616, 2311]. The ESR spectrum of cellulose shown in Fig. 4.20 can be resolved into following signals [971, 980]:

- doublet with 508 G splitting;
- doublet with 129 G splitting;
- doublet with 43 G splitting;
- triplet with 34 G splitting;
- quarter with overall width 88 G;
- doublet with 24 G splitting;
- singlet signals.

Table 4.8 describes the structures indicated by the different signals observed in an ESR spectrum of cellulose.

The ESR signals observed in UV irradiated cellulose are also present in cellulose derivatives when exposed to light (Table 4.9).

The lines shapes and intensities of ESR spectra depend very much on cellulose morphology [975] and reflect differences in the molecular arrangements and lattice types of various cellulose samples.



Fig. 4.20. ESR spectrum of free radicals formed in cellulose UV irradiated (253.7 nm) at 77 K [980]. (Reproduced with permission from [980]; published by John Wiley & Sons, Inc., 1979.)

•)	
Radical structure	Spectral characteristics	References
CH-0•	Singlet with a line width of 15 gauss	1467, 2311
ĊH	Doublet with a splitting of 23–24 gauss	2165
-0, 	Doublet with a splitting of 17 gauss due to the interaction between the unpaired electron of carbon and hydrogen	582
$\begin{array}{ccc} 0H & -CH - OH \\ -O & CH - and & -CH \\ -\dot{C} & CH - & CH \\ -\dot{C} & CH - & CH \\ OH & OH \end{array}$	These radicals yield triplet spectra due to the α protons, with a splitting of 34–35 gauss	1263
-cH - cH	These radicals yield doublet spectra and exhibit a hyperfine splitting about 43 gauss and a total line width of $68-70$ gauss	1616

Table 4.8 ESR spectra of free radicals formed during UV irradiation of cellulose

(Reproduced with permission from [981]; published by Chapman and Hall, 1981.)

Ta	ble 4.9 Ide	entified radica	als, obtain	ed during irra	adiation of:
(1)	cellulose;	(2) cellulose	acetate;	(3) cellulose	triacetate;
(4)	glucose; (5)) cellobiose; (6) cellobios	e octaacetate;	(7) maltose;
(8)	maltotrios	se and (9) star	ch [1467]		

Compounds	Recorded ESR sig	nals
~	1, 2, 3, 6, 7, 8, 9	singlet
o-↓o	1, 2, 3, 4, 5, 6, 7, 8, 9	singlet
·	1, 2, 3, 6, 7, 8, 9	doublet
└-o	1, 2, 3, 6, 7, 8, 9	triplet
CH ₃ •	2, 3, 5, 7	quartet

The photodegradation processes involved in cellulose are chain scission, dehydroxylation, dehydroxymethylation and dehydrogenation, which are responsible for the formation of different radicals [575, 618, 1254, 1466, 1467, 1499]:



Free radicals are also formed by chain scission reactions [1466, 1467, 1499]:



The formation of cellulose peroxy radicals (POO') was confirmed by ESR spectroscopy [970, 979, 1549].

The photo-oxidative degradation of cellulose is accelerated by moisture [576, 966, 975]. Water may play an important role in the formation of free radicals, which subsequently lead to degradation and yellowing of cellulose. At higher concentration of moisture (5-7%), the ESR signal intensities increase rapidly. The moisture content in the range of 5-7% represents the amount of water chemically bound in cellulose fibre. At moisture contents greater than 5-7%, the presence of water changes the semicrystalline structure of cellulose and the proportion of amorphous regions increases. Under UV irradiation, free radicals in cellulose are formed only in the amorphous regions. At moisture contents less than 5-7%, the amount of bound water, and hence the proportion of semicrystalline. The photodegradability of cellulose is heavily dependent upon its morphology [975]: the crystalline region is impervious to UV radiation.

Cellulose is oxidized during chemical and mechanical processing and storage [604]. The oxidation products of cellulose and traces of inorganic (metal salts) [972, 981] and organic impurities can photoinitiate and/or photosensitize the cellulose oxidative degradation mechanism. Depending on the types of these products and impurities, the mechanisms of photoinitiation of cellulose photo-oxidative degradation may differ significantly [967, 981].

Ozone remarkably accelerates the UV degradation of carboxymethyl cellulose [1041].

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Photodegradation (photo-oxidative degradation) of other cellulose derivatives such as:

- cellulose acetate and cellulose triacetate [1467];
- cellulose nitrate [983];
- acetyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropylmethyl cellulose, methyl cellulose and ethyl cellulose [530, 1467];
- oligosaccharides (glucose, glucose pentaacetate, cellobiose, cellobiose acetate, maltose and maltotriose [984];
- acetylated and phenyl hydrazine modified cellulose [1124];
- poly(methyl methacrylate) grafted cellulose and polystyrene grafted cellulose [980];

have been investigated by several authors.

4.18.4 Lignin

Lignin (4.124) has a basic structure that contains twelve coniferyl units [792]:



(4.124)

Lignin is an excellent light absorber; its absorption spectrum (Fig. 4.21) extends, with a tail, to over 400 nm.



Fig. 4.21. Ultraviolet absorption spectrum of lignin. (Reproduced with permission from [981]; published by Chapman and Hall, 1981.)

The photochemistry of lignin has been a subject of many publications [398-402, 605, 981, 1563, 1564, 2180].

Lignin always contains a small amount of stable phenoxy radicals, which



Fig. 4.22. ESR spectra of lignin UV irradiated (253.7 nm) at: (----) ambient temperature and $(-\cdot-)$ at 77 K. The dotted line signal is due to the naturally occurring free radicals in lignin. (Reproduced with permission from [981]; published by Chapman and Hall, 1981.)

may be generated during sample preparation, handling or storage in the presence of light. These stable free radicals give a singlet line ESR spectrum, characteristic of oxy radicals (Fig. 4.22).

During UV irradiation of lignin several other free radicals are formed, which were detected by ESR spectroscopy [981]. Because of the very complicated structure of lignin (4.124) it is difficult to identify the free-radical sites formed. The reactive groups available in lignin consists of various types of ether, primary and secondary hydroxyl groups, carbonyl groups, carboxyl and ester functions. There also exist a number of aromatic and phenolic sites where free radicals can be formed.

Because of the complexity of lignin structure, a number of the following lignin model compounds (containing phenolic and carbonyl functions) have been photolysed [33, 981, 2180]:



Computer modelling of the photoreactions of two other lignin model compounds, i.e. *tert*-butylguaiacylcarbinol (4.125) and *p*-methoxypropiophenone (4.126) shows the existence of 29 elementary reactions from 91 elementary steps with 58 different species formed [2164]:



Several important facts were elicited about the photodegradation of lignin from these model compound studies [981]:

- 1. Phenoxy radicals are readily produced from phenolic hydroxygroups by the action of light.
- 2. Phenoxy radicals are further transformed to *ortho*-quinoid structures which are responsible for the yellowing of lignin:



- 3. Carbon-carbon bonds adjacent to α -carbonyl groups are photodissociated via the Norrish Type I reaction.
- 4. The Norrish Type I reaction does not occur efficiently in those compounds with ether bonds adjacent to the α -carbonyl group. Photodissociation takes place at the ether bond.
- 5. Compounds bearing benzoyl alcohol groups are not susceptible to photodissociation, except when photosensitizers are present.
- 6. α -Carbonyl groups function as photosensitizers in the photodegradation of lignin.

Polyhydroxy structures formed by demethoxylation of the lignin portion of jute in sunlight, and the subsequent formation of quinone structures, are responsible for the discoloration of jute [351, 1304].

4.18.5 Wool

The exposure of wool keratin to sunlight results in a number of physical and chemical changes [166, 1576].

Wool and hair fibres consist mainly of keratin, which consists of polypetide chains bound by salt linkages between the functional groups of the amino acids (4.127) and by cystine (S-S) linkages (4.128):



The amino acid composition of wool fibres is given in Table 4.10. For different animal fibres, the cystine content of the keratin varies, but it is higher than in any other protein. There are differences in the structural positions of the amino acids in the keratin between the hair from different animal species, and also along the fibres.

Type of side chain	Acid	Mol%
Hydrocarbon (or hydrogen)	Glycine	10.5
	Alanine	5.4
	Valine	4.8
	Leucine	9.8
	β -Phenylalanine	2.6
Hvdroxy	Serine	11.0
5 5	Threonine	6.2
	Tyrosine	3.3
Acidic	Aspartic acid	6.1
	Glutamic acid	12.4
Basic	Lysine	2.2
	Arginine	8.4
	Histidine	1.0
Sulphur-containing	Cystine	10.3
1 8	Methionine	0.4
Heterocyclic	Proline	4.6
	Tryptophane	1.0

 Table 4.10
 The amino acid composition of wool [1461]

The absorption spectrum of wood (Fig. 4.23) depends very much on its origin, i.e. the composition of different amino acids. The absorption at 250-300 nm is due essentially to the presence of the amino acids tyrosine (4.129) and tryptophan (4.130), with minor contributions from cystine (4.131) and phenylalanine (4.132) [1576, 1578].

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Fig. 4.23. Ultraviolet absorption spectrum of merino-wool keratin [1578].



Under UV and even solar radiation wool becomes yellow. The degree of yellowing very much depends on the wavelength of radiation used [1287, 1324]. Much more extensive yellowing occurs in summer than in the winter months.

Oxygen plays an essential role in the yellowing of wool [1578]. Irradiation of dry wool in the absence of oxygen produces a green coloration, probably due to the formation of thiyl free radicals. On exposure to atmospheric oxygen these radicals decay, and the green colour of the wool turns to yellow [1324]. The presence of water vapour enhances yellowing; thus wet wool yellows much more rapidly than dry wool [1488].

Wool exhibits a weak fluorescence which can origin from tryptophan (4.130) [765, 1239]. The disulphide bonds present in wool are responsible for at least 50% quenching of wool's fluorescence [1305]. The phosphorescence observed in wool also originates from tryptophan [765, 1239, 1306, 1578].

During photo-oxidative degradation of wool several amino acids are formed, and the main photocleavage occurs between the side amino acid groups and the main chain [153, 965, 1469, 1470, 1578]. Determination of the free radicals so formed by ESR spectroscopy is difficult, due to a lack of distinct hyperfine structure in the resulting spectra [1684–1686, 1886].

The most widely accepted theory of wool yellowing proposes the photooxidation of the tryptophan groups (4.130) to yellow coloured N-formylkynurenine (4.133) and kynurenine (4.134) [964, 1576]:



In spite of considerable study, the mechanism of wool photo-oxidative degradation has not been fully elucidated.

4.18.6 Leather

Leather is an important natural polymer undergoing ageing when exposed to light, heat, oxygen, water and metal ions [167]. Degradation of collagen and changes in the mechanical properties of leather are the consequences of photo-oxidative processes. The ageing is influenced by the tanning process, by changes of pH due to chemical degradation and by losses of fat due to extraction or blooming.