CHAPTER I

DEGRADATION AND STABILIZATION OF ALIPHATIC POLYAMIDES

1.1 Introduction

Polymers bearing recurring amide groups in their backbone are defined as polyamides. Aliphatic polyamides can be synthesized by condensation of bifunctional monomers. The two principal commercial polyamides are poly(hexamethylene adipamide) [nylon 66] and polycaprolactam [nylon 6] widely used for variety of applications. Reactions of numerous combinations of diacids, diamines and amino acids have been reported and copolymers having various proportions of these have been prepared.

Carothers and co-workers[1] synthesized first high molecular weight polyamides. Nylon 66 was selected for furthers development because of its well-balanced properties and manufacturing cost. In 1937 samples of this polyamide fiber were made into experimental stockings. Plant scale manufacturing nylon was started in 1939 and nylon hosiery was put on general sale in 1940.

1.1.1 Aliphatic polyamides

Aliphatic polyamides are versatile engineering plastic and excellent fiber materials. As per their application aliphatic polyamides are categorized in two divisions: polyamide fibers and polyamide thermoplastics.

1.1.1.1 Polyamide fibers

Polyamide fibers are generally manufactured by melt-spun process. In melt spinning, molten polymer is delivered from an extruder or a metal-grid melter, through a filter to a meter pump. Molten polymer is then metered to the pack, which is a combination of small filter and spinnret. Molten filaments, coming out from the spinnret, pass into a vertical chimney where they are air-cooled and solidify.
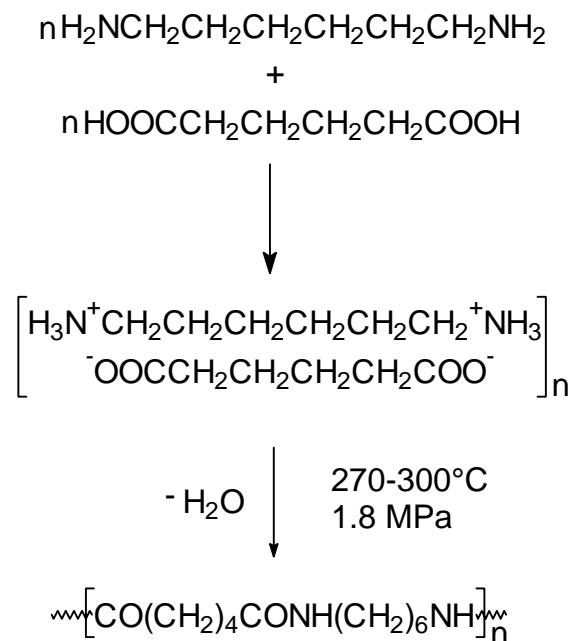
Nylon filaments are mainly used in carpets, apparel, tire reinforcement and in other industrial applications. Nylons are versatile fibers used in racing car tires and airplane tires owing to their excellent strength, adhesion to rubber and fatigue resistance in these demanding applications. Molecular weight, in case of nylon 66 fibers, is in the range of 12000 to 15000 for apparel fibers and 20000 for tire yarn is preferred.

1.1.1.2 Polyamide thermoplastics

Polyamides are important engineering plastics because of their toughness over wide range of temperatures. Also they have good resistance to impact and abrasion,

organic solvents and petroleum products. Polyamides can be processed by commonly used processing techniques for other thermoplastics, like injection molding, extrusion, blow molding etc. Due to their hygroscopic nature and hydrolytically unstable properties, polyamides are well dried before melt processing.

Thermoplastic polyamides are used in many automotive applications such as gears, bearings etc. Reinforced nylons are used for exterior body compartments such as fender extensions, decorative louvers, filler plates, head lamp housings, cross-over panels and many other applications. In electrical and electronic area, nylons are used in making plugs, sockets, switches, recelators and connectors. Nylon is commonly co-extruded with polyethylene for food packaging where the oxygen barrier characteristics of nylon and moisture barrier capabilities of PE are required. Other applications include shoes, ski boots, combs, bicycle wheels, cigarette lighters, racket frames, propellers, fans and toys.

$$n\,H_2NCH_2CH_2CH_2CH_2CH_2CH_2NH_2$$
$$+$$
$$n\,HOOCCH_2CH_2CH_2CH_2COOH$$

$$\left[\begin{array}{l} H_3N^+CH_2CH_2CH_2CH_2CH_2CH_2{}^+NH_3 \\ {}^-OOCCH_2CH_2CH_2CH_2COO^- \end{array}\right]_n$$

$$-H_2O \quad \Bigg| \quad \begin{array}{l} 270\text{-}300°C \\ 1.8\ MPa \end{array}$$

$$\sim\!\!\!\left[CO(CH_2)_4CONH(CH_2)_6NH\right]_n\!\!\!\sim$$

1.1.2 Methods of synthesis

Polyamides are synthesized by two main methods, a) is polycondensation of diacid and diamine and b) ring opening polymerization of lactams. Nylon 66 is manufactured[2, 3, 28] by a condensation reaction between hexamethylene diamine and adipic acid. In first step, hexamethylene diamine salt of adipic acid is prepared.

Solution of this salt is adjusted to proper pH and concentrated by evaporation of water. Concentrated solution is then charged to an autoclave. Polycondensation is carried out by increasing temperature and pressure to 250-300°C and 1.8 MPa. Water formed during this process is continuously removed. After completion of polymerization reaction, the molten polymer is discharged in the form of strands or sheet, which are cooled and cut in pallets.

1.2 Degradation of polymers

Aliphatic polyamides are excellent fiber materials and versatile engineering thermoplastics. Owing to their demanding applications, polyamides are often used in adverse environment where they are subjected to a variety of forces of degradation.

The degradation of polymers involves several chemical and physical processes accompanied by small structural changes, which lead to significant deterioration in useful properties of the polymeric materials. Degradation is an irreversible change, resembling the phenomenon of the metal corrosion. Degradation of the polymers is a very crucial aspect, which affects their performance in daily life. Throughout the life of a polymer, it encounters different kinds of degradation at various stages starting from the reactor where a polymer is synthesized, in extruder where it is processed, during service life and after its failure when it is discharged into the environment. The knowledge of the degradation mechanism has led to development of more efficient stabilizers[4-6] for better stabilization. On the other hand this knowledge also helped for development of some sensitizers to produce degradable plastics. A new emerging field, controlled degradation of commodity polymers is gaining much more importance these days[7-9]. Many useful products like, well defined telechelic oligomers and even monomers recoveries could be achieved by using the phenomenon of controlled degradation.

Thus, degradation of polymers is always not an unwanted phenomenon. Enough care has to be taken to check it otherwise it can be harmful to performance of a polymer and can lead even to safety hazards of fire and toxicity but if properly controlled, it can be used for producing new and better materials.

1.3 Manifestation of degradation

Effects of degradation on polymers may be assessed from the following

(i) Change in chemical structure:

Natural weathering is normally an oxidative degradation which produces hydroperoxy, hydroxy, carbonyl groups and cross-linkings, which can be detected by IR, UV and NMR spectroscopy.

(ii) Change on surface:

Most of the oxidative degradations take place at the surface of polymeric material because oxidative processes are more intense at surface due to greater availability of oxygen and high temperature. Thus a brittle outer layer is formed on polymer surface due to weathering and with the help of SEM or optical microscopy it can be observed.

(iii) Embrittlement: Many degradation processes cause embrittlement in polymers, which can be easily examined manually.

(iv) Generation of free radicals: Almost all the degradation processes are free radical reactions and generation of various types of free radicals can be detected by electron spin resonance spectroscopy.

(v) Change in molecular weight: Reduction in molecular weight due to chain scission processes is commonly observed phenomenon during degradation of polymers. Viscosity measurements and GPC are the commonly used techniques to study this aspect of polymer degradation.

(iv) Loss in mechanical properties: Change in chemical structure and chain scission processes are reflected in the loss in mechanical properties of a degraded polymeric material.

(vii) Impairment of transparency: This can be observed even manually that transparent polymeric material loses its transparency upon degradation. This is due to formation of different morphology upon degradation. This results in heterogeneity in bulk of a polymeric material, which scatters incident light rather than transmitting it. Eventually polymeric material loses its transparency.

1.4 Types of degradation

Based on the factors causing the degradation, various types of degradations are defined as follows:

1.4.1   Thermal degradation

Almost all polymers undergo thermal oxidative degradation[10-12] by the influence of heat. Thermal effects during service life significantly affect this phenomenon. If the

processing conditions are not well controlled, thermal effects prevailing during polymer processing can also cause significant degradation to polymers.

1.4.2 *Photo-oxidative degradation*[13-15]

In many polymeric materials chemical bonds can be cleaved by UV radiation of solar spectrum leading to their photodegradation. Many chemical processes start along with bond cleavage and one of the most important process is the oxygen attack on free radical formed as a result of bond cleavage. Thus, the degradation in presence of oxygen is mainly photo-oxidative degradation.

1.4.3 *Hydrolytic degradation*

Many polymers, mainly synthesized by polycondensation method, undergo hydrolysis and lead to degradation of polymeric material by scission of polymer backbone[16-18]. Polymers such as polyesters, polyamides, polycarbonates and polyacetals are prone to hydrolytic degradation which is caused in moist or acidic conditions present in the environment.

1.4.4 *Chemical degradation*

Most of the polymers undergo chemical degradation upon exposure to corrosive liquids and gases. Ozone, atmospheric pollutants (such as nitric oxide, sulfur oxides), acids like hydrochloric, nitric and sulfuric can attack and degrade most polymers.

1.4.5 *Mechanochemical degradation*

Mechanical energy applied in shear during melt processing of polymers can be converted into main chain bond energy resulting in bond scission and thus macro-radicals are formed. Owing to their reactive nature, macro-radicals react with oxygen and lead to further degradation processes[19-21]. This entire phenomenon is known as mechanochemical degradation.

1.4.6 *Radiation induced degradation*

In many polymers, energy transferred by gamma or electron radiation leads to severe degradation as manifested in post-irradiation embrittlement, discoloration and thermal instability[22-24]. This is an acute problem during the fabrication of disposable syringe barrels where embrittlement or lake of transparency can not be tolerated. It has been also found that packing material used in nuclear reactors are also prone to such kind of degradation.

1.4.7 Biodegradation

Biodegradation is a process by which enzymes produced by bacteria, fungi and yeast convert long polymer chains into small organic molecules, which in turn are consumed by these microorganisms as carbon source[25-27].

While most synthetic polymers are not biodegradable some additives may act as hosts for biodegradation. Enhanced photo-oxidation of polymers may also increase their biodegradability.

1.4.8 Degradation due to natural weathering

Depending on their composition, all polymers degrade to different extents when subjected to long term exposure to weather[29-31]. Natural weathering encompasses the effects almost all types of degradation. UV radiation is one of the important factors in weathering induced degradation. Apart from it, other climatic factors like rain, wind, thermal shock and air pollutants play a significant role in degradation.

1.4.9 Metal induced degradation

Metallic compounds present either as impurities (e.g. polymerization catalyst residues) or as additives, cause extensive degradation of polymers[32-33]. Copper wires are found to increase degradation of polyolefinic insulation for electrical cables. However, certain metallic compounds are well-reported stabilizers for polyamides and many other polymers.

1.5 Degradation of aliphatic polyamides

Prati[34] observed a decrease in intrinsic viscosity during UV degradation of nylon 66 at 128°C in acidic medium. The decrease in Huggin's constant is due to a decrease in solubility that indicated cross-linking. Bolton and Jackson[35, 36] found a decrease in breaking strength and extensibility and an increase in fluidity upon photo-oxidative degradation of nylon polymers. Nylon 66 photodecomposition[37] at long (365 nm) and short (253.7 nm) wavelengths has been studied. Long UV radiation can cause photodegradation in the presence of oxygen while short UV radiation can degrade nylon 66 in the absence of oxygen. Bernard *et al.*[38] found little increase in crystallinity on UV irradiation of nylon 66. The UV-irradiated samples were attacked more easily by water and alcohol. The UV-degraded nylon samples at room temperature did not impart any yellowing but when heated at 140°C imparted yellowing[39]. An increase in carboxylic groups and a decrease in amino groups was

found in yellowed samples. Yellowing is probably due to pyrrole formation during photo-degradation or thermal degradation. Stephenson et al.[40] studied the relative efficiencies of different wavelength of UV radiation in causing photoreactions in polymers upon irradiation in inert atmosphere. UV radiation of three different wavelengths was used for studies; 224 nm, 314 nm, and 369 nm. In case of other polymers, the lower wavelength radiation caused maximum deterioration too the mechanical properties of the polymer. However, data results were inconsistent in case of nylon 66. Nevertheless, the shorter wavelength band produced the greater changes in physical properties. In another study of this series they studied the effect of atmosphere during photo-irradiation of nylon 66. They observed that nylon degrades fast in presence of nitrogen than they do in vacuum, but not as fast as when irradiated in oxygen. They also calculated scission-to-crosslinking ratio for a variety of irradiation conditions. This ratio was found less for film samples (0.6) in comparison to fiber samples (1.17).

The acid hydrolysis[42] of photodegraded nylon 66 showed traces of acetic acid, propionic acid, butanoic acid, malonic acid, succinic acid, glutaric acid and adipic acid. Ammonia, methyl amine, ethyl amine, propyl amine, butyl amine, pentyl amine, allyl amine, α, ω amino carboxylic acids of two to six carbon atoms and nitrate were also detected in the final product. These results confirmed that the primary attack occurs on the methylene group next to the -NH- group. The model amide (*N,N*′-diacetyl hexamethylene adipamide) and (*N,N*′- diethyl adipamide) showed yellowing on photo-oxidation. Moore[43] studied the photo-oxidation of nylon 66, and it was characterized by tenacity losses, intrinsic viscosity changes, UV absorption and end- group analysis. Analysis of hydrolyzed nylon 66 after photo-oxidation indicated the formation of aldehyde and primary amide end groups. The polymer showed photolysis at a shorter wavelength, which is independent of oxygen concentration. At longer wavelengths, a photosensitized auto-oxidation occurred, involving oxidative attack predominantly at the methylene group adjacent to the *N*- atom of the molecule. *N*-alkylamide, a model, also gave analogous products of nylon 66 upon exposure to UV radiation in oxygen or under anaerobic conditions. Progressive degradation of nylon 66 was observed with exposure time, which is indicative of more degradation and chain cleavage, but titanium dioxide as a delustrant enhances the photo-oxidative degradation, which means that it acts as a photosensitizer. The titanium dioxide absorbs radiation (>300 nm) and produces

free radicals and/or peroxides that can attack nylon 66 chemically. Thus, titanium dioxide produces a new route to initiate nylon 66 degradation. Mechanism suggested by Moore for photo-oxidation of nylon 66 is shown in *Scheme 1.1.*

Mark and Lerch[44] confirmed the dicarbonyl compounds (e.g., dialdehyde and γ-diketones) as intermediates during the exposure of nylon 66 to UV irradiation. They cause yellowing of photo-degraded polyamide and react easily with substances containing free amino groups, forming pyrroles, which are primarily responsible for the yellowing in nylon 66. The pyrroles are formed by the oxidation of hexamethylene diamine unit in the sample. Shah *et al.*[45] also confirmed the above results with nylon 66. They suggested that the pyrrole formation mechanism went through degradation steps that proceed through the secondary diamide of 2,5-dioxoadipic acid, succinic acid, succinaldehyde and finally pyrrole.
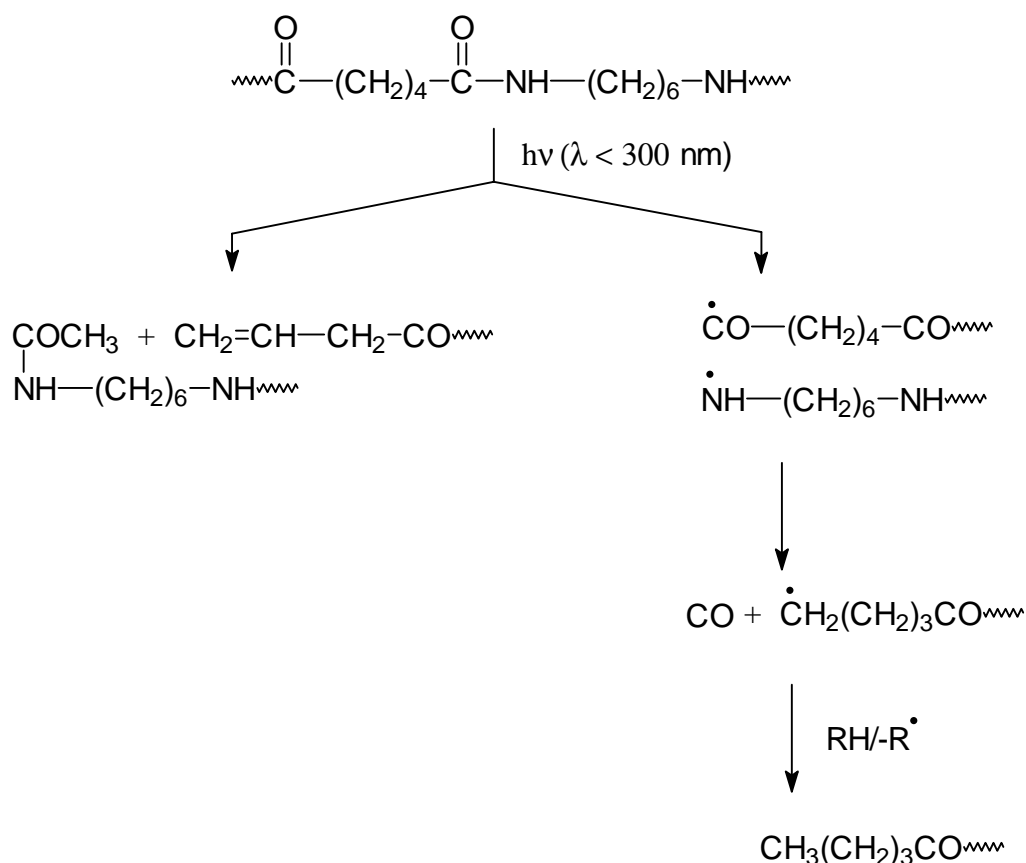
Scheme 1.1

Taylor et al.[46] studied photo-oxidation of nylon 66 in the absence and presence of titanium dioxide. They observed that the phototendering effect of titanium dioxide proceeded by a chemical, rather than energy transfer mechanism. In this mechanism, titanium dioxide absorbs radiation and produces free radicals and/or peroxides that chemically attack the nylon 66. Peebles and Hoffman[47] studied the gel and color formation in nylon 66 in thermal degradation. The rate depended on the removal of degradative volatile products. Upon heating (~ T_m) even for long time in sealed tubes, the material remained white and soluble, while the escape of volatile material caused gelation and color formation. Degradation of nylon 66 was characterized by differential scanning calorimetry, which showed peaks of a double melting point. The ratio of peak heights was correlated with elongation and Izod impact strength[48.] Jellineck and Chaudhari[49] found random degradation upon exposure to near UV radiation ($\lambda \geq 290$ nm) of nylon 66 film cast from formic acid solution, but random degradation was inhibited in the film cast from benzyl alcohol due to the protection of peptide groups (C−N bond) by hydrogen bonding formed by benzaldehyde or benzoic acid, the oxidation products of benzyl alcohol.

Figure 1.1 shows the degree of degradation in different environments versus exposure time. Practically, no degradation occurs in vacuum. The degradation increased with temperature and air pressure. The degradation rates in NO_2 and air atmosphere are diffusion controlled. The UV radiation ($\lambda \geq 290$ nm) and ozone accelerated the degradation as compared to air alone. A saturation limit in degradation is reached at 15 h exposure in all the cases.

Fornes and coworkers[50] studied the rate of loss of breaking strength and percentage elongation at break of nylon 66 fibers exposed to near-UV irradiation (350 nm). The rate was much slower when samples were exposed to far-UV radiation. This was attributed to the increased crystallinity that results from chain scission during exposure to near-UV irradiation.

Allen et al.[51] observed that, during thermal oxidation, short-lived longer wavelength phosphorescent species were formed in nylon 66 film that gradually decomposed during photo-oxidation. The same authors indicated that carbonyl groups are reactive intermediates in thermal and photochemical oxidation. In contrast to other nylons, Allen and coworkers[52] found two distinct phosphorescence bands in nylon 66 at 420 and 465 nm. They also identified that carbonyl species

Figure 1.1 Degree of degradation versus exposure time during photodegradation of nylon 66 different environmental conditions.
(1) 35°C, 1 atm. air plus 19 ppm O_3, (2) 55°C, NO_2, (3) 35°C, UV irradiation, (4) 35°C, 11 ppm O_3, (5) 45°C, NO_2 (6) 35°C, 1 atm. air, (7) 35°C, NO_2, (8) UV irradiation, vacuum.

were responsible for these emissions. These groups (carbonyl species) were developed into the polyamide backbone during thermal/photochemical oxidation. These carbonyl species, on further exposure to thermal/photochemical treatments, decompose to diketones and dialdehydes, which are precursors to the pyrrole compound formation[53]. Koenig and Roberts[54] studied the mechanism of dye-sensitized photodegradation of nylon 66 by means of excitation and emission spectra of polymer dyed with C. I. Acid Blue 40. The spectra indicated that a ground-state complex was formed between the dye and polyamide on dyeing. The energy levels of the complex's electronic states favor triplet-triplet energy transfer from the nylon to the complex. The energy is transferred by an exchange mechanism. An additional energy transfer occurred between the excited dye and the complex by either a singlet-triplet or triplet-triplet mechanism. The dye-nylon complex sensitizes the polyamide photo-oxidative degradation at its own expense

without dye photobleaching. The subsequent photo-oxidation of the thermally oxidized polyamide results in a distinct shift in phosphorescence at a shorter wavelength and a shortening of the emission lifetime[55]. Thermal oxidation caused a new longer wavelength phosphorescence bands in aliphatic polyamides. These caused reduction in mean phosphorescence lifetime for new longer wavelength bands and in original phosphorescence as well. Photo-irradiation to thermally oxidized samples vanishes the emission maxima of longer wavelength. Also the yellow discolouration caused by thermal oxidation was gradually decreased upon photo-irradiation. Phosphorescence species can impart greater absorption of sunlight in the near ultra-violet region and in turn reduces the photostability of the substrate. Moreover, strain relieving in crystalline region can cause chain restructuring upon thermal treatment. This will also contribute to make polymer susceptible to photo-oxidation.
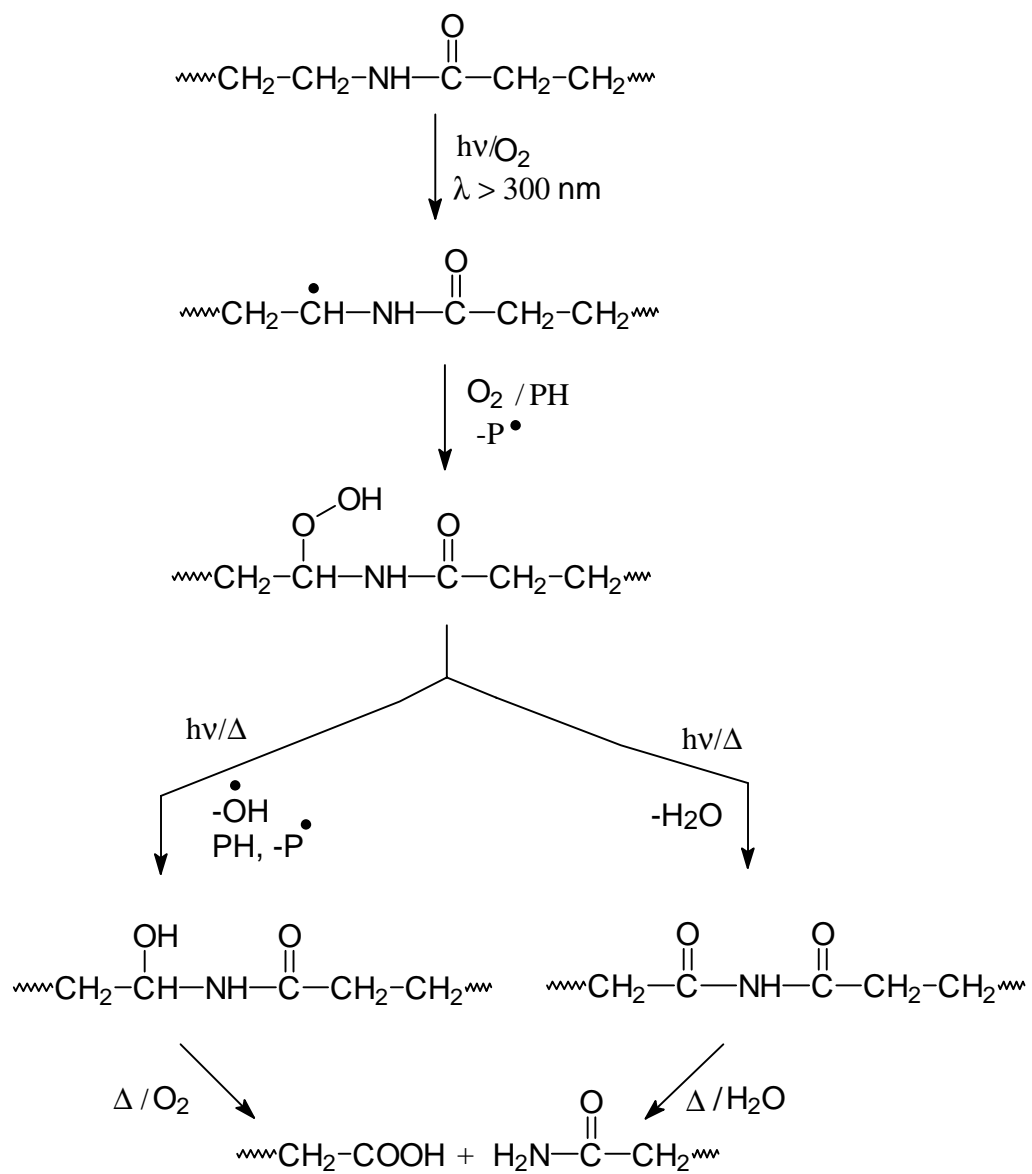
Allen *et al.*[56] studied the thermal and photochemical oxidation of nylon 66 by luminescence spectroscopy. Nylon exhibited phosphorescence emission in the wavelength region 400-500 nm. The phosphorescence probably originated from the impurities formed due to thermal oxidation during polymerization and processing. Mild oxidation of model amide compounds produces a phosphorescent species with an emission spectrum that is closely matched to that of the polymer. On the basis of composition of the phosphorescence excitation spectrum of the oxidized model amides with absorption spectra of two possible general types of model α, β-unsaturated carbonyls, the phosphorescence was controlled to originate from dienone choromophoric units. They remarked that these species are responsible for the sunlight-induced oxidation of nylon 66. Allen and coworkers[57] presented the evidence for a triplet-singlet resonance energy transfer process between the α, β-unsaturated carbonyl impurities in nylon 66 and a photoactive disperse dye (3-methoxybenzanthrone, Disperse Yellow 13). The dye showed poor lightfastness and strong phototendering action on nylon fiber due to the high charge transfer content of the dye in its first excited singlet state. The dye is also capable of being photoexcited into its first excited singlet state by the triplet-singlet resonance transfer, which is possible only with radiation absorbed by the α, β-unsaturated carbonyl impurities in the spectral range of 290 to 330 nm. The dye also showed significant effect on the photo-induced change in the viscosity of the polymer. Initially, the solution viscosity increased up to 100 h UV irradiation due to cross-

linking between the polymer chains. Same authors[58] studied the effect of light on luminating compounds. 2-Amino anthraquinone exhibited fluorescence, 2-hydroxyanthraquinone exhibited phosphorescence in various solvents, but 2-amino-3-hydroxylanthraquinone was found completely nonluminescent. Nylon 66 incorporated with these luminescent compounds faded very fast compared to nonluminescent compound (2-amino-3-hydroxyanthraquinone) upon UV irradiation. This nonluminescent compound is light stable because of the 2- and 3- positions of the amino and hydroxyl groups, respectively, which leads to extremely rapid deactivation within the singlet and triplet manifolds; this gives a dye of much higher light stability than the corresponding individually 2-substituted compounds, in which deactivation is slower.
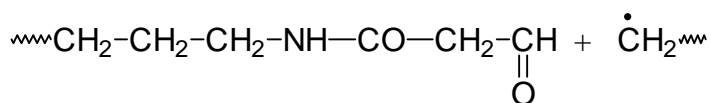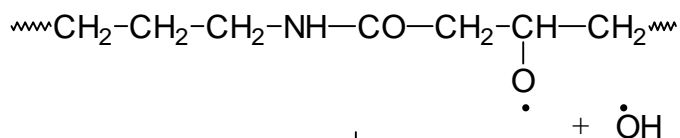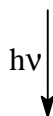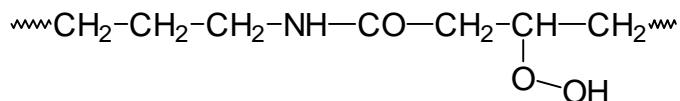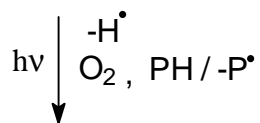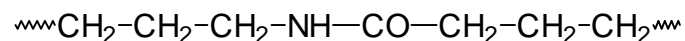
The surface photo-oxidation studies[59] of nylon 66 with electron spectroscopy for chemical analysis (ESCA) showed an increase in oxygen content on the surface during the UV irradiation. The added oxygen is present mainly as carboxylic groups. The photo-oxidation studies[60] of the oven-aged nylon 66 films resulted in an initial increase in viscosity due to cross-linking, followed by a rapid decrease due to chain scission, indicating that the latter is induced by hydroperoxide, which results in β-bond scission to give a free macroalkyl radical and carbonyl group. A new intense absorption band was observed, which was centered at 230 nm and a much weaker band at 290 nm. After a certain period of photo-exposure, both the bands shifted simultaneously to shorter wavelengths and were also reduced in intensity. Both the bands behaved in the similar manner. Thus, confirming that they were the low and high-energy transitions associated with α, β-unsaturated carbonyl species.   A higher concentration of hydroperoxides, > 200 ppm, led to chain scission due to β-scission processes. Mechanism for β-scission, which leads to an aldehyde and a free macroalkyl radical, is shown in *Scheme 1.3*.

Lemaire and co-workers[60a] studied the photochemistry of various aliphatic polyamides. Polyamides were irradiated to UV radiation of 254 and >300 nm wavelength. Mechanism suggested for photo-oxidation of polyamides is shown in *Scheme 1.2*.

Allen *et al.*[61] analyzed the fluorescent and phosphorescent species in nylon 66. One of those species showed excitation maximum at 290 nm and corresponding emission at 326 nm. This species were extracted from polymer by iso-propanol

$$\underset{\text{O}}{\overset{\|}{\text{wwCH}_2\text{-CH}_2\text{-NH-C-CH}_2\text{-CH}_2\text{ww}}}$$

$\downarrow$ hν/O$_2$
$\lambda > 300$ nm

$$\underset{\text{O}}{\overset{\bullet}{\text{wwCH}_2\text{-CH-NH-C-CH}_2\text{-CH}_2\text{ww}}}$$

$\downarrow$ O$_2$ / PH
$-$P$^\bullet$

$$\text{wwCH}_2\text{-CH-NH-C-CH}_2\text{-CH}_2\text{ww}$$
O-OH, O

hν/Δ   hν/Δ

$\bullet$OH   -H$_2$O
PH, -P$^\bullet$

OH   O   O   O

$$\text{wwCH}_2\text{-CH-NH-C-CH}_2\text{-CH}_2\text{ww} \qquad \text{wwCH}_2\text{-C-NH-C-CH}_2\text{-CH}_2\text{ww}$$

Δ / O$_2$ Δ / H$_2$O

$$\text{wwCH}_2\text{-COOH} + \text{H}_2\text{N-C-CH}_2\text{ww}$$

Scheme 1.2

wwwCH$_2$–CH$_2$–CH$_2$–NH—CO—CH$_2$–CH$_2$–CH$_2$www

$h\nu$ $\Big|$ $\begin{array}{l}\text{-H}^\bullet\\ \text{O}_2, \ \text{PH}/\text{-P}^\bullet\end{array}$

wwwCH$_2$–CH$_2$–CH$_2$–NH—CO—CH$_2$-CH—CH$_2$www
|
O~OH

$h\nu$ $\Big|$

wwwCH$_2$–CH$_2$–CH$_2$–NH—CO—CH$_2$-CH—CH$_2$www
|
O
$^\bullet$ + $^\bullet$OH

wwwCH$_2$–CH$_2$–CH$_2$–NH—CO—CH$_2$-CH + $^\bullet$CH$_2$www
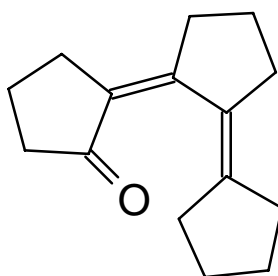‖
O

Scheme 1.3

whereas another species had an excitation maximum at 390 and 420 nm and could not be isolated. The latter one was reported to be associated with the presence of α-ketoimide structures formed during thermal oxidation of nylon 66. Extracted products were separated by   TLC and analyzed using GC-mass spectrometry. They confirmed the presence of cyclic enone dimer and dienone trimer of cyclopentanone amongst other products.
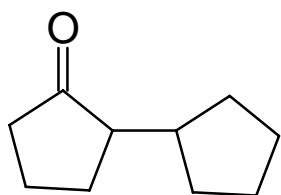
Cyclopentyl-
cyclopentanone

Cyclopentylidine-
cyclopentanone
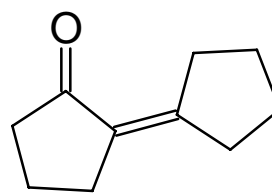
Cyclopentylidene
(2'-cyclopentylidene)
cyclopentanone

Allen *et al.*[61a] studied the influence of amine end groups on nylon 66 stability and observed that a higher concentration of amine end groups resulted in an increase in polymer stability both thermally and photochemically. This phenomenon was associated with the radical or oxygen-scavenging ability of the amine group and was confirmed by the observation that sulfur dioxide treatment of nylon 66 films generated sulfonamides and sensitized the photochemical oxidation of the polymer.

The thermal and photochemical degradation of nylon 66 in different atmospheres is compared in *Figure 1.2* by the percentage change in viscosity number. Figure shows two interesting features. Compared to the control samples all the post-heated samples in nitrogen and steam display a more rapid decrease in viscosity number except for samples 5, 6, and 9. Of the two post-thermal treatments, the effect of steam is quite dramatic in the case of sample 2, for which a rapid change in viscosity number is observed that is certainly associated with a higher concentration of degradation products generated in the polymer.

Figure 1.2 Thermal and photochemical degradation of nylon 66 in different atmospheric conditions.

(1), (3), (5) before; (2), (4), (6) after heating in steam at 275°C; and (7), (8), (9) in N$_2$ at 200°C.

The viscosity changes also show that the post-heated samples exhibit a higher level of UV absorbing fluorescent and phosphorescent species at 294 nm. The shapes of carbonyl envelope[62] of the IR spectrum formed in thermal and photo-oxidation were similar, suggesting that both the oxidation mechanisms are the same. The broadness of these bands indicated that the carbonyl group spectra arise from more than one species. The presence of keto and part of *N*-alkyl amide groups made nylon susceptible to a degradation reaction entailing mainly a Norrish type II mechanism. Evolution of carbon monoxide, methane and formation of the primary amide groups was observed in the photodegraded sample under vacuum. The same authors compared the photodegradation of nylon 6 and nylon 66. The only difference in nylon 6 and nylon 66 photodegradation reported was evolution of ammonia during

the photolysis of the former. The amorphous region (1148 cm^{-1}) of nylon 66 degraded faster compared with the crystalline region (935 cm^{-1}). They also studied the photodegradation of model amides. The imide formation was the main observation during the photo-oxidation of both the nylons and amides, therefore, model imide compounds were also studied. The degradation products were identical in model amides and nylons, but model imide compounds generated carbon monoxide and 1-butene upon photodegradation. They also studied the photodegradation of thermally oxidized samples. Photolysis caused a decrease in intensity of absorption between 1800 and 1700 cm^{-1} and also reduced the peak intensities of —NH—, —CH$_2$—, Amide I and Amide II bands. This is because of the decomposition of short-lived emitting species formed during thermal oxidation of nylon 66.

Allen *et al.*[63] studied the relative rates of photofading of three azo dyes (C. I. Acid Blue 62, C. I. Acid Red 266, C. I. Acid Yellow 135) and four azo acid metal complex dyes (C. I. Acid Brown 226, C. I. Acid Blue 171, C. I. Acid Orange 162 and C. I. Acid Black 107) in nylon 66 films. They correlated the rate of photofading of the dyes with their ability to photostabilize the polymer. Amongst first three dyes the stabilizing efficiency was in the order yellow > blue > red. Metal complex dyes also photostabilize the polymer in the order blue > black > orange > brown. The nature of the central metal atom was identified to be an important factor. Normally terminal amine groups have an influencing effect on photostability of nylon 66. However, in presence of dyes, terminal amine group concentration did not show any significant effect on photostability of nylon 66. Acid complex dyes were found more than two order of magnitude more stable than the acid dyes, and this was reflected in their ability to impart greater stability to the polymer. Photofading of acid complex dyes was found to be decreased with increasing the cobalt content. Chromium was observed less efficient in this respect. They also found the close relationship between the ability of the dyes to quench luminescent chromophores and polymer stability. They suggested that triplet energy transfer may be important in stabilization of the polymer with dye. They also reported[64] in their another studies that C. I. Acid Yellow 135 and C. I. Acid Brown 226 dyes were having quenching effects on the phosphorescence of α, β-unsaturated carbonyl species in nylon 66. The rate of photo-oxidation of nylon 66 was found to be inversely proportional to the dye concentration in both the cases, and the rate of dye fading

exhibited a similar, but slower, trend. This result confirmed previous findings on the importance of triplet energy transfer in the stabilization of dyed nylon 66 polymer, with the metal complex types being the most effective. Allen[65] studied the commercial problems of photofading and photostability of dyed and pigmented polymers. The electron-withdrawing and electron-donating groups in the dye will influence its photo-physical and photochemical behavior. In the case of electron-donating groups intramolecular hydrogen bonding is significant for anthraquinone chromophores and enhances lightfastness of nylon polymer. The electron-withdrawing groups, on the other hand, reduce the lightfastness. Brasington and Gadala-Maria[66] examined the luminescent impurities in nylon 66 using image processing. Samples were irradiated to light ($\lambda \leq 366$ nm) and changes in fluorescence and phosphorescence intensities were studied. They observed that fluorescence emission from the green and red gel particles decreased in intensity exponentially with irradiation time. The decay constants for the two types of gel particles were found to be in the same range. Based on this observation they concluded that a similar mechanism is responsible for the decrease in the intensity of the fluorescence emissions from both the gel. The phosphorescence intensity of the gel particles also decreased with irradiation time. The phosphorescence intensity did not return back to its original value after a long period of irradiation. This indicated that the structure of the gel had been permanently altered. According to them still more efforts are needed to establish the relationship between the decay of fluorescence and phosphorescence emissions and the structure of the gel. They also suggested that the effect of temperature on the decay of the fluorescence properties should be examined because it may be possible to distinguish the polymer degradation from the gel decomposition and to distinguish between different structures of gel.

1.6 Types of stabilization

At the time of heating, milling, or kneading, polymer may degrade or depolymerize. On exposure to the natural and induced environmental conditions, UV radiation, either alone or in combination with oxygen, heavy metal or the like, profoundly deteriorates the mechanical properties of most polymers. A small amount of compounds called stabilizers are added into the polymer matrix to retard degradation or depolymerization and to impart long-term outdoor stability to the polymer. The stabilizers quench the electronic excitation energy associated with

specific chromophores as a result of photon absorption. Polymer stabilization may be achieved by light screeners, UV absorbers, antioxidants, peroxide decomposers and excited-state quenchers.

1.6.1 Light screeners

The light screeners are interposed as shields between the radiation and the polymer. They function either (1) by absorbing the radiation before it reaches the photoactive species in the polymer or (2) by limiting the damaging radiations penetration into the polymer matrix. Reflection of radiation can be achieved by the selection of suitable paints, coatings or pigments or by metallizing the surface[67, 68]. The pigments are used in dispersed form in the polymer matrix as screeners. Schonhorn and Luongo[69] assumed that, due to their low surface energy, the pigments show protective activity. The pigments also quench certain photoactive species in the polymer[70]. Carbon black is commonly used as a pigment because it is the most-effective light screen[67], especially at high temperatures. Several theories have been advanced to explain its technically important behavior in the polymer[71].

1.6.2 Ultraviolet absorbers

The function of the ultraviolet absorber is the absorption and harmless dissipation of ultraviolet radiation, which would otherwise initiate degradation of polymer material. The ultraviolet absorbers act through photophysical processes like intersystem crossing, internal conversion and molecular rearrangements. The *o*-hydroxybenzophenones and *o*-hydroxybenzotriazoles are important groups of UV absorbers since both the groups absorb strongly in the UV region. The photostabilization mechanism[72, 73] of *o*-hydroxybenzophenone and *o*-hydroxybenzotriazoles are believed to be a rapid tautomerism of the excited state as it is shown in *Scheme 1.4.*

The more basic the hetero atom (O) in the ground state, the more light stable is the compound. It is assumed that, in the ground state, the enol form is energetically preferred, whereas the reverse is true for the first excited singlet. An argument for this viewpoint is the fact that, in the exited state, phenol becomes much more acidic, whereas the hetero atom O becomes more basic than in the ground state.
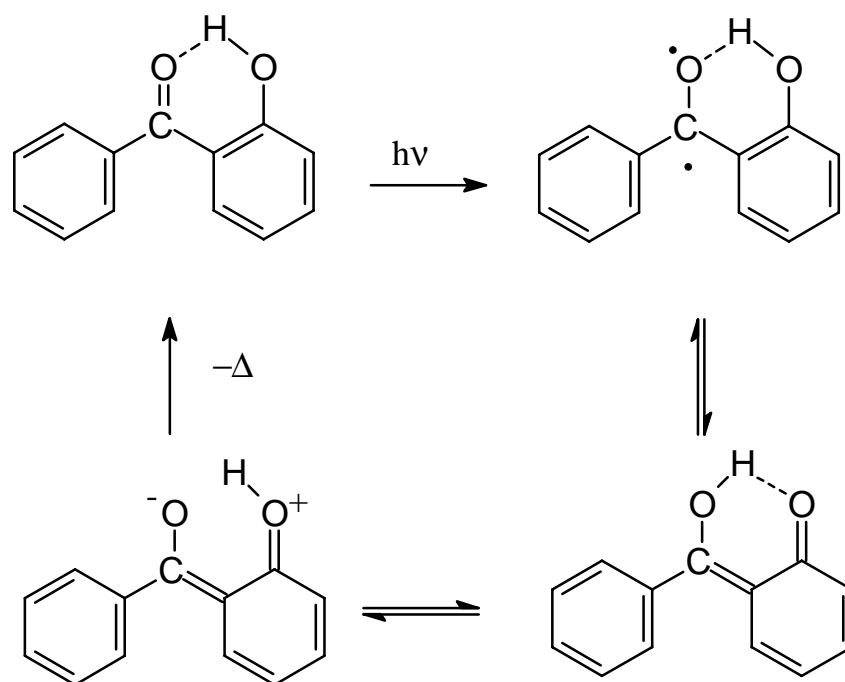
Scheme 1.4

1.6.3 Antioxidants

The antioxidant (AH) may inhibit oxidation processes by the following proposed mechanism:
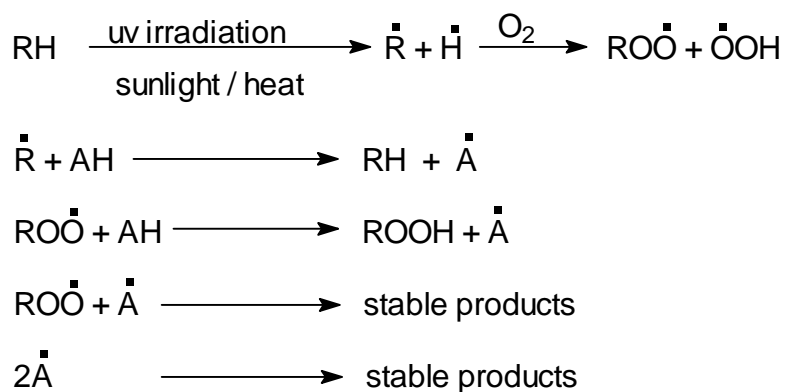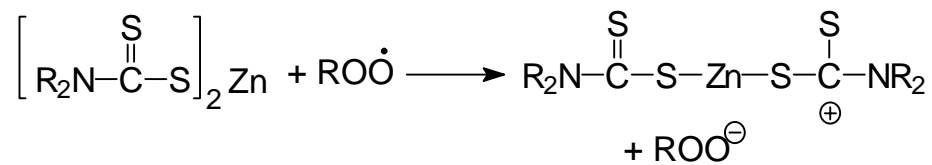

The antioxidants act as a chain-terminating agent. The antioxidants react faster with peroxide radical (ROO$^{\bullet}$) then with macroradical (R$^{\bullet}$) and the activity depends upon their structure[74-76].

1.6.4 Peroxide decomposers

The salts of alkyl xanthates, *N, N´*-disubstituted dithiocarbamates and diethyl dithiophosphonates are effective peroxide decomposers[77]. Since no

active hydrogen is present in these compounds, an electron transfer mechanism was suggested. The peroxide radical is capable of abstracting an electron from the electron-rich sulfur atom and is converted into a peroxy anion as illustrated below for zinc dialkyl dithiocarbamate[78]:

$$
\left[R_2N-\overset{\overset{S}{\|}}{C}-S \right]_2 Zn \ + ROO\cdot \longrightarrow R_2N-\overset{\overset{S}{\|}}{C}-S-Zn-S-\overset{\overset{S}{|}}{\underset{\oplus}{C}}-NR_2
$$
$$
+ ROO^{\ominus}
$$

1.6.5   *Excited-state quenchers*

The excited-state quenchers deactivate the photoactive chromophoric species in the polymer before it undergoes degradation. Generally, the metal chelates with a variety of legends are excellent quenchers for the exited states[79]. The photo-oxidative degradation is promoted by an electronically exited oxygen molecule (singlet oxygen $^1O_2$) formed in the polymer. The quenching of $^1O_2$ is necessary for effective stabilization and nickel chelates[80-82] have proved to be effective quenchers for exited states of singlet oxygen. The quenching may occur either by energy transfer or by the formation of excited state complexes[83]. They also act as scavengers for hydroxyl and oxy radicals formed during the photo- and the thermal decomposition of polymeric hydroperoxides.

1.6.6   *Synergistic mixtures*

The combined effects of all the above-proposed processes are known as *synergism* when the cooperative action is greater than the individual effects[84] taken independently. The mechanism of synergism is unknown, but it is believed that the synergistic mixture functions in several ways (i.e., as UV absorbers, antioxidants, quenchers, or peroxide decomposers).

1.7   Stabilization of aliphatic polyamides

The loss in strength of nylon due to UV and/or sunlight exposure is of importance and has been minimized by a number of workers. The lightfastness[85] of model polyamide is increased by treatment with polyhydroxy benzophenones, benzotriazoles, or benzo-oxazoles, which react with polyamide. Strobel[86] studied the effect of UV absorbers in relation to lightfastness of dyed nylon fabric and

concluded that penetration of dye into the fiber is a prerequisite to satisfactory stabilization of dyes by UV absorbers. Polyamides were photostabilized[87] by incorporating additives such as the Mn (II) salts of ethane phosphonic acid, phenyl ethyl sulfonic acid, and the like during polymerization. Polyamides were stabilized[88] against light and heat by incorporating 0.1% w/w of phenylphosphorus dihalide during manufacturing. The polymer retained 33% to 69% tenacity, and 27% to 52% elongation before and after 100 h exposure, respectively, in Fade-o-meter.

The oxalic acid bis (anilide) derivatives[89] have been used as UV stabilizers for polyamide and other polymer. The salts of hydrohalic acids have been used as stabilizers[90] in polyamides, the most effective being potassium iodide, sodium bromide, potassium bromide and copper bromide. Nylon 66 is delustered with titanium dioxide, but it enhances the photodegradation upon exposure to equal to or more than 300 nm, therefore, manganese salts are added to a delustered sample to counteract the photocatalytic action of titanium dioxide[43, 44]. The manganese salt (300 ppm manganese) prevented the formation of pyrrole precursor upon exposure to UV-visible radiation. The protective action of manganese consists essentially of the destruction of peroxide or a change in the course of reaction so that the photodegradation by the radical mechanism is considerably slowed.

Nylon and other textile materials were stabilized against light by *o*-hydroxy-*s*-triazines and their derivatives[91]. Organic or inorganic derivatives of copper and tin (20-100 ppm) were reported as light and heat stabilizers for polyamides[92]. Some *N*-acyl-*p*-phenylene diamines[93] were observed to be suitable additives for nylons and rubbers to improve their resistance to heat, light and oxidation. Uvilhelm *et al.*[94] stabilized nylon 6 and nylon 66 against thermal and photodegradation by incorporating into their matrix, the copper salt of $(CH_2-CH_2-NH-CH_2-Ph-COOH)_2$ and potassium iodide. Light stable polyamides were obtained by blending polyamides with hydroxybenzoic acids, optionally substituted with one or two alkyl, alkoxy, aryl, hydroxy, or fluroalkyl gruops[95].

The sensitizing effect of dyes in accelerating the degradation of nylon fabric is well known, but the disperse dyes decreased the rate of photochemical decomposition of polyamides[96]. Thus, the protective as well as accelerated action in nylon 66 yarns depends on the dye and methods of application. Nylon 66 pigmented[97] with titanium dioxide upon treatment with manganese acetate, a

phosphorus-containing compound, hexamethylene diammonium dihydrophosphite, bis(nonylphenyl) phenyl phosphite, triisodecyl phosphate or diethanol ammonium hypophosphite and 1,1,3-tris(2-methyl-4-hydroxy-5-tert butyl phenyl)butane, 2(α-methyl cyclohexyl)-4,6-dimethyl phenol; 1,3,5-trimethyl-2,4,6-tris(3,5-ditetra butyl-4-hydroxy benzyl benzene, or 1,1,5,5-tetrakis(2-methyl-4-hydroxy-5-tert-butyl phenyl)pentane improved the oxidative stability. Metallized dyes[98] of the Amichrome type, containing cobalt such as C. I. Acid Yellow 119, protected nylon 66 fibers against thermal and photochemical degradation. The chromium-containing Amichrome light dyes such as C. I. Acid Violet 74 also stabilized nylon 66, while others like C. I. Acid Red 226 had no protective effect on nylon 66. All the nonprotective dyes contained a pyrazolone ring, which enolized and released chromium. Nylon 66 textiles[99] finished with sodium diethyl dithiocarbamate and 2-mercaptobenzothiazole sodium salt showed improved heat and light stability. The textiles were impregnated with aqueous or benzene solutions of the stabilizers.

Jellineck and Chaudhari[49] studied the effect of the solvent from which nylon 66 film was cast. The nylon 66 films cast from benzyl alcohol showed more stability toward ozone, nitric oxide, oxygen and near UV irrdiation. They also explained that hydrogen bonding of benzaldehyde or benzoic acid with an amide group prevented the degradation of nylon 66. Light and heat resistance[100] of nylon 66 were improved by conducting the polymerization in the presence of bis (o-diaminophenyls) or bis (o-amino hydroxyphenyls). Reaction of the terminal carboxyl groups in polyamides with these compounds yielded benzimidazole or benzo-oxazole groups, respectively, that imparted greater stability to polyamides. Several metal salts[101] of 3-(3,5-ditert-butyl-4-hydroxyphenyl)propionate were used to stabilize polyolefins and nylon 66 against decomposition by the action of heat and light.

Knell *et al.*[102] stabilized polyolefins, nylon 66 and polyacetal resins against thermo-oxidative degradation by the addition of 0.005% to 0.5% tris (hydroxy alkyl phenyl) derivatives of thiopropinyl hexahydrotriazines. Thiophines and their derivatives were reported to impart oxidative stability to polyamides[103]. Yellow-color polyamides were obtained[104] with addition of 0.005 to 1.5 parts of tetrachlorophthalic acid or its mixture in liquid phase. These resins possess good colorfastness and light resistance when compared to polyamides containing dyes or pigment. Furukawa and Yoshihira[105] incorporated iodonitrobenzene to nylon 6 and

nylon 66 to give a composition with good oxidative degradation resistance. Spivack and Klemechuk[106] used a synergistic mixture of nickel bis(3,5-di-tertbutyl-4-hydroxybenzoate), benzophenone derivatives, benzotriazole derivatives and/or phenolic propionate to stabilize nylon 66 against photo-oxidation.

Allen *et al.*[107] studied the effect of titanium dioxide (anatase and rutile) on the photodegradation of nylon 66. Phosphorescence spectra of nylon 66 containing anatase titanium dioxide shows luminescence at 540 nm, while rutile titanium dioxide did not show any luminescence. The reduction in the intensity of the nylon phosphorescence by rutile titanium dioxide is probably a screening effect. The luminating compounds are prone to sensitize the photo-oxidation of many polymers, therefore, the anatase form of titanium dioxide sensitizes nylon 66 photo-oxidation. Manganese salts quenched the luminescence of anatase titanium dioxide and showed no luminescence in the visible region. The coated titanium dioxide (anatase) suppressed the intensity of phosphorescence emission from nylon 66, but the emission lifetimes remained unchanged. It means that manganese ions quench the excited state of the anatase form of titanium dioxide. The photoconductivity of titania pigments is related to their semiconductor properties, therefore, one possible way of quenching is that manganese(II) ions are trapping electrons from the conduction bands of photoexcited titania. The addition of manganese salt prior to polymerization as manganese (II) acetate, together with anatase, did not quench the anatase luminescence at 540 nm, but coated anatase suppressed/screened the photoexcitation of the impurity species in the polymer. Thus, the precoated titanium dioxide with manganese(II) compound acts as a photostabilizer.

Acylated derivatives of 2, 6, dihydroxy-9-azobicyclo[3, 3, 1] nonane are reported as light stabilizers and antioxidants for nylon fibers and rubbers[108]. The 2-aminoanthraquinone and 2-hydroxyanthraquinone gave strong transient absorption on flash photolysis in 2-propanol due to the formation of dye radical anion whereas 2-amino-3-hydroxyanthraquinone gave strong transient absorption due to the
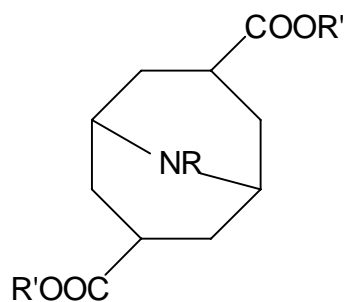
semiquinone radical[41]. This difference causes higher lightfastness of the latter in the polymer. The substitution in the 2- and 3- positions by an amine and a hydroxyl group, respectively, leads to extremely rapid deactivation within the singlet and triplet manifolds, and this gives much higher light stability to a dye than the corresponding individually 2-substituted compounds, in which deactivation is slower. Spivack and Dexter[109] reported 2,4,6-trialkyl-3-hydroxy phenyl phosphonates and phosphinates used as stabilizers for nylon 66 subjected to oxidation in thermal and UV exposures. Spivack[110] used 2,3,5-trialkyl-4-hydroxy benzylphosphonates and phosphinates also during thermal and photochemical degradation. Nylon 66 shows fluorescence and phosphorescence[56] due to some impurities that are generated during melt processing. Alkali metal halide can quench fluorescent species in nylon 66. Allen *et al.*[111] correlated the fluorescence and phosphorescence quenching properties of some light stabilizers. Alkali metal halides quenched fluorescent species in nylon 66 in the following order:

$$I > Br > Cl > F$$
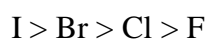
Alkali and transition metal salicylates quench the phosphorescent species and are effective photostabilizers for polyamides. The manganese compounds in the anatase form of titanium dioxide pigment also quench the phosphorescence emission from the pigment and the polymer.

Allen and coworkers[112] stabilized nylon 66 against light by incorporating various hindered piperidine stabilizers. The effectiveness of stabilizers was evaluated by viscosity, ultraviolet absorption and luminescence spectroscopy. *Figure 1.3* shows

Figure 1.3 Percentage Change in Viscosity Number versus Irradiation Time for nylon 66 films: (1) neat, with 2 wt. % each of (2) Cyasorb UV 3346, (3) 4-carboxy piperidine and with 0.25 wt. % after heating in steam at 275°C (50 mins) each of (4) Tinuvin 770, (5) Chimassorb 994, (6) Tinuvin 622, (7) Tinuvin 765.

the photostability of nylon 66 films as measured by percentage decrease in viscosity number as a function of irradiation time. The most effective stabilizer is Tinuvin 770 followed by Tinuvin 756, 4-carboxy piperidine, Cyasorb UV 3346, Tinuvin 622 and Chimassorb 944, in that order. The two monomeric stabilizers are most effective probably due to their better solubility and compatibility with the polar crystalline nylon 66 polymer. An interesting result is the greater stabilizing effect of Tinuvin 770 compared with that of Tinuvin 765. This is because the former is a secondary amine and the latter a tertiary amine. Thus, the Tinuvin 770 is more likely to undergo reaction with the terminal carboxylic end group in the polymer and impart greater stability. The steam treatment (275°C) of the stabilized nylon 66

films increased the viscosity number. Furthermore, the viscosity changes correlate well with the UV absorption spectra at 294 nm and fluorescence/phosphorescence values at excitation and emission maxima at 297/330 nm and 290/410 nm, respectively. These commercial stabilizers inhibited the formation of photoactive chromophores during UV irradiation. The photobleaching of the dyed and/or pigmented polyamides is a complex phenomenon, but conventional UV absorbers and hindered piperidine additives have provided effective stabilization for nylon 66 containing dyes and pigments[65].

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