

**PHOTO-OXIDATIVE DEGRADATION AND
STABILIZATION OF NYLON 66 IN PRESENCE
OF ACID BLUE DYES**

**A Thesis submitted to the
UNIVERSITY OF POONA
for the degree of
DOCTOR OF PHILOSOPHY
in
CHEMISTRY**

by

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July 1999

3 SEP 2005

DECLARATION

Certified that the work incorporated in thesis “**Photo-oxidative Degradation and Stabilization of nylon 66 in presence of Acid Blue dyes**” submitted by Mr. Thanki P. N. was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged.



(R. P. Singh)

Research guide



Acknowledgement

Today when I repose in peace contemplating about my experiences & achievements as a researcher, my highest gratitude goes to Dr. R. P. Singh – my research supervisor – a euphemism for the one who has righted my floundering ship. He deserves all the credit of escalating my career to the height I stand today. It is he, who saw me past every hurdle, big & small with utmost patience & understanding. I shall be grateful to him for imparting me full freedom to explore the world of chemistry from books to bench. Through this little eulogy I would like to express my everlasting gratitude toward him.

I owe a word of gratitude to Dr. S. Sivaram, Deputy Director and Head, Polymer Chemistry Division, N.C.L., for his useful discussions, valuable suggestions & remarkable research inputs. I shall always admire his art of envisaging Chemistry. Without his critical evaluation & constant encouragement this thesis would not have become a reality.

How can I forget Dr. C. G. Joshi of Maharshi Dayanand Science College, Porbandar who had sown the seed of chemistry in me & nourished it all the way through, for me, to harvest the fruits today.

I thank Dr. C. Ramesh, Dr. B. D. Sarwade and Dr. A. Vishwa Prasad of the Polymer Chemistry Division for their special help during the course of this work.

I also thank Ramnathan, Shailendra, Shrojal, Pandey, Birajdar, Nirmala, Sandhya, Yanjarappa, Rajesh, Shruti, Shyamroy, Saptarshi, Sunita, Snehlata, Raghunath, Nita, Mahuva, Zinu, Mr. Shaikh, Ms. Gracy and all my senior colleagues of the Polymer Chemistry Divisions for their timely help during the course of my stay at N.C.L.

My thanks are due to Dr. R. Mani, Dr. B. B. Idage, Dr. S. Balamurugan, Dr. Sreelatha, Dr. N. Sarkar, Dr. K. Radhakrishnan and Dr. Sensharma for their constant encouragement.

My friends Upadhaya, Sanjay Modha, Nabi, Mohan, Rao, CV, Bhusan, Pujar, Milu, Bhargav, Sanjay, Dhvani, Bharat, Manoj, Dharmesh, Tejas, Manish and Ashok for their direct or indirect support during the entire course of this work.

I am indebted to my mother, brothers', sister and sisters' in-law for the timely advise, support and freedom given to me.

Finally, I am thankful to the Council of Scientific and Industrial Research, New Delhi for the awarding a research fellowship and the Director, N.C.L., for permitting me to submit this work in the form of a thesis.

*Thanks & w
5/7/99*

Thanki P. N.

ABSTRACT

This thesis presents the results on the degradation and stabilization in presence of anthraquinone acid blue dyes. Chemical and physical changes associated with the photo-oxidative degradation of nylon 66 were characterized in details. Photo-oxidative degradation in nylon 66 causes the formation of imide groups. Unlike many other polymers, nylon 66 did not exhibit the increase in hydroxy/hydroperoxy group concentrations. FT-IR and UV spectroscopic methods were used to characterize these chemical changes in nylon 66 caused by photo-oxidative degradation.

Morphological changes associated with the photo-oxidative degradation of nylon 66 were characterized by DSC, XRD and SEM techniques. We found the formation of new crystalline morphology. However, the DSC results showed that the formation of new crystalline morphology was at the loss of existing morphology whereas the XRD study did not indicate the same. SEM studies showed that there was a significant chemi-crystallization upon prolong photoirradiation. Study also showed the formation of various surface morphologies as a result of photoirradiation.

Thermal oxidative degradation is a very crucial phenomenon in nylon 66, which influences the photo-oxidative stability of the thermally treated samples. The α , β -unsaturated carbonyl species which were formed upon thermal oxidative degradation are known for sensitizing photo oxidative degradation in polyamides. We observed that formation of α , β -unsaturated carbonyl species is controlled by the aging temperature. The higher aging temperature (160°C and above) was found to enhance the formation of α , β -unsaturated carbonyl species whereas at the lower aging temperature (120°C) was observed to form only carbonyl species in thermally treated nylon 66.

Effect of dyebath pH was found to have a peculiar effect on the photostability of nylon 66 dyed with an anthraquinone acid blue dye. We examined the photostability of the nylon 66 films dyed at various pHs ranging from 2 to 7. Samples dyed at and above pH 3 were found photochemically stable whereas, the samples dyed at pH < 3 showed enhanced photo-oxidation as compared to neat samples.

We also examined two different class of photostabilizers on nylon 66 to prevent the photo-oxidation of polymer and colour fading of a dye. Dye, UV absorber and HALS were observed to impart photostability to nylon 66. UV absorber and HALS showed the greater photostability at higher loading whereas in case of dye, the

0.2 % was observed as the optimum concentration and beyond that its photostabilizing efficiency is deteriorated. Fading of dye was increased with increasing dye concentration. UV absorber imparted higher lightfastness to the dye as compared to HALS. Substitution on pendant phenyl ring of anthraquinone acid blue dyes was found to be ineffective for the photostabilizing efficiency of these dyes.

Novel water-soluble UV absorbers were designed synthesized. Their property evaluation was carried out on neat and dyed nylon 66. We observed that water-soluble UV absorber with sulfonic acid moiety was water-soluble even at neutral pH and could be easily applied onto the polyamide substrate. However, the UV absorber with carboxylic acid group was having limited diffusivity in polyamide substrate and was water insoluble in its acid form. UV absorber with sulfonic acid group showed the considerable photostabilizing effect on the nylon 66 substrate. Polyamide containing water-soluble UV absorber showed poor lightfastness when they were dyed with anthraquinone acid blue dyes. This could be due to the increase interaction of UV absorber with polar polyamide substrate. Thus, the more dispersed form of UV absorber had shown the detrimental effect on its efficiency to photostabilize the polymer and colour.

ABBREVIATIONS

AH	Antioxidant
Atm	Atmospheric
A U	Arbitrary Unit
C. I.	Colour Index
DMF	Di methyl formamide
DMSO	Di methyl sulphoxide
DSC	Differential Scanning Calorimetry
ESCA	Electron Spectroscopy for Chemical Analysis
FTIR	Fourier Transform Infrared Spectroscopy
g	Grams
HALS	Hindered Amine Light Stabilizers
IR	Infrared Spectroscopy
∞	Infinite
h	Hour
J/g	Joule per gram
kg	Kilogram
kV	Kilo Volt
L	Litre
M	Mole
mA	Mili Ampere
mg	Miligram
MPa	Mega Pascal
μm	Micrometer
nm	Nanometer
NMR	Nuclear Magnetic Resonance
<i>o</i> -	Ortho
<i>p</i> -	Para
PP	Polypropylene
ppm	Parts per million
SEM	Scanning Electron Microscopy
t	Time
<i>tert</i>	Tertiary
T_m	Melting temperature
UV	Ultra violet
wt	weight
w/w	Weight by weight
XRD	X- Ray Diffraction

ABSTRACT



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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-workers¹ synthesized first high molecular weight polyamides. Nylon 66 was selected for further 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

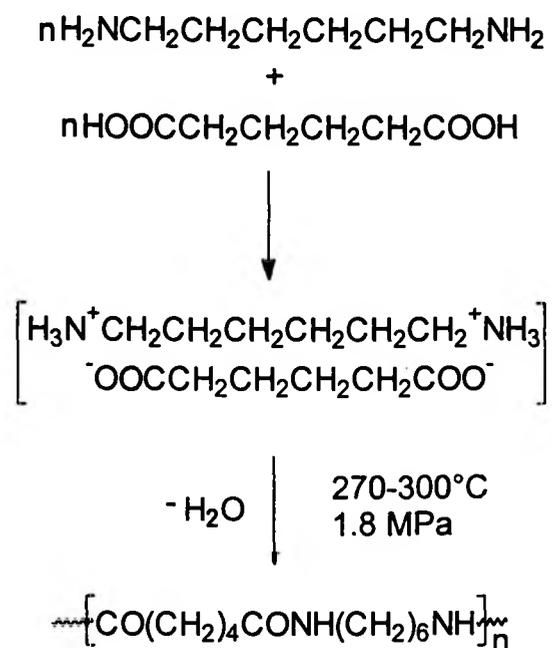
Polyamides are important engineering plastics because of their toughness over wide range of temperatures. Also they have good resistance to impact and abrasion,

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.

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 stabilizers⁴⁻⁶ 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 days⁷⁻⁹. 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 degradation¹⁰⁻¹² 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 degradation¹³⁻¹⁵

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 backbone¹⁶⁻¹⁸. 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 processes¹⁹⁻²¹. 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 instability²²⁻²⁴. This is an acute problem during the fabrication of disposable syringe barrels where embrittlement or lack 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 source²⁵⁻²⁷.

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 weather²⁹⁻³¹. 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 polymers³²⁻³³. 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

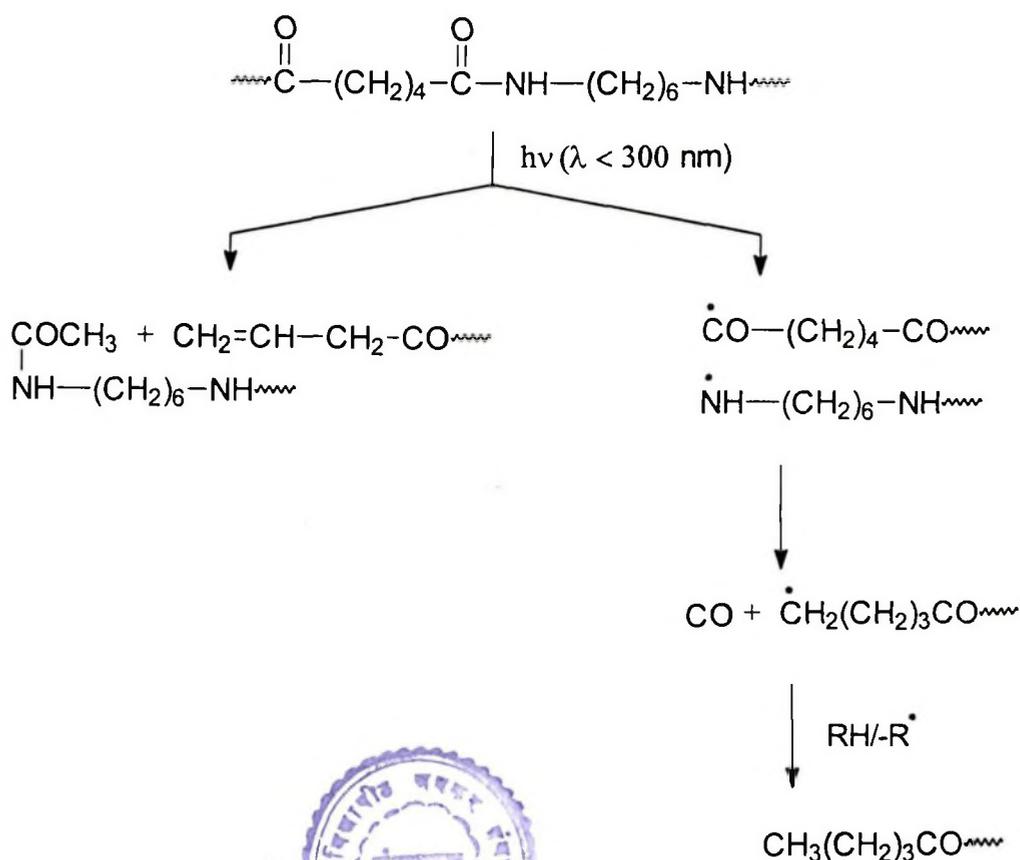
Prati³⁴ observed a decrease in intrinsic viscosity during UV degradation of nylon 66 at 128°C in acidic medium. The decrease in Huggin's constant is due to a decrease in solubility that indicated cross-linking. Bolton and Jackson^{35, 36} found a decrease in breaking strength and extensibility and an increase in fluidity upon photo-oxidative degradation of nylon polymers. Nylon 66 photodecomposition³⁷ 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 yellowing³⁹. 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 hydrolysis⁴² 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. Moore⁴³ 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 Lerch⁴⁴ 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 Hoffman⁴⁷ studied the gel and color formation in nylon 66 in thermal degradation. The rate depended on the removal of degradative volatile products. Upon heating ($\sim T_m$) 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 strength⁴⁸. Jellineck and Chaudhari⁴⁹ 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 NO₂ 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 coworkers⁵⁰ 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 coworkers⁵² found two distinct phosphorescence bands in nylon 66 at 420 and 465 nm. They also identified that carbonyl species

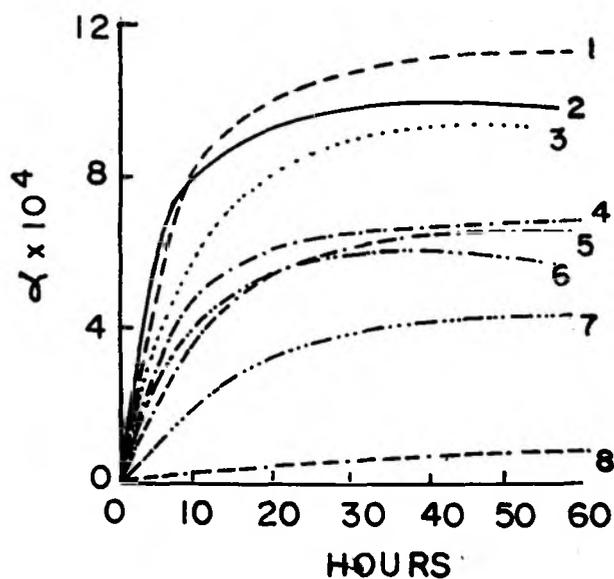


Figure 1.1 Degree of degradation versus exposure time during photodegradation of nylon 66 different environmental conditions.

(1) 35°C, 1 atm. air plus 19 ppm O₃, (2) 55°C, NO₂, (3) 35°C, UV irradiation, (4) 35°C, 11 ppm O₃, (5) 45°C, NO₂ (6) 35°C, 1 atm. air, (7) 35°C, NO₂, (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 formation⁵³. Koenig and Roberts⁵⁴ 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 lifetime⁵⁵. 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.

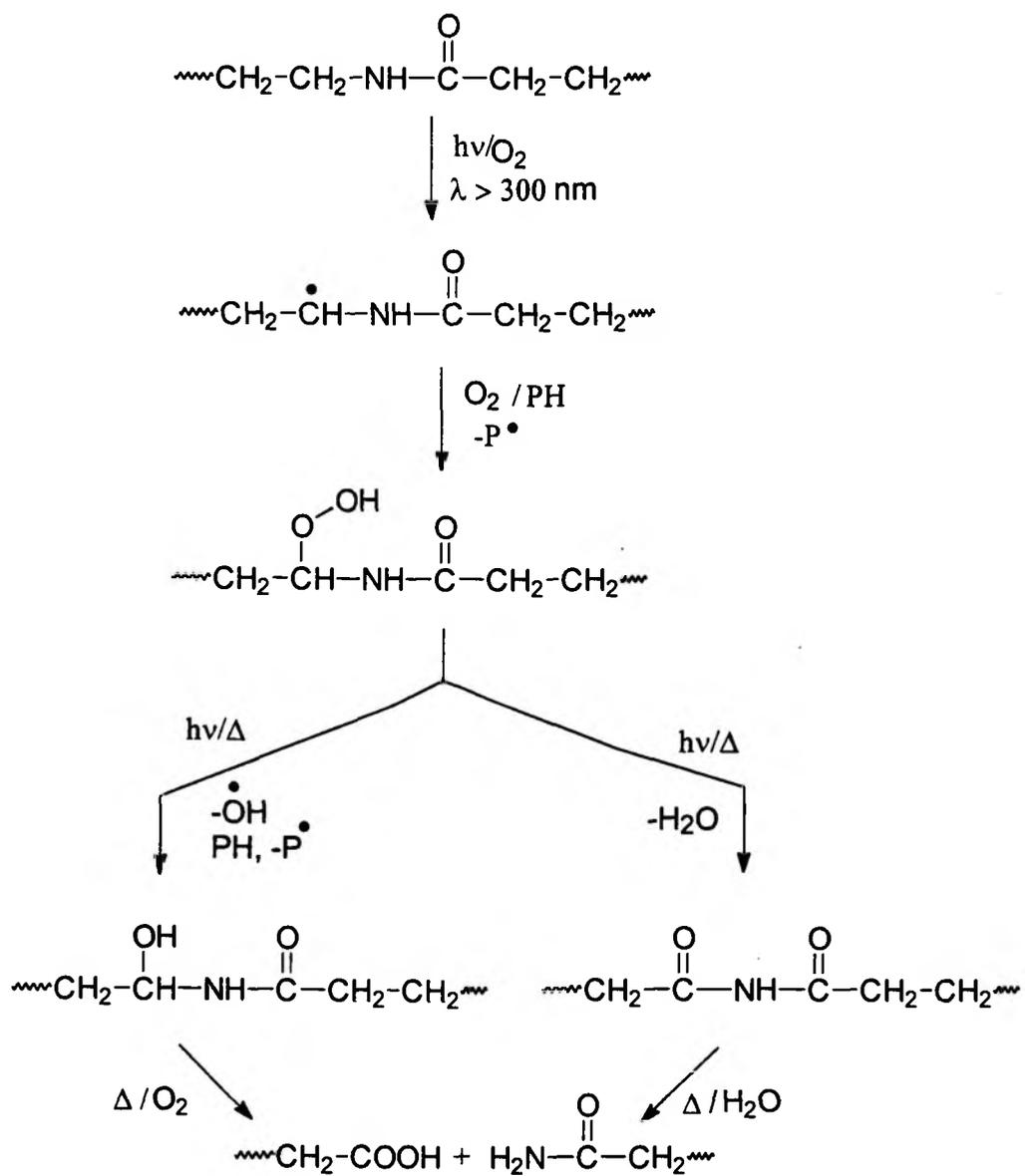
Allen *et al.*⁵⁶ studied the thermal and photochemical oxidation of nylon 66 by luminescence spectroscopy. Nylon exhibited phosphorescence emission in the wavelength region 400-500 nm. The phosphorescence probably originated from the impurities formed due to thermal oxidation during polymerization and 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 chromophoric units. They remarked that these species are responsible for the sunlight-induced oxidation of nylon 66. Allen and coworkers⁵⁷ 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 authors⁵⁸ studied the effect of light on luminating compounds. 2-Amino anthraquinone exhibited fluorescence, 2-hydroxyanthraquinone exhibited phosphorescence in various solvents, but 2-amino-3-hydroxyanthraquinone 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.

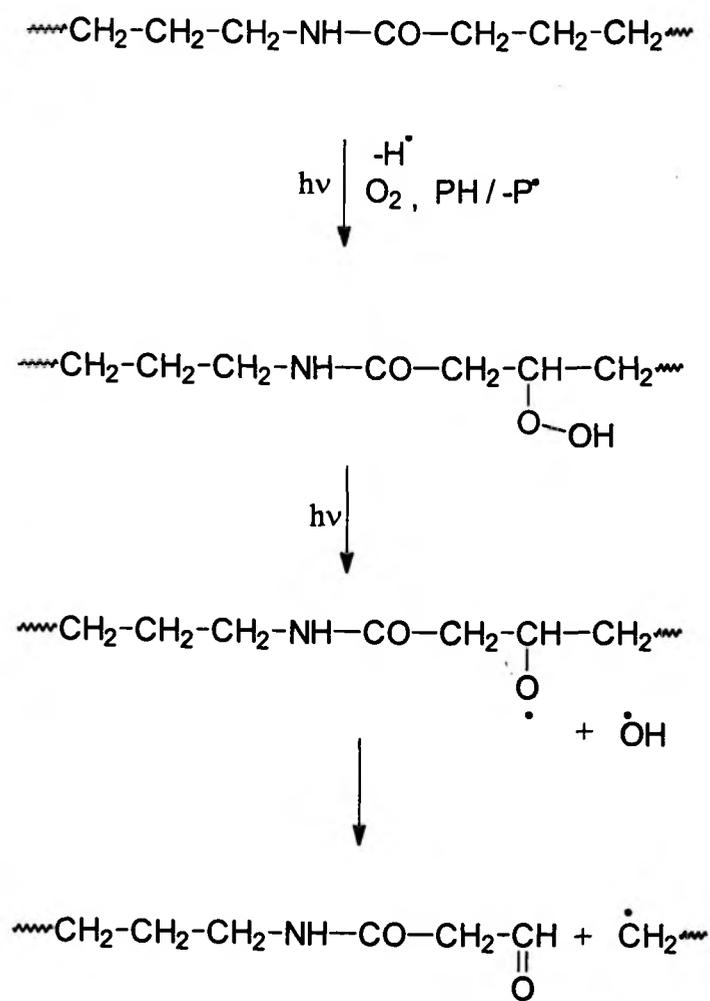
The surface photo-oxidation studies⁵⁹ of nylon 66 with electron spectroscopy for chemical analysis (ESCA) showed an increase in oxygen content on the surface during the UV irradiation. The added oxygen is present mainly as carboxylic groups. The photo-oxidation studies⁶⁰ of the oven-aged nylon 66 films 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

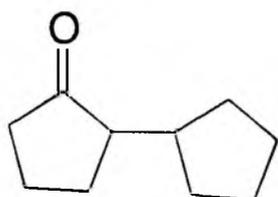


Scheme 1.2

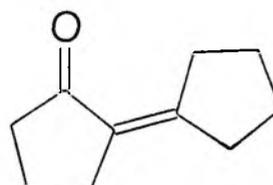


Scheme 1.3

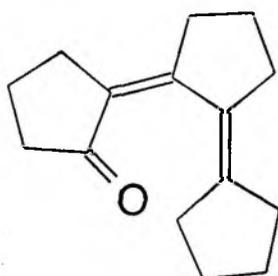
whereas another species had an excitation maximum at 390 and 420 nm and could not be isolated. The latter one was reported to be associated with the presence of α -ketoimide structures formed during thermal oxidation of nylon 66. Extracted products were separated by TLC and analyzed using GC-mass spectrometry.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



Cyclopentyl-
cyclopentanone



Cyclopentylidene-
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.

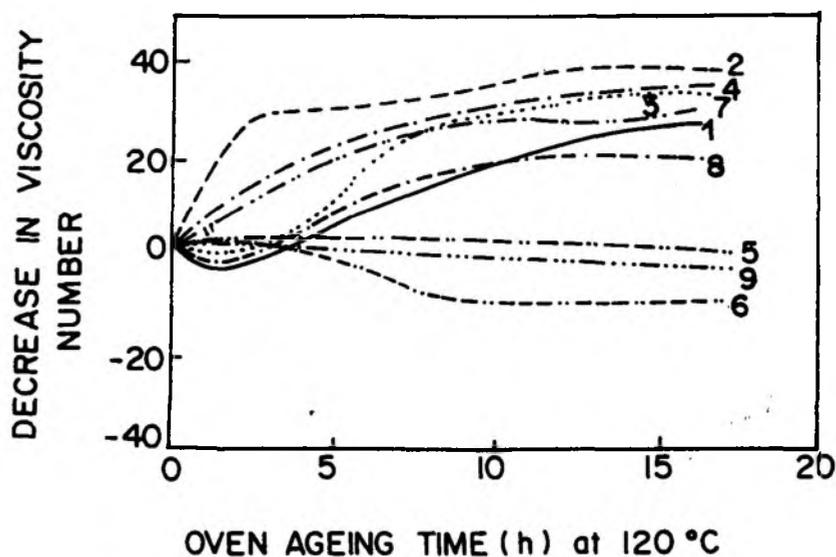


Figure 1.2 Thermal and photochemical degradation of nylon 66 in different atmospheric conditions.

(1), (3), (5) before; (2), (4), (6) after heating in steam at 275°C; and (7), (8), (9) in N₂ 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 envelope⁶² 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— , $\text{—CH}_2\text{—}$, 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 reported⁶⁴ 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. Allen⁶⁵ 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-Maria⁶⁶ 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.

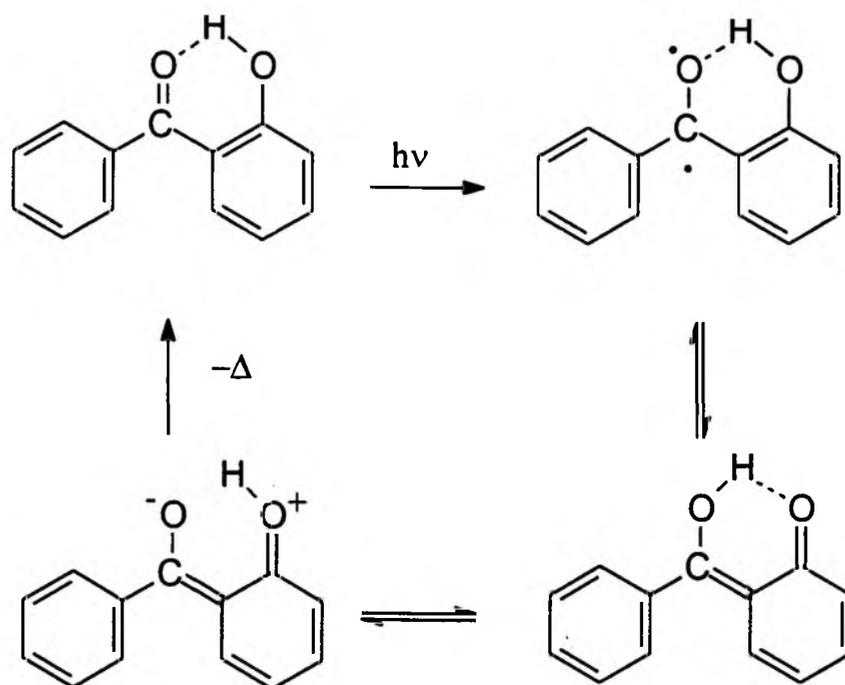
1.6.1 Light screeners

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 Luongo⁶⁹ assumed that, due to their low surface energy, the pigments show protective activity. The pigments also quench certain photoactive species in the polymer⁷⁰. Carbon black is commonly used as a pigment because it is the most-effective light screen⁶⁷, especially at high temperatures. Several theories have been advanced to explain its technically important behavior in the polymer⁷¹.

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*.

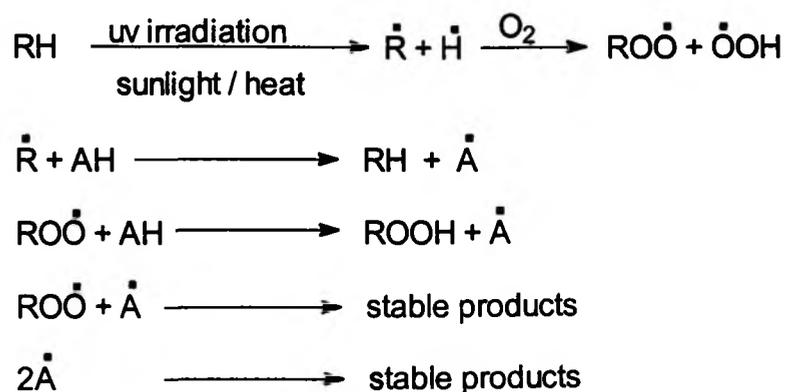
The more basic the hetero atom (O) in the ground state, the more light stable is the compound. It is assumed that, in the ground state, the enol form is energetically preferred, whereas the reverse is true for the first excited singlet. An argument for this viewpoint is the fact that, in the excited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

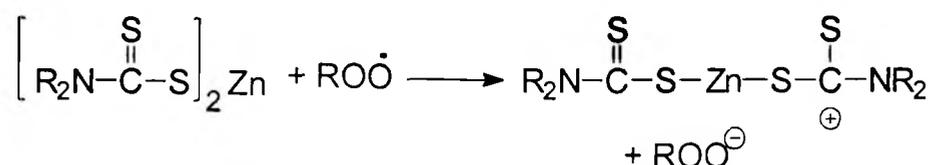
The antioxidant (AH) may inhibit oxidation processes by the following proposed mechanism:



The antioxidants act as a chain-terminating agent. The antioxidants react faster with peroxide radical (ROO $\dot{\text{O}}$) than with macroradical (R $\dot{\text{}}$) and the activity depends upon their structure⁷⁴⁻⁷⁶.

1.6.4 Peroxide decomposers

The salts of alkyl xanthates, *N*, *N'*-disubstituted dithiocarbamates and diethyl dithiophosphonates are effective peroxide decomposers⁷⁷. 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 dithiocarbamate⁷⁸:



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 legands are excellent quenchers for the excited states⁷⁹. The photo-oxidative degradation is promoted by an electronically excited oxygen molecule (singlet oxygen ¹O₂) formed in the polymer. The quenching of ¹O₂ is necessary for effective stabilization and nickel chelates⁸⁰⁻⁸² have proved to be effective quenchers for excited states of singlet oxygen. The quenching may occur either by energy transfer or by the formation of excited state complexes⁸³. 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 effects⁸⁴ 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 lightfastness⁸⁵ of model polyamide is increased by treatment with polyhydroxy benzophenones, benzotriazoles, or benzo-oxazoles, which react with polyamide. Strobel⁸⁶ 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 photostabilized⁸⁷ by incorporating additives such as the Mn (II) salts of ethane phosphonic acid, phenyl ethyl sulfonic acid, and the like during polymerization. Polyamides were stabilized⁸⁸ 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) derivatives⁸⁹ have been used as UV stabilizers for polyamide and other polymer. The salts of hydrohalic acids have been used as stabilizers⁹⁰ 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 derivatives⁹¹. Organic or inorganic derivatives of copper and tin (20-100 ppm) were reported as light and heat stabilizers for polyamides⁹². Some *N*-acyl-*p*-phenylene diamines⁹³ 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 $(\text{CH}_2\text{-CH}_2\text{-NH-CH}_2\text{-Ph-COOH})_2$ 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 fluoroalkyl groups⁹⁵.

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 polyamides⁹⁶. Thus, the protective as well as accelerated action in nylon 66 yarns depends on the dye and methods of application. Nylon 66 pigmented⁹⁷ with titanium dioxide upon treatment with manganese acetate, a phosphorus-containing compound, hexamethylene diammonium dihydrophosphate, 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-ditert-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 dyes⁹⁸ 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 textiles⁹⁹ 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.

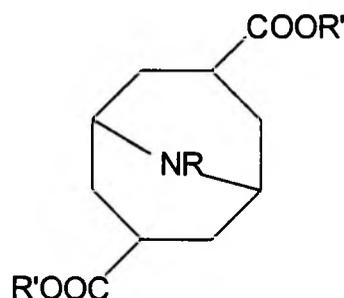
Jellineck and Chaudhari⁴⁹ studied the effect of the solvent from which nylon 66 film was cast. The nylon 66 films cast from benzyl alcohol showed more stability toward ozone, nitric oxide, oxygen and near UV irradiation. They also explained that hydrogen bonding of benzaldehyde or benzoic acid with an amide group prevented the degradation of nylon 66. Light and heat resistance¹⁰⁰ 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 salts¹⁰¹ 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 polyamides¹⁰³. Yellow-color polyamides were obtained¹⁰⁴ 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 Yoshihira¹⁰⁵ incorporated iodonitrobenzene to nylon 6 and nylon 66 to give a composition with good oxidative degradation resistance. Spivack and Klemechuk¹⁰⁶ 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.

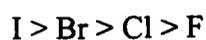
Allen *et al.*¹⁰⁷ studied the effect of titanium dioxide (anatase and rutile) on the photodegradation of nylon 66. Phosphorescence spectra of nylon 66 containing anatase titanium dioxide shows luminescence at 540 nm, while rutile titanium dioxide did not show any luminescence. The reduction in the intensity 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 rubbers¹⁰⁸. 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 radical⁴¹. 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 Dexter¹⁰⁹ 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. Spivack¹¹⁰ used 2,3,5-trialkyl-4-hydroxy benzylphosphonates and phosphinates also during thermal and photochemical degradation. Nylon 66 shows fluorescence and phosphorescence⁵⁶ 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:



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 coworkers¹¹² 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

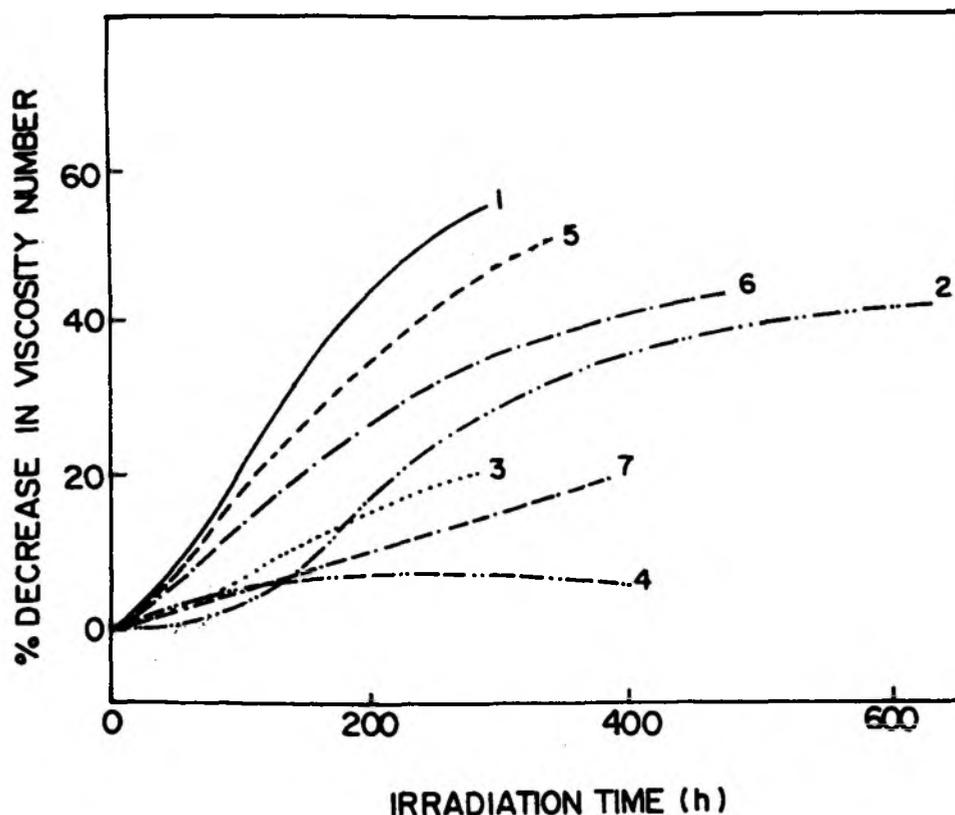


Figure 1.3 Percentage Change in Viscosity Number versus Irradiation Time for nylon 66 films: (1) neat, with 2 wt. % each of (2) Cyasorb UV 3346, (3) 4-carboxy piperidine and with 0.25 wt. % after heating in steam at 275°C (50 mins) each of (4) Tinuvin 770, (5) Chimassorb 994, (6) Tinuvin 622, (7) Tinuvin 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 pigments⁶⁵.

1.8 References

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CHAPTER II

SCOPE AND OBJECTIVES OF THE PRESENT

INVESTIGATION

2.1 Introduction

Now-a-days the production of polymers and plastics is increasing. Nylon 66 is a widely used yarn as well as engineering resin. Moreover, it is used in outdoor applications and sometimes in the hostile conditions of temperature and mechanical stress. All this can cause various degree of degradation depending on hostility of environment and presence of oxygen. Knowledge of the degradation chemistry of polymers has led to the development of more efficient stabilizers¹ for improving performance in one hand and on other hand the development of sensitizers^{2, 3} to produce degradable plastics which may be environmental friendly on the other hand⁴.

The prime factors causing degradation of polymers are UV radiation or heating effects of solar radiation. Additional relevant factors include ozone, atmospheric contaminants, and high-energy radiations. The impurities present in the commercial polymers are known to initiate photochemical reactions. The main light absorbing species may be carbonyls⁵, metallic impurities⁶, dienes⁷, trienes⁸, hydroperoxides⁹ and oxygen-polymer charge transfer complexes^{10, 11}.

Photochemistry of aliphatic polyamides has been a matter of great interest for researchers during last three decades¹²⁻²⁴. Unlike other polymers, nylon 66 has very complicated photodegradation behavior. Certain impurities (mainly α , β -unsaturated carbonyls) formed during melt processing or thermal degradation are reported^{16, 17, 20, 21, 24} to sensitize the photo-oxidation of nylon 66. Ultimately, in the melt processed nylon 66, the presence of these impurities become the major factor, which determines the rate of photo oxidative degradation in nylon 66.

Photosensitized oxidation of nylon 66 in the presence of dyes is also an important area of research^{19, 25-27}. Photochemical behavior of anthraquinone acid blue dyes in polyamides as well as in model amides has been studied^{19, 28}. However, there is a lack of basic understanding of dual behavior of this class of dyes. Photostabilization of nylon 66 is also widely studied²⁹⁻³⁹, which includes hindered amine light stabilizers²⁹, UV absorbers³⁰⁻³², transition metal salts³³⁻³⁵, alkali metal salts³⁶ and inorganic pigments³⁷⁻³⁹ etc.

2.2 Objectives of the present investigation

The objective of the present investigation is to study the degradation mechanism of nylon 66 upon thermal and photoirradiation. This would provide a basic

understanding to the phenomenon of stabilization of this polymer against degradation.

The following aspects of degradation and stabilization have been studied:

1. To examine the photo-oxidative degradation in nylon 66. Chemical and physical changes associated with degradation to be studied in details.
2. To study thermal oxidative degradation in nylon 66 at various temperatures and the formation of oxidative products at all these temperatures are to be compared.
3. To examine the photostability of nylon 66 in the presence of anthraquinone acid blue dyes and also to examine the factors affecting the photochemical behavior of this class of dyes.
4. To study the effect of conventional photostabilizers on the photostability of nylon 66 in the presence of anthraquinone acid blue dyes.
5. To design, synthesize and property evolution of specific water soluble UV absorbers in nylon 66.

2.3 Approaches

2.3.1 Degradation studies of nylon 66

- 2.3.1.1 Detailed photoproducts formation during photo-irradiation of nylon 66 will be studied by IR and UV spectroscopy.
- 2.3.1.2 Changes in the surface and bulk morphology upon photo-irradiation will be studied and compared with their respective unirradiated samples. Surface morphology will be studied by SEM and bulk morphology will be studied with the help of DSC and XRD techniques.
- 2.3.1.3 Chemical processes associated with thermal oxidative degradation will be studied and compared with their respective neat samples. IR and UV spectroscopy will be used for the characterization of thermal oxidative products being formed during the thermal oxidative degradation of nylon 66.
- 2.3.1.4 Effect of dyebath pH on the photochemical behavior of dyed nylon 66 will be studied with the help of FTIR spectroscopy. Nylon 66 samples will be dyed at a range of pH and the rate of photo-oxidation will be studied.

2.3.2 Stabilization studies of nylon 66

2.3.2.1 Photostabilization of nylon 66, in presence of various combinations of a dye, UV absorber and HALS will be studied in details. This is an empirical approach, which enables us to judge the efficiency and optimum quantity of a stabilizer required for the stabilization of a particular substrate.

2.3.2.2 Water-soluble UV absorbers with carboxylic acid and sulfonic acid functional groups will be designed and synthesized. Photo-oxidation of nylon 66, dyed and treated with the aqueous solution of these UV absorbers will be studied in details.

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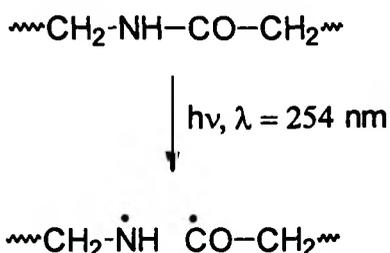
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CHAPTER III

PHOTO OXIDATIVE DEGRADATION OF NYLON 66

3.1 Introduction

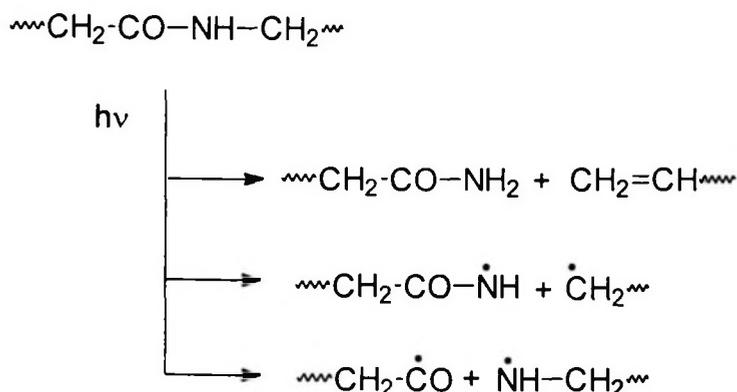
Aliphatic polyamides have got very good applications as engineering plastic as well as fiber material. During its normal use it is exposed to sunlight, which causes extensive degradation to the polymer. Degradation is a very crucial factor and deteriorate the useful properties of polymeric materials. Nylon 66 degradation is studied widely during the past several decades by several authors¹⁻⁴. It causes severe changes in its chemical, physical and mechanical properties upon natural/artificial weathering. The degree of changes depends on the wavelength of the UV light and the atmospheric conditions. Various techniques have been used to characterize the photodegradation in nylon 66. Moore² compared the photodegradation products obtained from the model amides and polyamides and characterized them by several techniques like loss in tenacity, change in intrinsic viscosity, UV spectroscopy and end group analysis. The hydroperoxide analysis and second derivative of UV spectroscopy are also important and have been used to characterize photodegradation in polyamides⁵⁻⁸. Allen *et al.*⁹⁻¹² have studied the photochemistry of nylon polymers in details. Kinetics of photoaging has been widely studied^{2,4,10,12} for nylon 66. It was observed that wavelength of light has significant influence on photoproduct formation during photodegradation of nylon polymers^{6,7}. Chromophore defects and impurities initiate the hydroperoxidation when nylon polymers are exposed to light of higher wavelength ($\lambda > 340$ nm). Whereas at lower wavelength ($\lambda = 254$ nm) direct photoscission occurs, which is independent of the length of carbon chain.



Presence of water was the another important factor plays ver crucial role during the photo-oxidation of aliphatic polyamides.

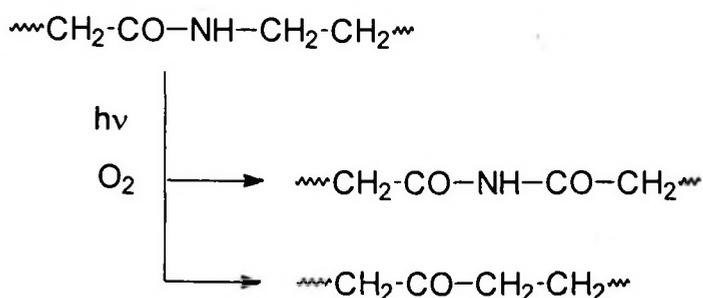
Chain scission upon photo-irradiation is also widely studied in nylon polymers. Do *et al.*¹³ studied the photodegradation and photo-oxidation in nylon films at shorter wavelength ($\lambda = 254$ nm) by FT-IR spectroscopy. They also studied the evolution of the gases and changes in crystallinity with UV exposure. They observed

that photo-irradiation of nylon polymers in nitrogen atmosphere gives extensive chain cleavage.



While photo-oxidative degradation gives the following photoproducts.

Th 8690



Although a few workers have studied photo-oxidation¹⁴⁻¹⁶ of nylon 66 but the photo-oxidative kinetics is not well defined. To improve all aspects of the stability of polymers, a fundamental understanding of degradation process involved is essential, therefore in present study we have made an attempt to study the chemical and physical changes in nylon 66 with polychromatic irradiation ($\lambda \geq 290$ nm).

3.2 Experimental

3.2.1 Materials

Commercial samples of nylon 66 (Zytel 101 L NC 10) were received from M/s E.I. du Pont de Nemours, USA and used without further purification.

3.2.2 Sample preparation

Thin films (thickness ~ 50 μm) of commercial nylon 66 were prepared by pressing the polymers in preheated *Carver* press at 270°C under ~ 14 kg/cm^2 pressure for two minutes. The films were quench cooled rapidly in the press.

3.2.3 Photo-irradiation

All samples were irradiated in a SEPAP 12/24 (an accelerated photoirradiation chamber $\lambda \geq 290$ nm) at 60°C for different time intervals. The details of this equipment are given elsewhere¹⁷.

3.3 Analysis

3.3.1 FT-IR analysis

Photo-oxidative products and kinetics of photodegradation were studied by FT-IR (Fourier Transform Infrared 16 PC spectrometer).

3.3.2 UV absorption analysis

The ultra-violet absorption measurement for thin films (~ 50 μm) were carried out on Hewlett Packard 8452A Diode Array Spectrophotometer.

3.4 Results and Discussion

3.4.1. Change in hydroxyl regions

FT-IR spectroscopic technique was used to characterize the photo-oxidation in the polymer films. Changes in hydroxyl region ($3700\text{-}3200$ cm^{-1}) during the

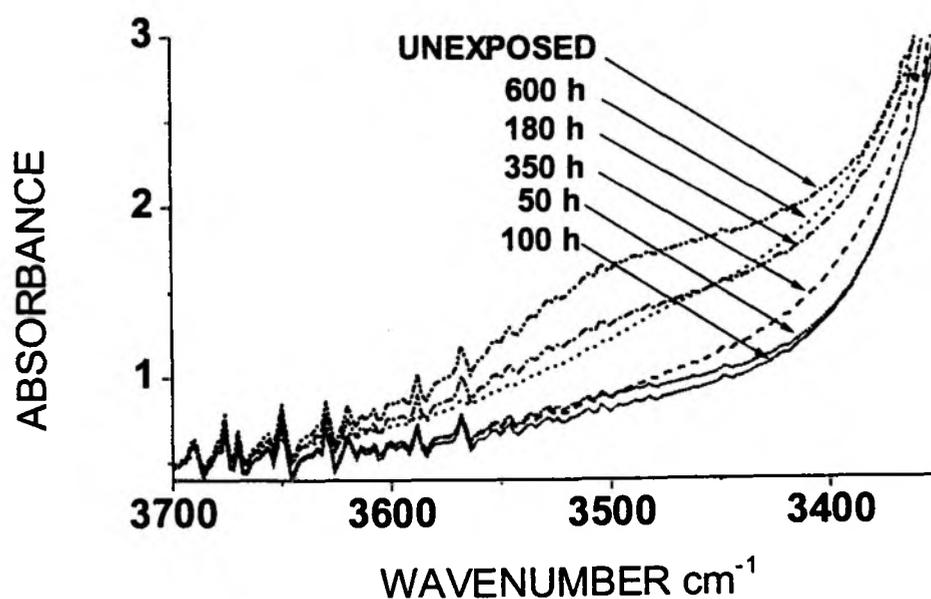


Figure 3.1 Change in hydroxyl region of IR spectra of photo-irradiated nylon 66 sample.

photo-irradiation are quite different than what usually observed in polyolefines and styrenic polymers^{18,19}. *Figure 3.1* shows that already formed hydroperoxides, which might have been generated during the melt processing of the polymer and are decomposed upon photo-irradiation. The rate of decomposition of hydroperoxide/hydroxyl groups is much faster than that of generation during the initial period of photo-oxidation, which leads to a decrease in the absorbance range 3700-3200 cm^{-1} in the initial 100 h. irradiation but after that there is no consistency in the changes as shown in *Figure 3.2*. Here the peak intensity in case of hydroxyl/hydroperoxy absorption is an integrated partial area from 3700 to 3350 cm^{-1} calculated using base line from 3700 to 2200 cm^{-1} . In case of carbonyl absorption, the peak intensity is also an integrated partial area from 1820 to 1690 cm^{-1} calculated using baseline from 1800 to 972 cm^{-1} . Decomposition of hydroperoxide/hydroxyl species can form imide or aldehyde respectively²⁰.

Existence of hydroperoxy/hydroxyl species in unexposed sample is due to the

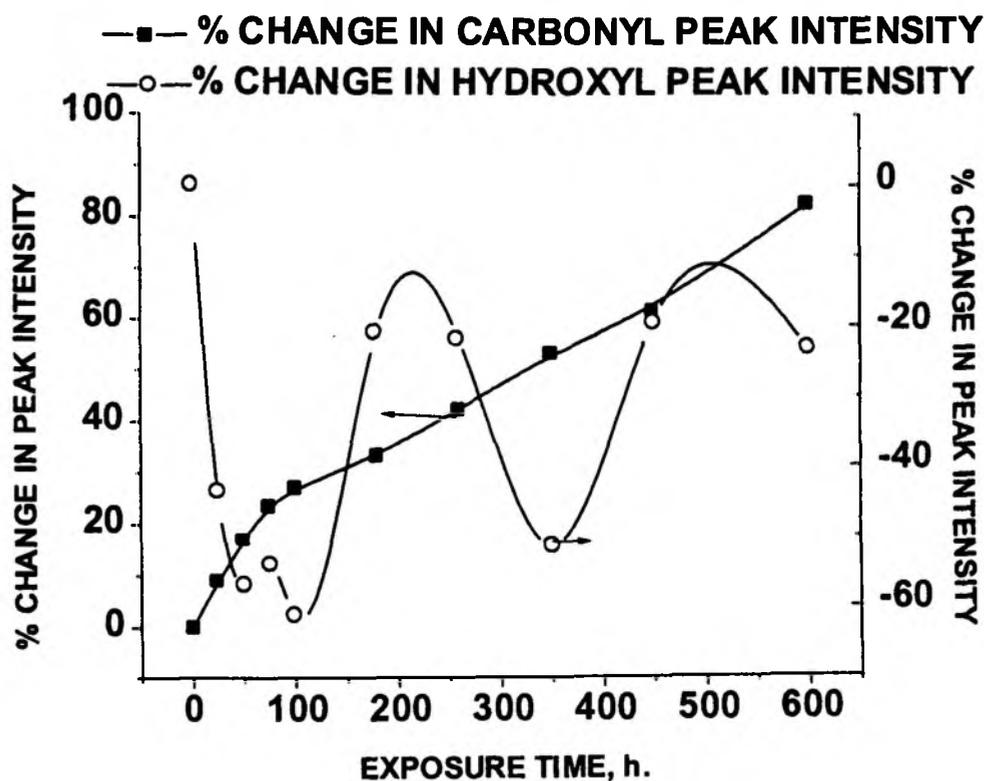


Figure 3.2. Change in hydroxyl and carbonyl peak absorption of nylon 66 with exposure time.

formation of these groups during melt processing (while preparing the films) of nylon 66. Moreover, these species are stable at room temperature and easily detected in unexposed samples. We did not observe the presence of these species in solution-cast films.

In a separate study we tried to examine the decomposition behavior of hydroperoxy/hydroxyl species during the initial period of photo-irradiation. Pre-existing hydroperoxy/hydroxyl species started getting decomposed with increasing exposure time (*Figure 3.3*) up to 25 h. During that period there was a rapid increase in carbonyl population. After 25 h, the hydroperoxy/hydroxyl species started increasing while carbonyl population remained rather constant. After 90 h again

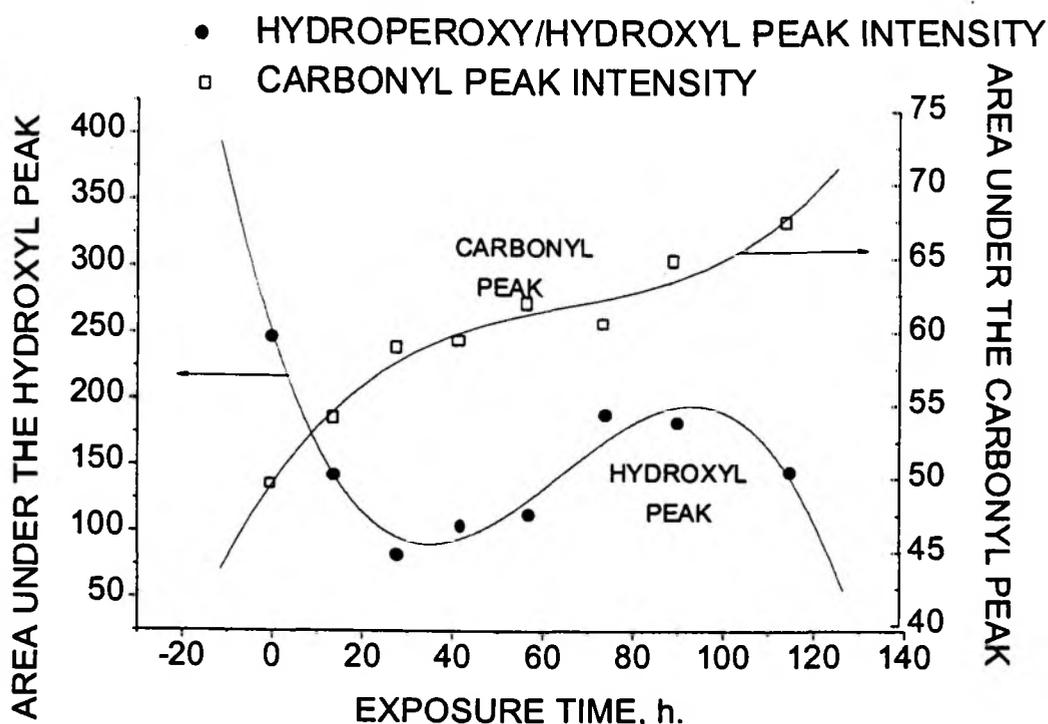


Figure 3.2. Change in hydroxyl and carbonyl peak absorption of nylon 66 with photo-irradiation during initial period of exposure.

hydroperoxy/hydroxyl species started getting decomposed and the carbonyl population increased sharply. Thus, decomposition of hydroperoxy/hydroxyl species resulted in the formation of carbonyl species.

3.4.2 Change in carbonyl regions

The IR spectral changes in the $1800\text{-}1690\text{ cm}^{-1}$ region with exposure time are shown in *Figure 3.4*. The increase in the absorbance with irradiation time in this region indicates an increase in the imide group population. From *Figure 3.2* also, it is clear

that there is a continuous increase in carbonyl absorption, moreover, this increase is more rapid during initial period of exposure (up to 100 h) after that it continues to increase but with slower rate. This observation, again, gives perfect evidence about the decomposition of hydroperoxide/hydroxyl groups in the carbonyl groups. Straight increase in carbonyl group concentration with irradiation time is an indication for the prevalence of single photo-oxidation mechanism throughout the photo-oxidation process.

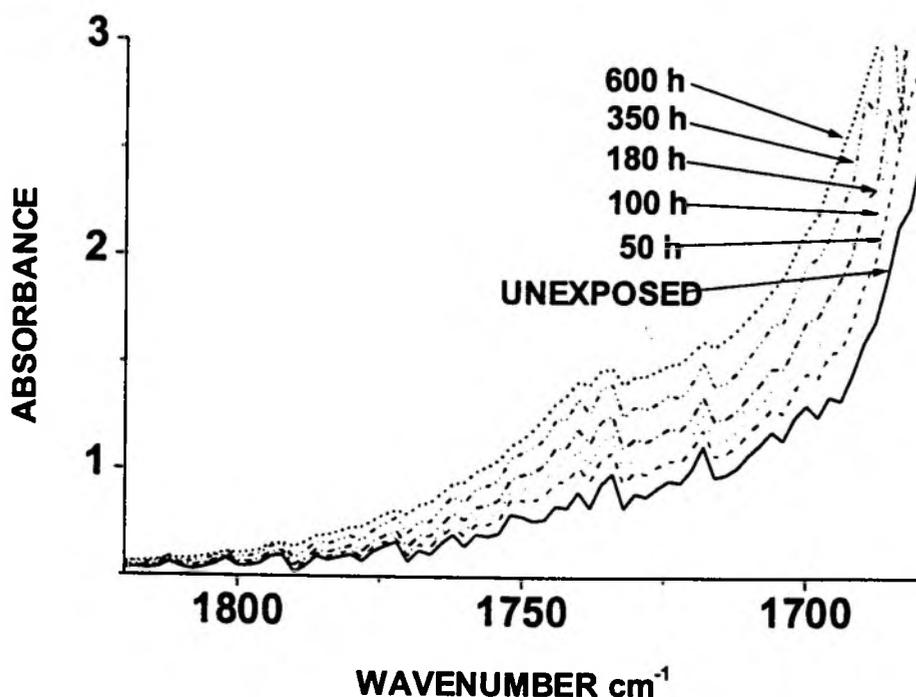
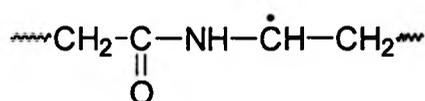


Figure 3.4 Change in carbonyl region of IR spectra of photo-irradiated nylon 66 sample.

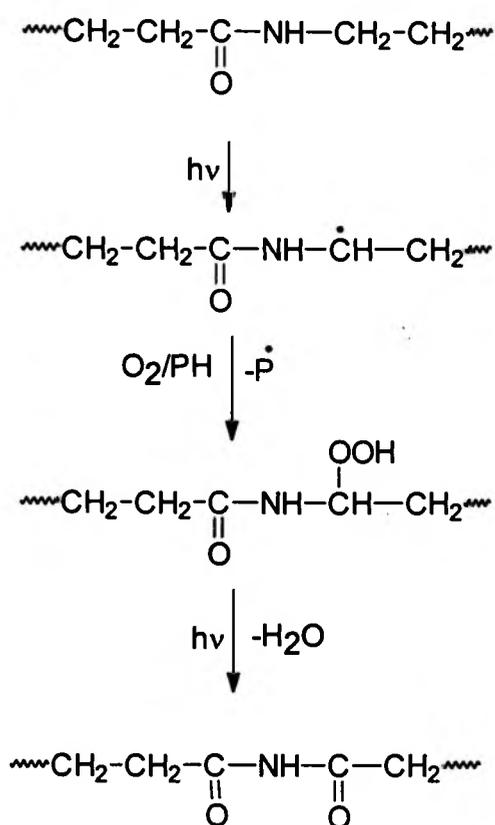
3.4.3 Change in methylene regions

As per mechanism suggested^{2,19,20} for photo-oxidation of model polyamides, it was observed that the primary free radical formed upon UV irradiation is:



which suggests that there should be continuous decay of methylene group adjacent to —NH— group [—CH₂—(NH)—] population. We have also tried to study the

kinetics of $\text{—CH}_2\text{—(NH)—}$ decomposition with exposure time. The absorption band at 1180 cm^{-1} is due to $\text{—CH}_2\text{—(NH)—}$ group²⁴ and we found that population of methylene group, vicinal to —NH— group, decreases linearly with irradiation time (Figure 3.5). This is an additional evidence to the mechanism suggested by Do *et al.*¹³ that decomposition of hydroperoxides leads to the formation of carbonyl groups:



IR 1690 cm^{-1}
UV 244 nm

Absorption of methylene groups linked both the side with carbon atom show absorption at 2900 cm^{-1} . We did not observe any significant change in this particular band intensity.

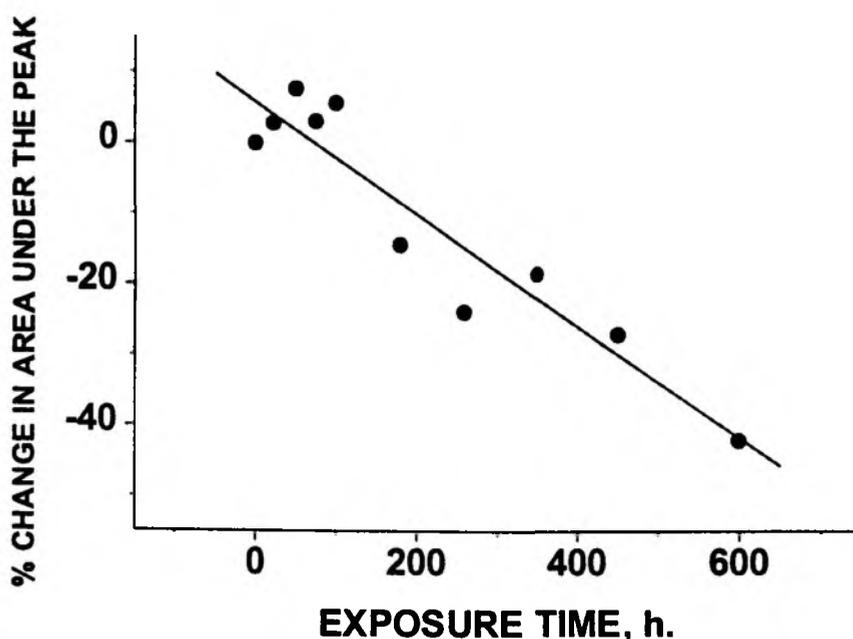


Figure 3.5 Change (%) in the methylene group, adjacent to the —NH— group, population with photo-irradiation time.

3.4.4 Change in amorphous and crystalline regions

Many semicrystalline polymers show infrared absorption bands corresponding to motions in the crystalline and amorphous phase. In case of nylon 66 crystalline and amorphous bands appear at 936 and 1140 cm^{-1} , respectively²¹. The origin of this bands has been assigned^{21a} to a CO twist (1140 cm^{-1}) and —C— CO stretch (936 cm^{-1}). Figure 3.6 shows that intensity of this peak decreases with exposure time.

In Figure 3.7 amorphous and crystalline peak intensity is plotted against the exposure time and from this figure it is very much clear that the amorphous region is the only site for photo-oxidation, which decomposes continuously with exposure time. Somewhat similar results were observed by Do *et al.*¹³ during exposure of nylon 66 by short wavelength irradiation ($\lambda = 254\text{ nm}$). The reason for decomposition of amorphous region, exclusively, can be justified by the lower oxygen diffusivity and permeability for nylon 66. This phenomenon might have limited photo-oxidation to amorphous region only where oxygen diffusion would be sufficient to oxidize the polymer.

Aliphatic polyamides are reported to have very less oxygen diffusivity as compared to polyolefines. Importance of oxygen diffusion in determining the rate

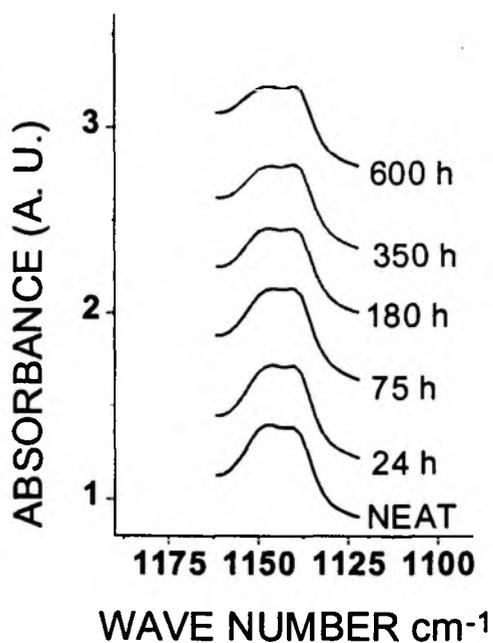


Figure 3.6 Changes in amorphous region of IR spectra with photo-irradiation.

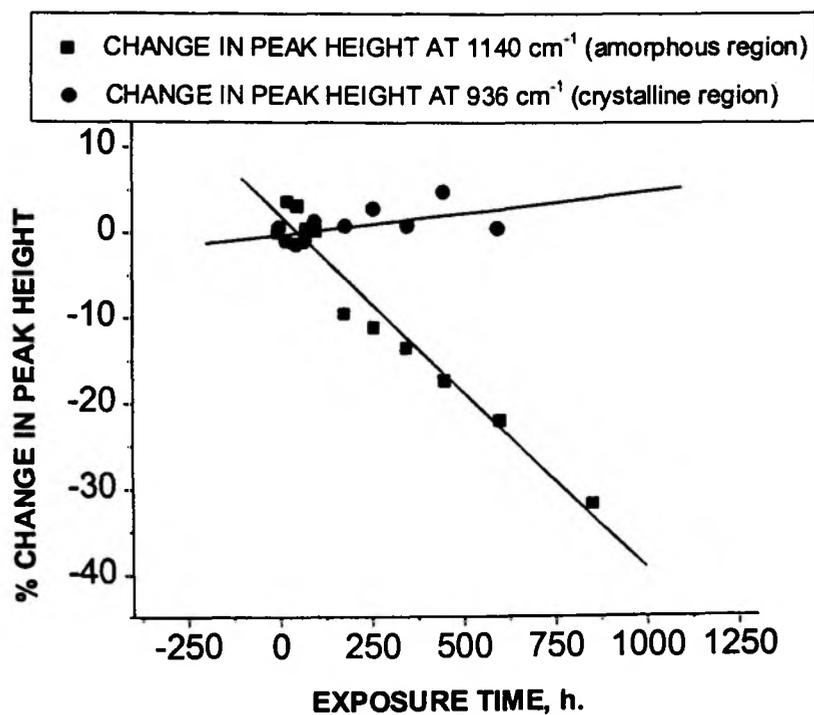


Figure 3.7 Change in crystalline and amorphous peak intensity with exposure time.

of thermal and photo-oxidation of polymers has been discussed in details²²⁻²⁶. Carlsson and Wiles observed²⁶ very high surface oxidation of during the photo-irradiation of polyolefines and indicated that oxygen availability at the surface of polymer causes very high degree of oxidation. Furneaux *et al.*²⁷ studied the natural and accelerated artificial weathering of low density polyethylene. The natural and artificial samples showed very similar reaction profiles. They found that there was a significant drop in photo-oxidation reaction at the center of the sample. They too concluded that this particular behavior was due to the limited supply of oxygen at the core of sample. It is fact that gas diffusion in any semicrystalline polymer is limited to the amorphous phase of the polymer. As crystallinity increases the gas diffusivity is declined. Prevalence of photo-oxidative processes in amorphous region supports the fact that oxygen diffusivity is one of the important factor that can control the rate of oxidative degradation in any polymer.

Do *et al.* also reported the emergence of absorption band at 1620 cm^{-1} during photo-oxidation of nylon 66, according to them this band is due to absorption of certain species bearing double bonds. However, in our study we did not observe such kind of absorption at $\sim 1620\text{ cm}^{-1}$.

3.4.5 Change in UV absorption

Exposure of nylon 66 films to polychromatic radiation led to the development of UV absorption band at $\sim 244\text{ nm}$. The spectra shown in *Figure 3.8* are in the form of spectral subtraction of unexposed sample spectra from each of the spectra of the photo-oxidized sample at different time duration.

Figure 3.9 shows that the peak height ($\lambda = 244\text{ nm}$) is increasing continuously with exposure time. Increase in peak height with exposure time is due to the formation of imide groups as it is already reported²⁸ that open chain imides show a peak in the region of 250 nm and 230 nm with a tail extended out to 280 nm . Also the nature of kinetic curves in *Figure 3.4* and *Figure 3.9* are similar, which again confirms the formation of, mainly, imide species as a result of photo-oxidation in nylon 66. Allen reported²⁹ the UV absorption bands at $\sim 230\text{ nm}$ and 294 nm in photo-oxidized nylon 66 (due to formation of α , β -unsaturated carbonyl species) but we did not observe the same in our studies.

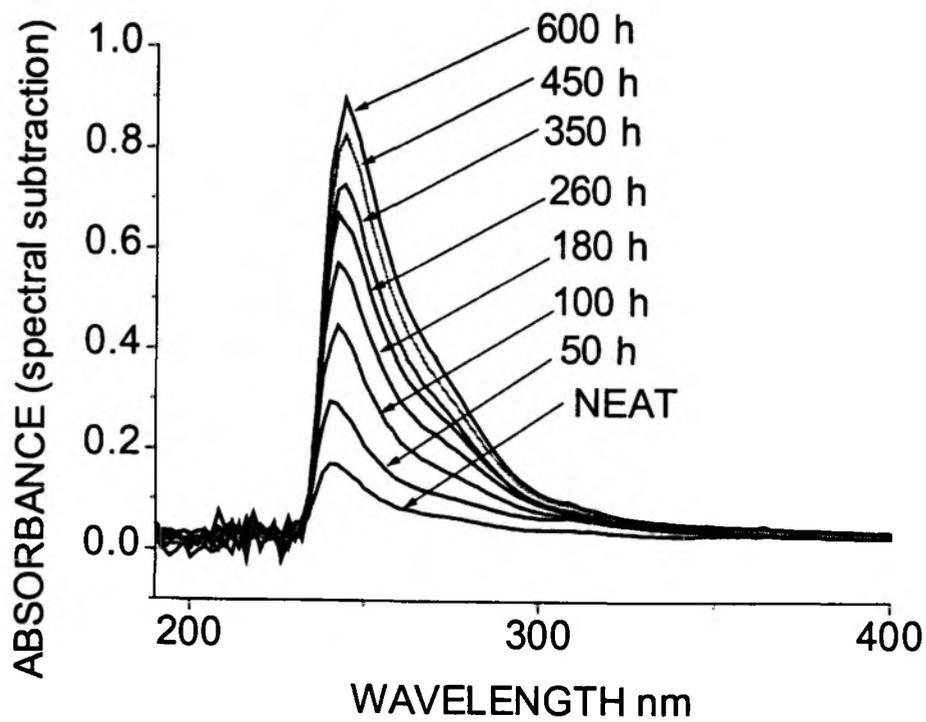


Figure 3.8 Change in UV absorption nylon 66 photo-irradiated at different time intervals.

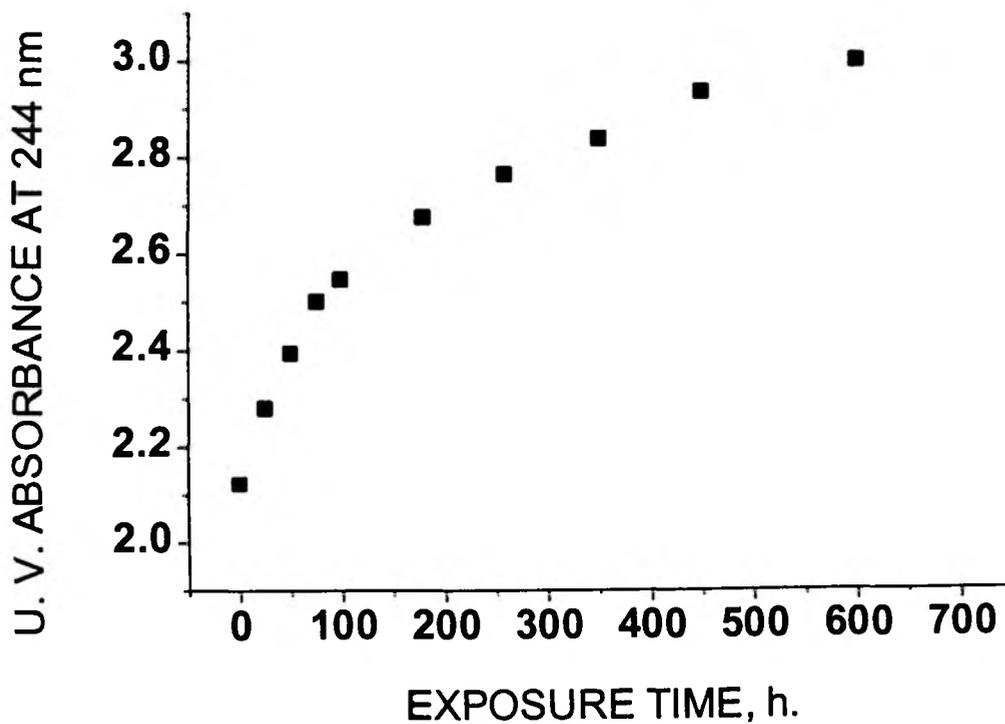


Figure 3.9 Increase in UV absorption at 244 nm with exposure time

3.5 Conclusions

The presence of hydroxy/hydroperoxide groups in melt processed film was found in quite a higher concentration and according to us that is the main driving force for the higher rate of photo-oxidation during the initial period of exposure. The continuous increase in carbonyl group concentration concludes the existence of a single photo-oxidation mechanism throughout the oxidation process. Primary photo-oxidation process in polyamide is the oxidation of methylene group adjacent to the —NH— group. Physical changes in polymer matrix like disappearance of amorphous phase with exposure time is the main evidence for effectiveness of photo-oxidation in amorphous phase. Finally, the UV absorption study suggests that the increase in UV absorption at ~244 nm is due to the imide formation.

3.6 References

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4.1 Introduction

Photo-oxidation in nylon 66 has been studied widely. Several authors have characterized photo-oxidation in polyamides using various analytical techniques. Moore¹ characterized photo-oxidation by intrinsic viscosity changes, UV absorption and end-group analysis. Surface oxidation in nylon 66 was also characterized² by ESCA. The effects of photo-irradiation were characterized in detail^{3,4} by FT-IR spectroscopy. Polymer morphology is one of the major factors, which marginally affects the degradation kinetics of the polymeric materials⁵⁻⁸. Moreover, all useful mechanical properties of a polymeric material depend on its morphology. The studies of changes in polymer morphology upon degradation have always been remained as an important area of research⁹⁻¹⁷. In present study we have made an effort to look at the morphological changes in nylon 66 induced by photo-irradiation. Some interesting observations are highlighted in this chapter.

There has been also a keen interest to study degradation-induced microstructure changes on the polymer surface. Scanning electron microscopy (SEM) is most often used for studying such kinds of microstructural changes¹⁸⁻²⁴. In the present report, we have also studied photoirradiation induced microstructure changes on nylon 66 surface by SEM. At different stages of photo-oxidation various microstructures were observed. Surface swelling was observed in initial stages of photo-oxidation, which was followed by micro-cracks. Development of extended parallel cracks, chemi-crystallization and the formation of fractals was observed on the intensely photo-oxidized surface of nylon 66.

4.2 Experimental

4.2.1 Materials

Nylon 66 (Zytel 101 L NC 10) was received from M/s du Pont de Nemours (USA) and used without further purification.

4.2.2 Experimental procedure

Thin films of (thickness ~50 μm) of nylon 66 were prepared by pressing the polymer in between two preheated plates in a hydraulic press at 270°C under ~ 14 kg/cm² pressure for 2 minutes. The films were quench cooled rapidly in the press. Films for optical microscopic study were prepared on glass slides by heating slides at 270°C on hot-plate. All the samples were irradiated in an accelerated photo-irradiation chamber

(SEPA 12/24, $\lambda \geq 300$ nm) at 60°C for different time intervals. The details of this equipment are given elsewhere¹⁷.

4.2.3 X-ray diffraction measurements

The X-ray diffraction experiments were performed using Rigaku Dmax 2500 diffractometer. The system consists of a rotating anode generator, wide-angle powder goniometer and a slit collimated small angle goniometer. The generator was operated at 40 KV and 150 mA. The samples were scanned between $2\theta = 10$ to 35 deg. and the scan speed was 1deg/min. The crystallinity was calculated as the ratio of the area of the crystalline peaks to the total area.

4.2.4 DSC measurements

The calorimetric measurements were done using Perkin-Elmer DSC-7. The samples were heated/cooled at a rate of 10°/min. under nitrogen environment. The melting temperature and heat of fusion were obtained from the heating thermogram.

4.2.5 SEM analysis

Surface changes on nylon 66 films were studied by using Leica Cambridge (Stereoscan 440) scanning electron microscope (Cambridge, UK). Polymer film specimens were coated with gold (thickness 50 μm) in an automatic sputter coater (Polaron Equipment Ltd., scanning electron microscope coating unit E 5000, UK) and accelerating potential was 10 kV. Micrographs of representative areas of the sample were taken at different magnifications.

4.3 Results and Discussion

Photo-oxidation processes in polyamides consist chain scissions, formation of hydroxy/hydroperoxy and various carbonyl species²⁵⁻²⁷. It was observed⁴ that initiation of photo-oxidation starts with a proton abstraction from methylene group adjacent to $-\text{NH}-$ group and amorphous region was identified as initial site of photo-oxidation in nylon 66.

In order to study morphological changes occurred as a result of photo-oxidative processes in nylon 66, samples were analyzed by DSC. *Figure 4.1* shows the DSC heating thermograms of nylon samples photo-irradiated for different time intervals. There is a systematic variation of the melting peak with irradiation. The melting endotherm of the control sample shows two peaks, a broad peak starting from

220°C and a sharp peak at 265°C. The sharper peak at higher temperature corresponds to the

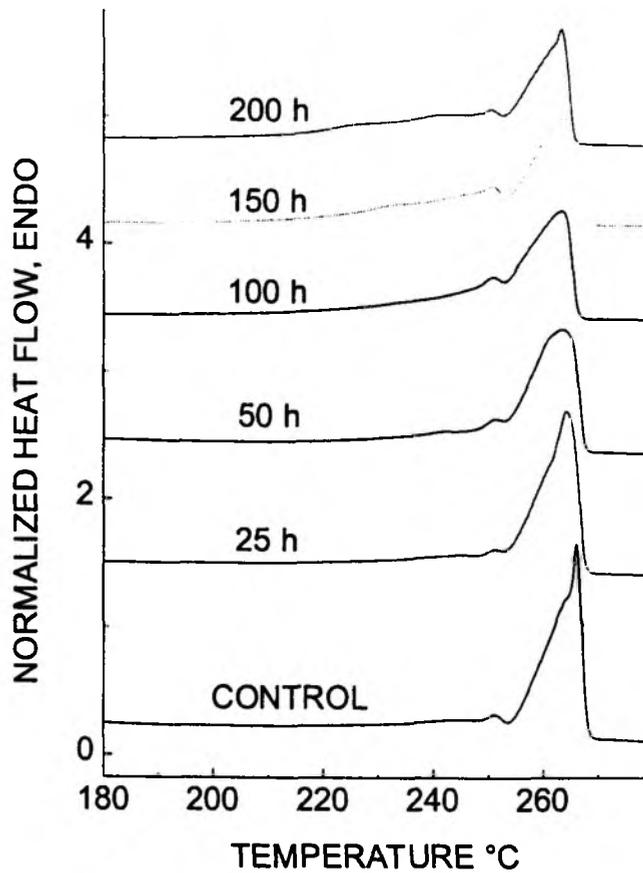


Figure 4.1 Melting thermograms of nylon 66 photoirradiate for different time intervals

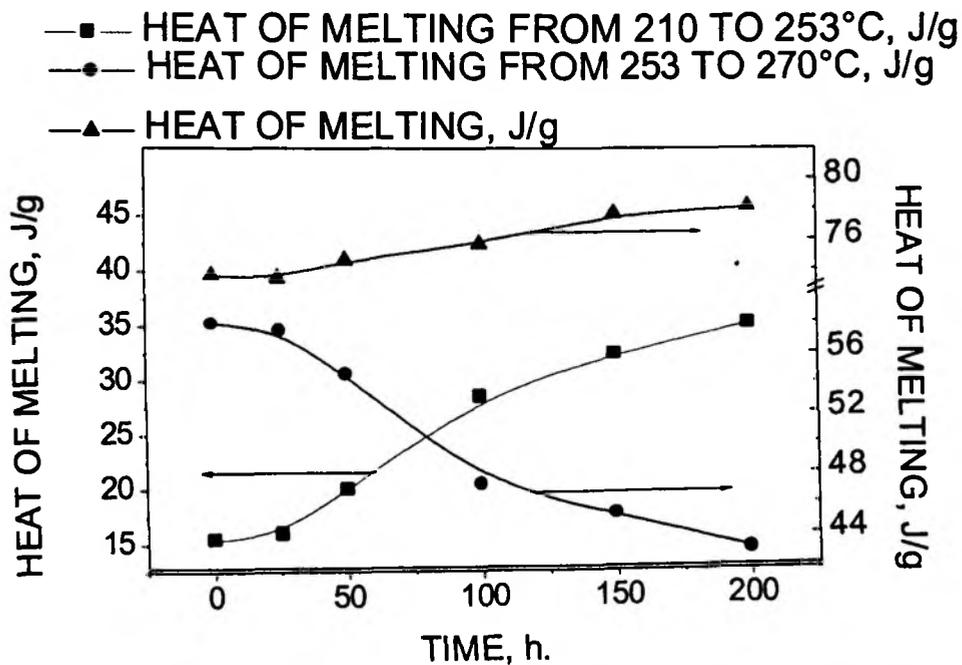


Figure 4.2 Change in Heat of Metling with exposure time

melting of the lamellae that is formed at the crystallization temperature on cooling and can undergo partial melting and recrystallization resulting in the double peak. A careful inspection of the sharper peak reveals that the sharper peak is composed of two peaks. The broad peak starting at 220°C corresponds to the melting of thin lamellae that crystallize at a lower temperature than the normal crystallization temperature on cooling to room temperature. This lamellae, in general, reside within the spherulites and between the thicker lamellae and cannot undergo reorganization and melts at lower temperature.

The partial area of the low temperature broad peak and the higher temperature sharp peak are shown in the *Figure 4.2* as a function of irradiation time. It is seen from the Figure that the area under the low temperature peak increases while the high temperature peak decreases. However, the total area remains fairly constant. This indicates a modification of semi-crystalline morphology due to photo-irradiation. The melting temperature also shows a small decrease with exposure time and is given in *Table 4.1*.

Table 4.1 Decrease in melting temperature with exposure time:

Exposure time, hrs	Melting temp. °C
0	266
25	264
50	264
100	264
150	264
200	263

The room temperature X-ray diffraction patterns of the various samples are shown in *Figure 4.3* where the positions of the characteristic peaks of nylon 66 at $2\theta = 20^\circ$ and 24° remains unchanged. The intensity of the peak at $2\theta = 24^\circ$ shows a

decrease during initial stages of photo-irradiation as seen from the pattern of the sample irradiated for 25 hours. However the intensity of the peak at $2\theta = 24^\circ$ does not

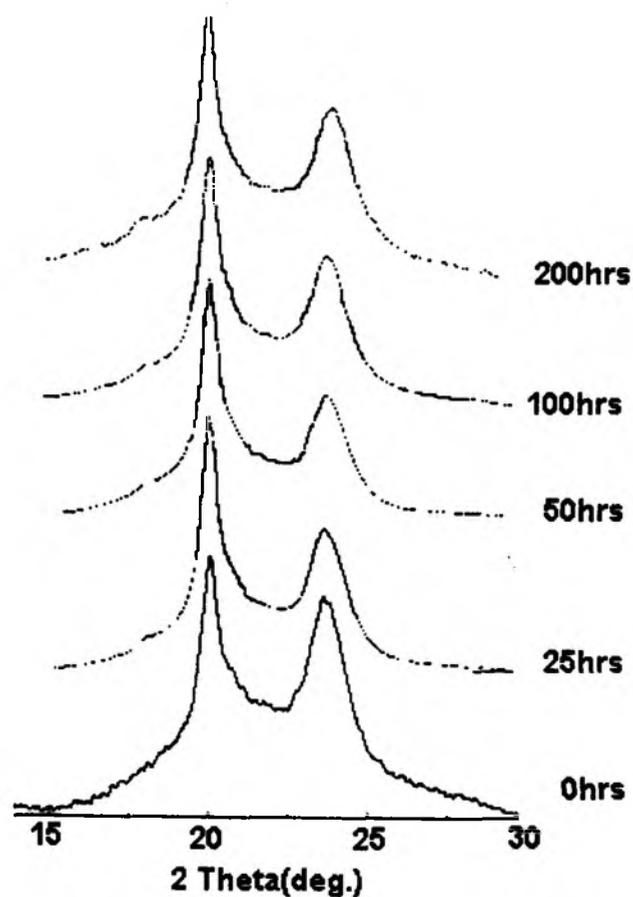


Figure 4.3 Change in X-ray diffraction patterns of nylon 66 with exposure time

show any significant variation above 25 hours of irradiation. The intensity of the peak at $2\theta = 20^\circ$ seems to be not affected by irradiation. The crystallinity calculated from the pattern of the various samples are shown in *Table 4.2* and seen that crystallinity increases marginally during very early stages of irradiation and then remains unchanged.

The general shape and d-spacings of the 100 and 010/110 reflections suggest that the photo-irradiation does not induce any variation to the α -phase crystalline structure of nylon 66. DSC studies on polymer degradation show emergence of new melting peak as a result of degradation processes^{13, 16, 28-32}. Modification of crystalline

Table 4.2 Change in crystallinity with exposure time measured using XRD technique.

No.	Exposure Time, h	% Crystallinity (XRD)
1.	0	36
3.	50	40
4.	100	42
5.	150	43
6.	200	44

morphology can be explained by chemi-crystallization phenomenon. In case of nylon 66, at 60°C, the molecule segments in the amorphous region have enough mobility. However, further crystallization is restricted because of chain entanglements. When semicrystalline nylon 66 is exposed to UV irradiation in presence of oxygen, oxidation reactions occur resulting in the chain scissions. Since amorphous region has higher oxygen permeability and diffusivity, photo-oxidation preferentially takes place in the amorphous phase of polymer. The entangled molecules are released as a result of chain scission. These released molecule segments crystallize by the rearrangement. In this study, we find decrease in the heat of fusion of the high temperature peak and this indicates that the radiation affects the crystalline region as well. However, there is no decrease in crystallinity (*Figure 4.2*) even after 200 h of photo-irradiation whereas chemi-crystallization is known to increase the crystallinity²⁶. Similar fact was observed by Aslanian *et al.*²³, when LDPE is irradiated with γ -radiation, which showed the emergence of a low temperature endothermal peak in DSC thermogram. Kostoski *et al.*¹³ also found that the oriented PP with increasing γ -irradiation dose showed the melting temperature decreases and area under the lower melting peak increases at the expense of the area under higher melting temperature.

It is observed⁴ in the case of nylon 66 that photo-oxidative processes are prevailing in amorphous phase. Damage observed in crystalline region, the decrease in the melting peak area of high temperature peak, is due to scission of tie molecules and chain folds at crystal surfaces and subsequent cleavage of chains from the crystal surface. Moreover, both tie molecules and chain folds are likely to contain heavily strained bonds and making them prone to photo-oxidation. These oxidative processes will cause bond breaking and lead to the lowering of melting point. Ogier *et al.*¹⁴ also observed the similar phenomenon during photo-oxidation studies on PP. Increase in the area under lower melting peak with irradiation time is mainly due to the formation

of new thin lamellae. The emergence and destabilization of defects in crystalline region of spherulite composition can result in a decrease in melting temperature of the main endotherm peak.

Kostoski *et al.*¹³ also found similar phenomenon and suggested that increase in crystallinity with absorbed dose can probably be attributed to the scission of highly strained molecules followed by chemi-crystallization. Detailed explanation for similar fact was given by Rabello *et al.*,⁹ according to them the crystals formed as a result of photoirradiation grew with the same orientation distribution as pre-existing ones. This occurs if the overgrowth predominates over formation of new crystals. This is in agreement with the theory of chain scissions to occur within or near to the interphase, suggesting the involvement of short-range movements of the molecules during molecular ordering upon photoexposure.

Optical microscopic studies show (*Figure 4.4.a, b, and c*) that there is cracks formation with photo-irradiation. It is interesting to note that all the cracks originated from the center of spherulites and grow in size with exposure time. This suggests that there is further crystallization within the spherulites during oxidation, which causes the shrinkage within the spherulites. The center of a spherulite becomes the point with maximum strain and giving rise to a crack. Thus this is an additional evidence for chemi-crystallization process.

SEM showed the variety of surface features upon photoirradiation of nylon 66. *Figure 4.5* shows the surface characteristics of controlled sample. Straight parallel marks visible on the sample surface are believed to be generated during melt processing of the polymers. After 100 h of photo-irradiation, there are distinct features developed on the surface. *Figure 4.6 (a)* shows a spot, which is due to localized swelling of the surface. Localized degradation could be due to the impurities present in the polymer sample. These impurity centers are believed to be formed during polymerization or melt processing of polymers, which sensitize photo-oxidative processes in the polymer. As a result of this, there will be an intense damage at some portions of the polymer surface. Swelling of the surface is due to the increase in the surface-volume as a result of photo-oxidative process. Photo-oxidation causes formation of hydroxy/hydroperoxy, imide and other carbonyl species, which occupies more volume than existing macromolecule chains. Eventually, this causes the surface swelling as a result of photo-exposure. Microstructure of the swelled surface is shown in *Figure 4.6 (b)*, which shows the formation of some irregular

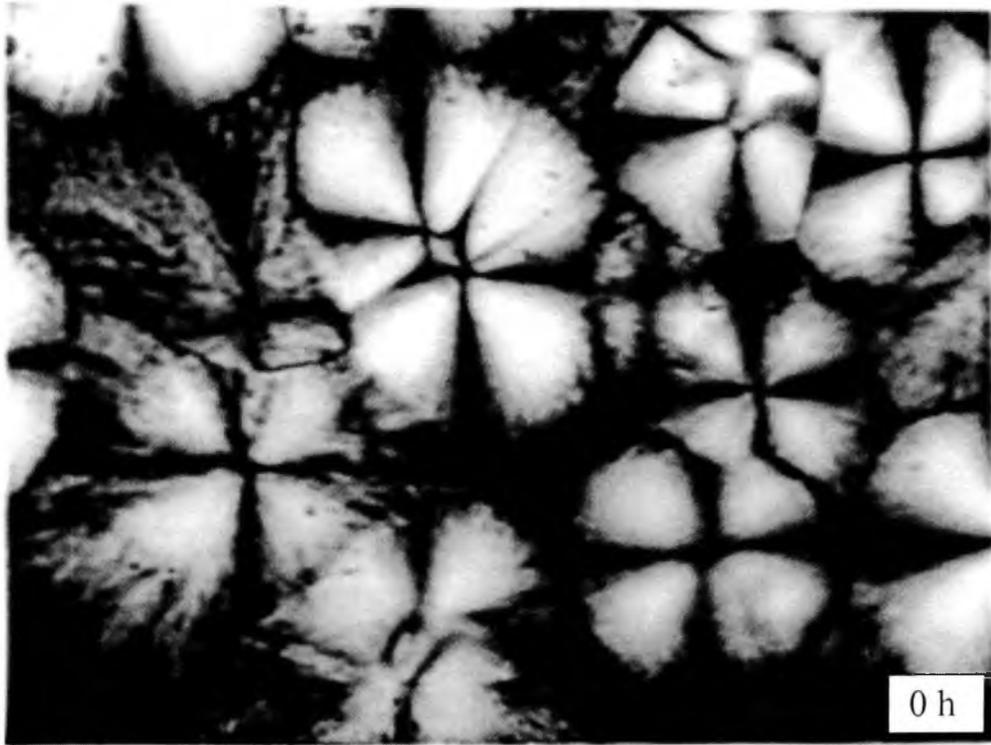


Figure 4.4.a

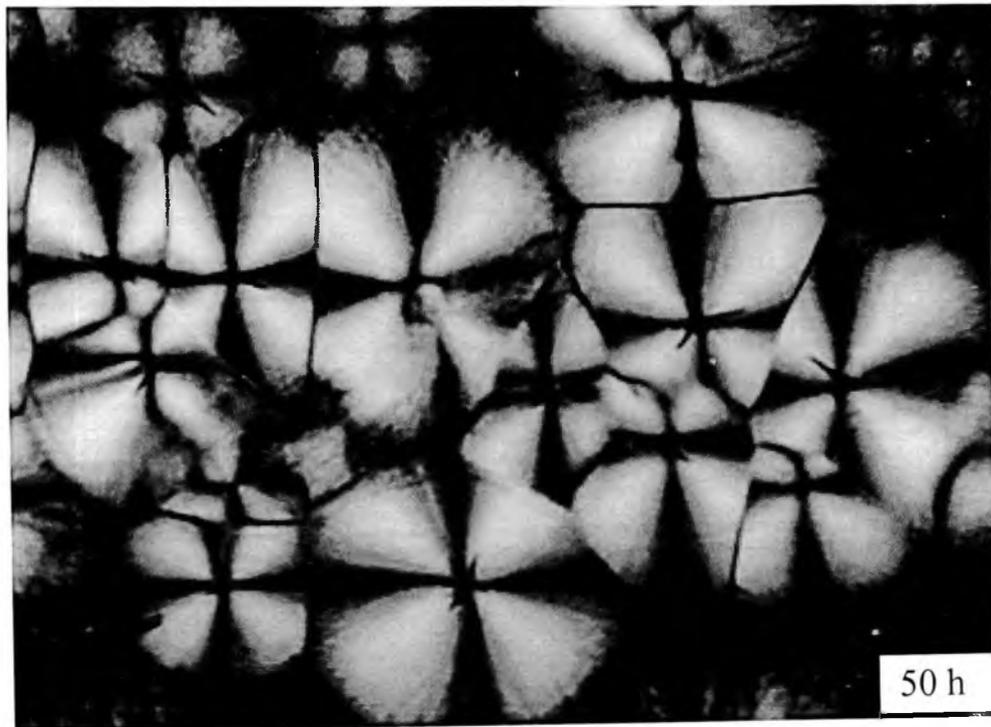


Figure 4.4.b

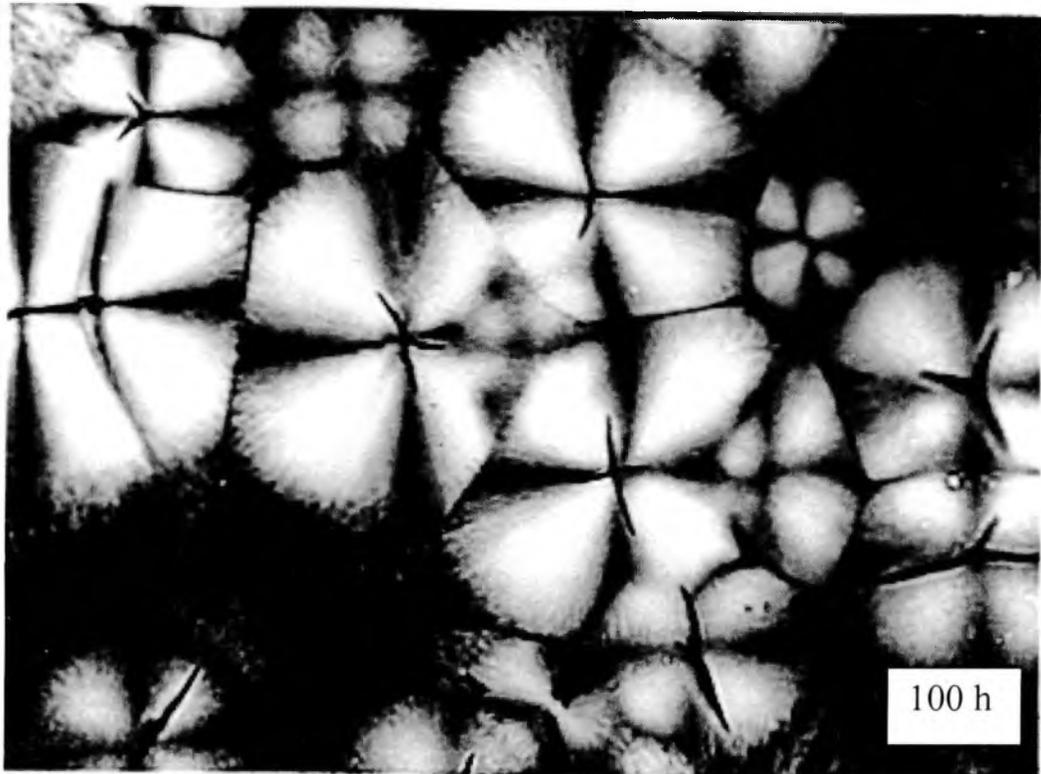


Figure 4.4.c

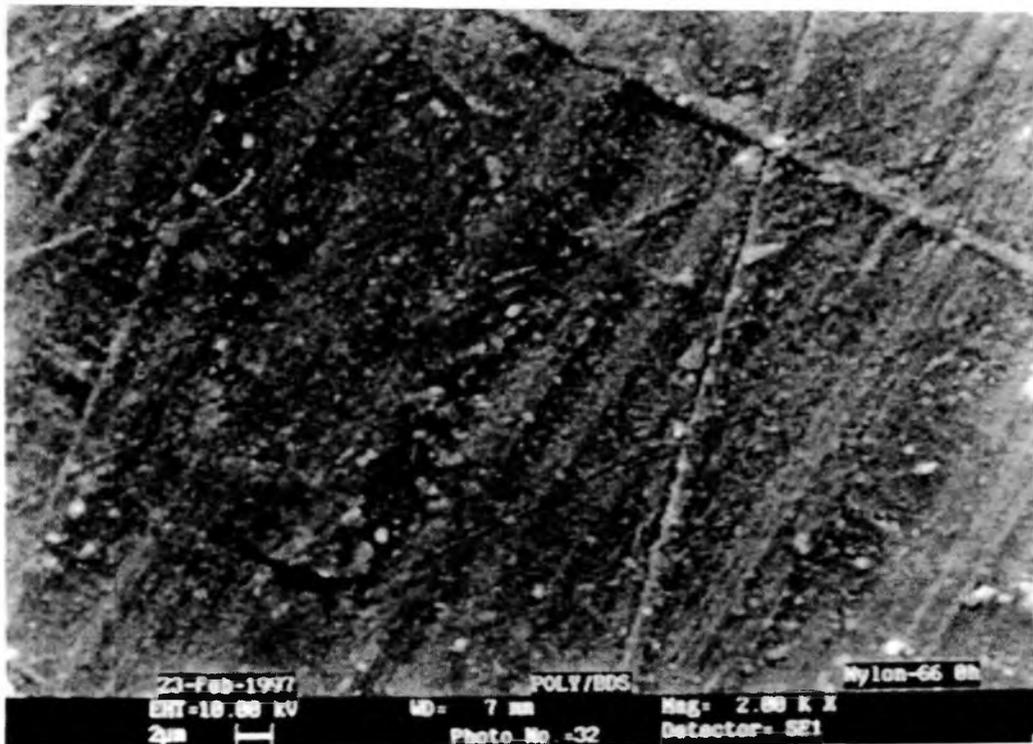


Figure 4.5

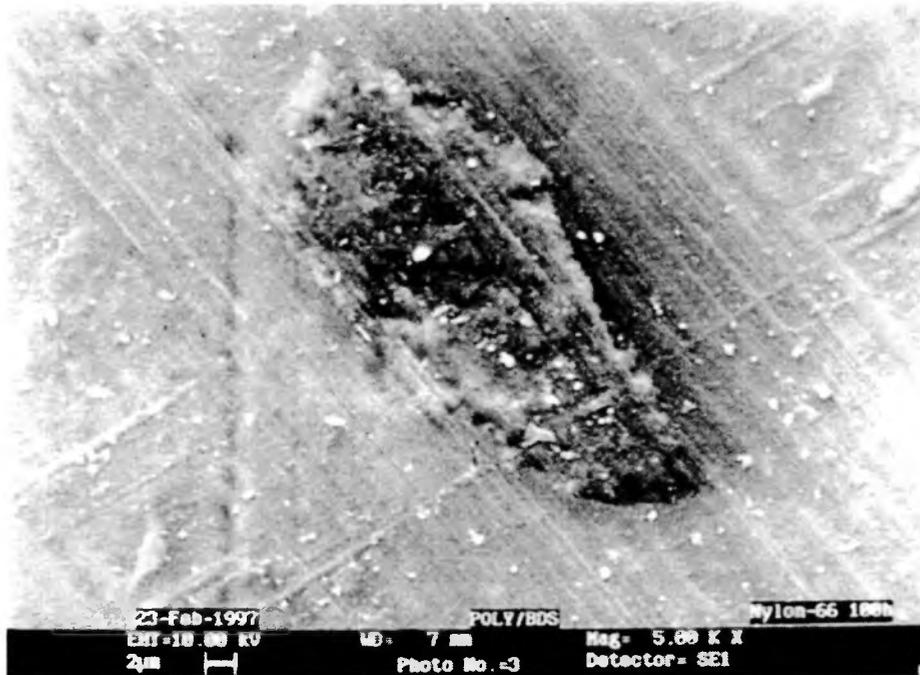


Figure 4.6.a



Figure 4.6 (b)

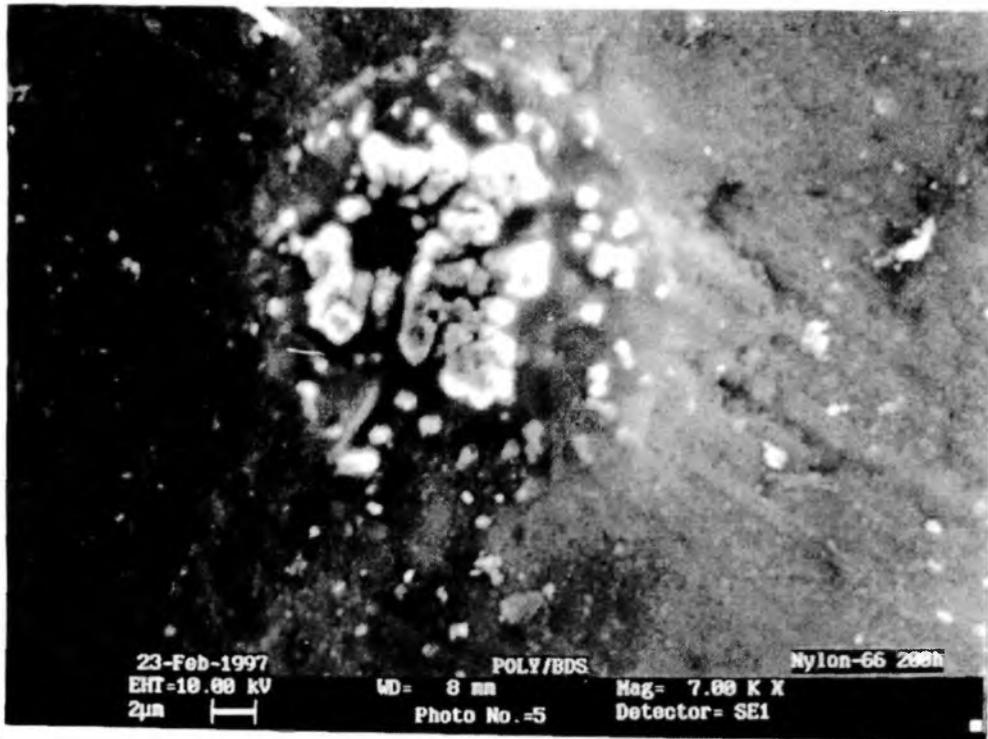


Figure 4.7 (a)

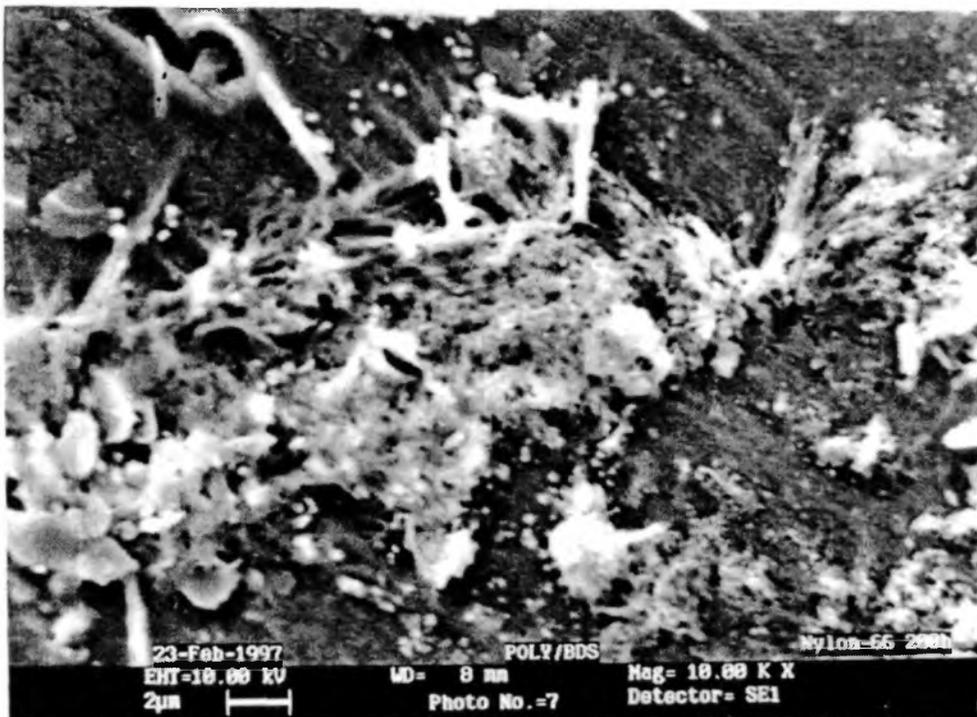


Figure 4.7 (b)

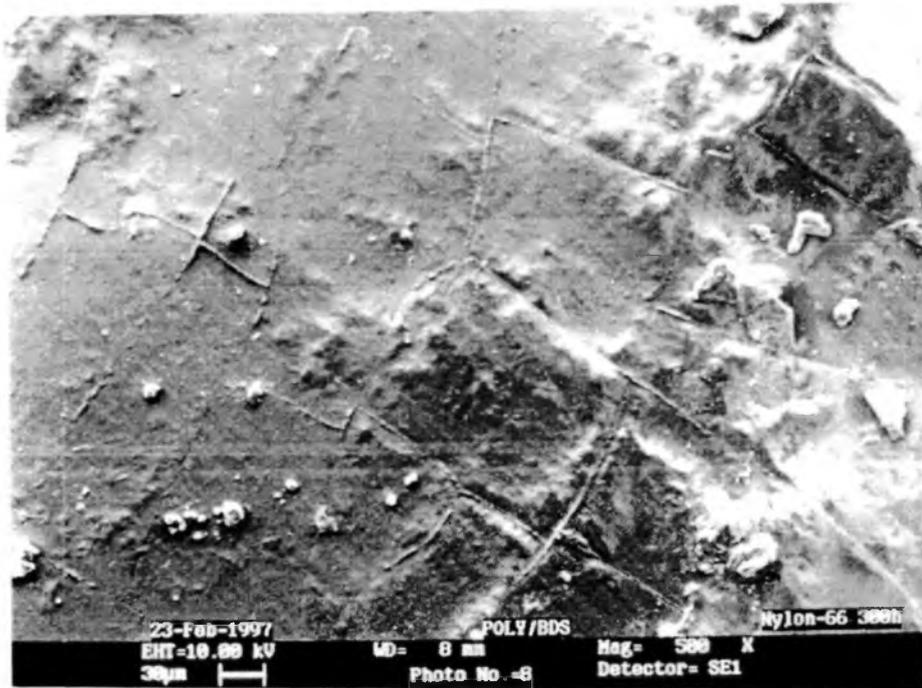


Figure 4.8

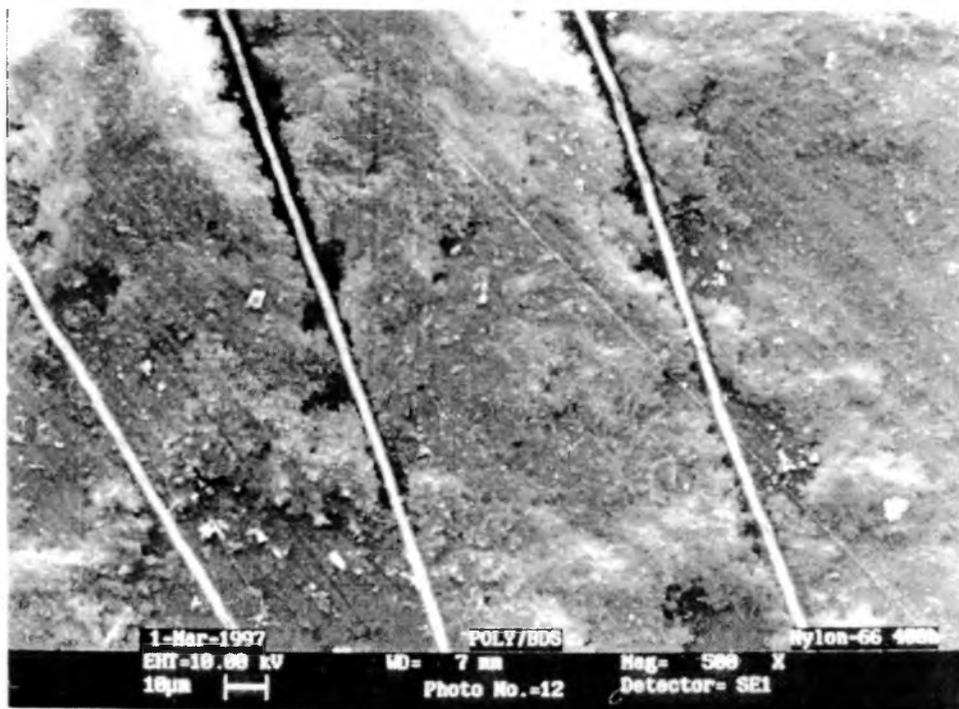


Figure 4.9 (a)



Figure 4.9 (b)

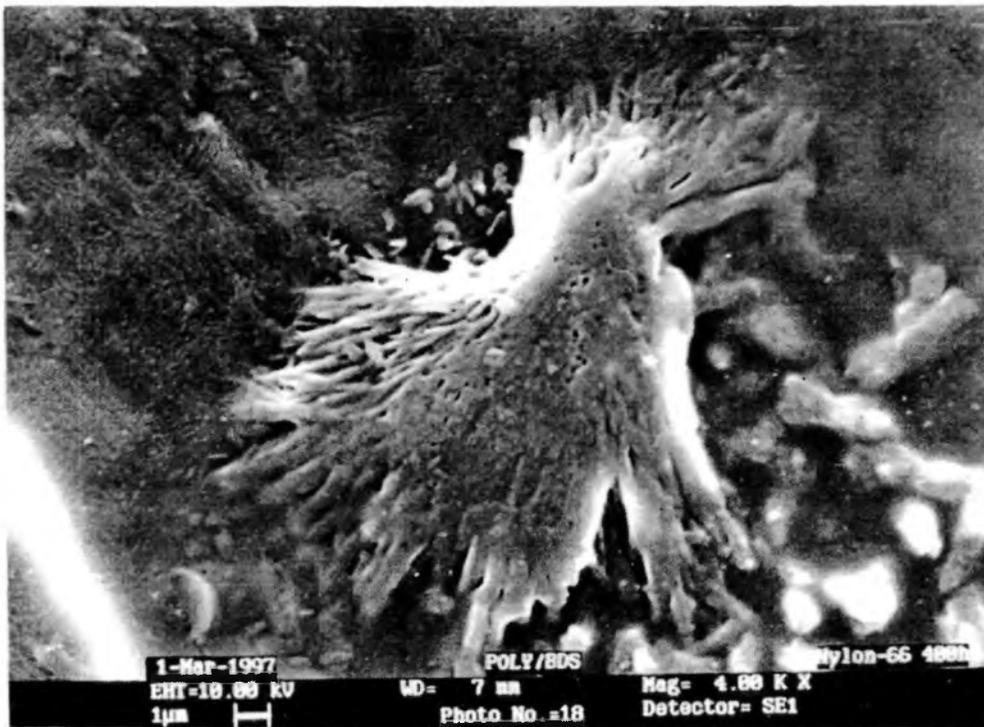


Figure 4.9 (c)

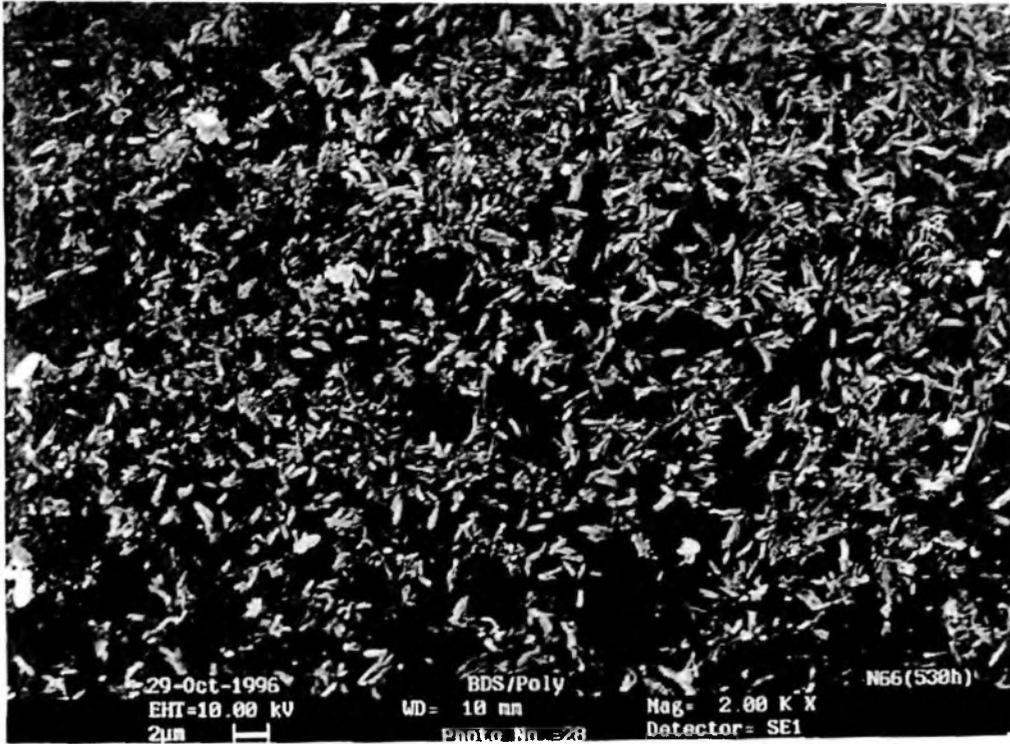


Figure 4.10 (a)

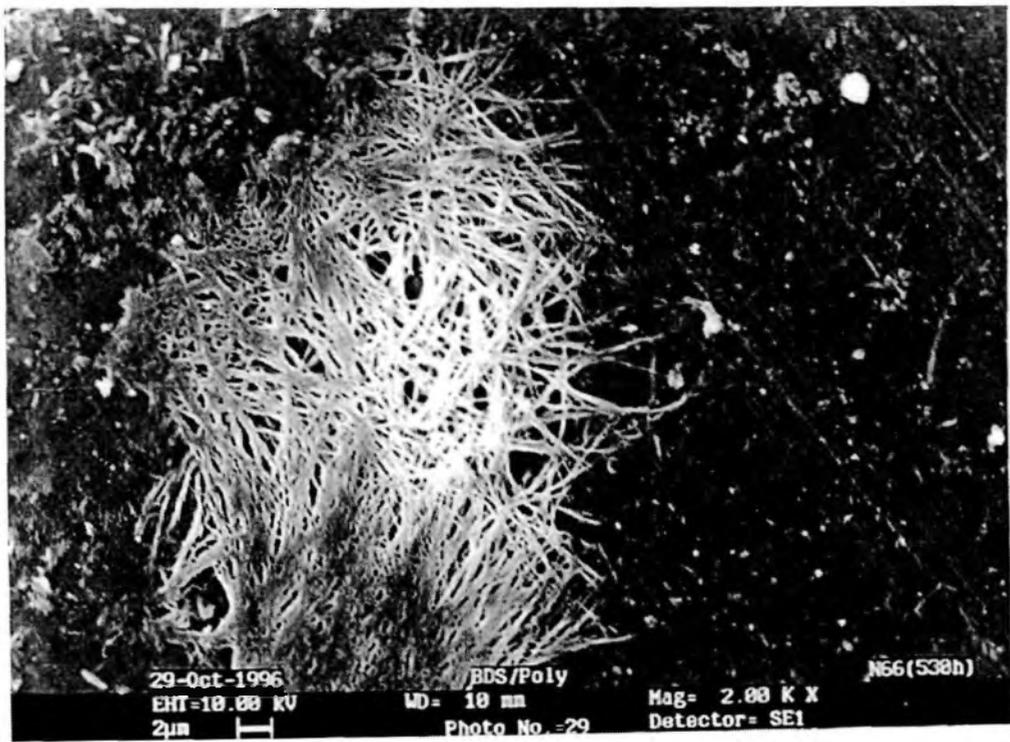


Figure 4.10 (b)

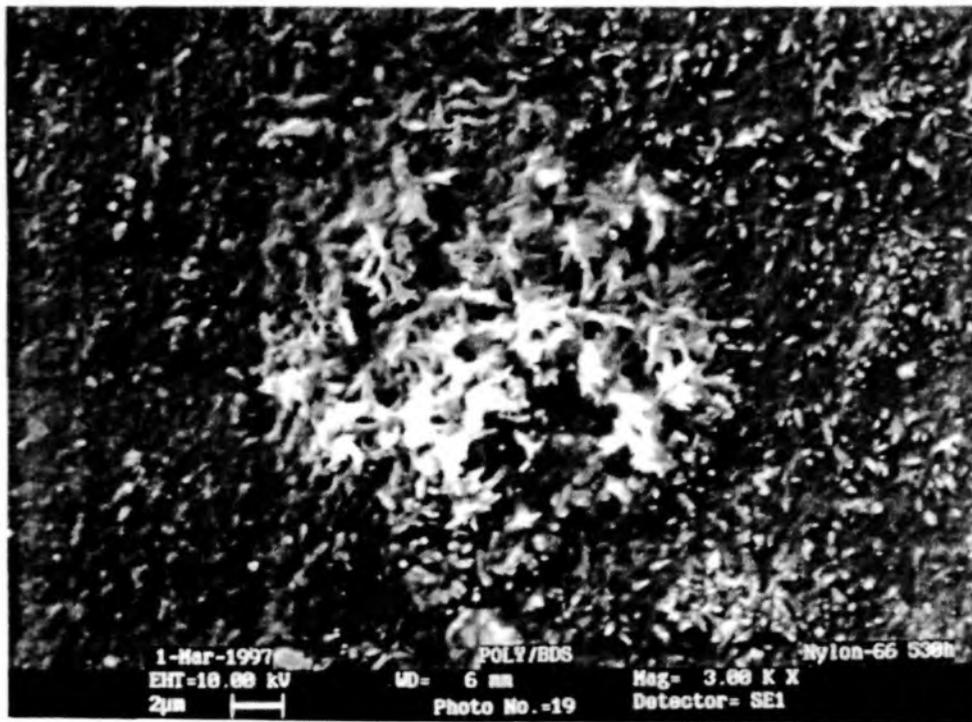


Figure 4.10 (c)

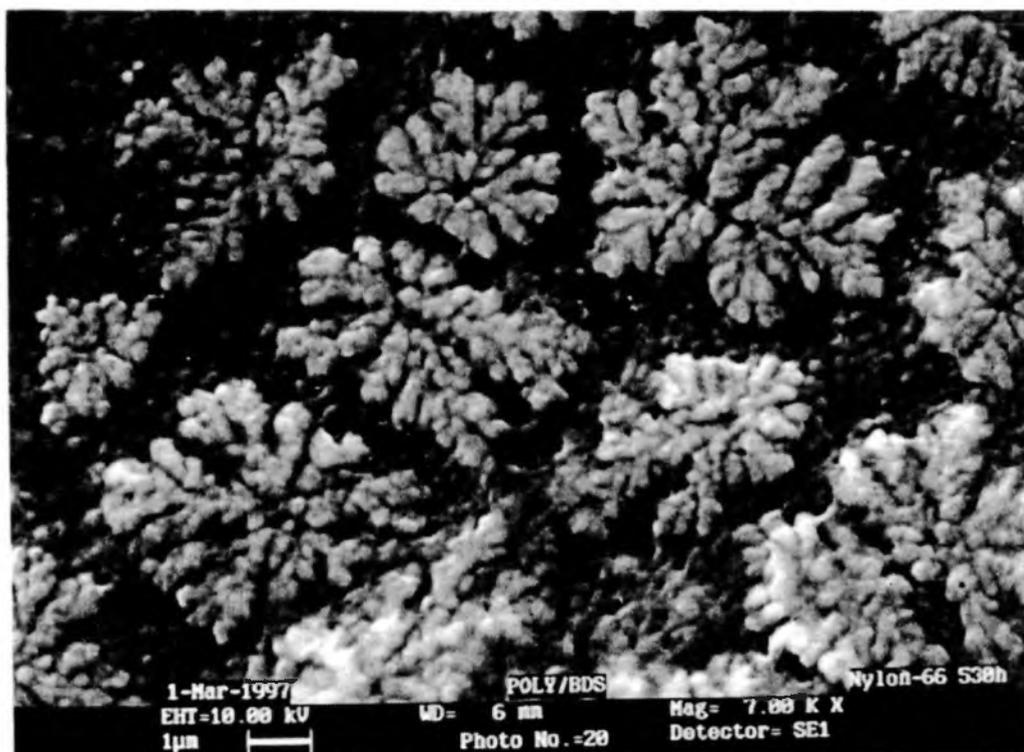


Figure 4.10 (d)

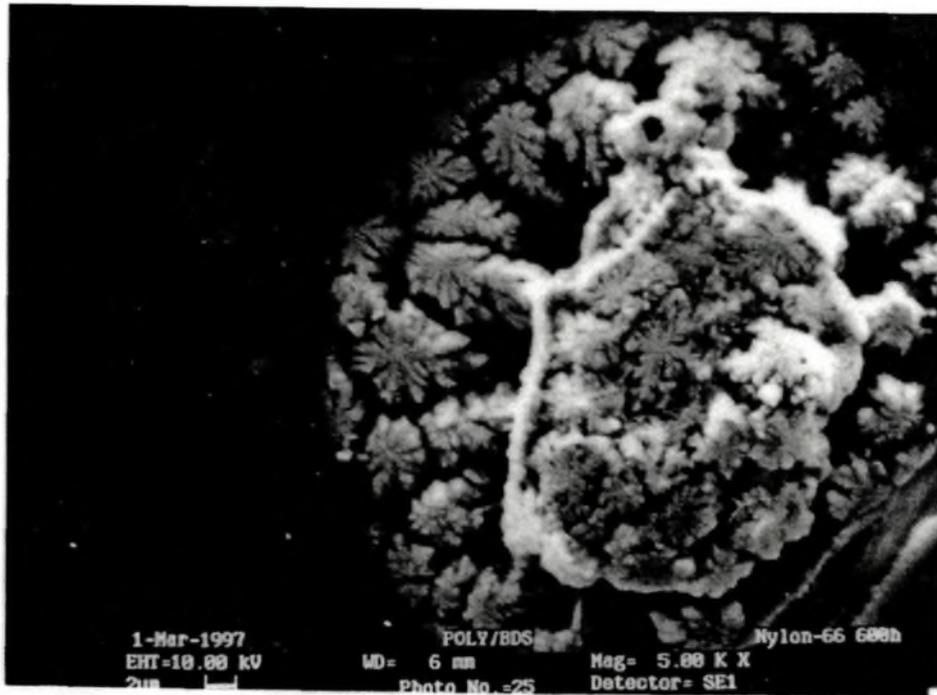


Figure 4.11



structures. Formation of microcracks is also quite visible from this micrograph, which is due to the stress and strain, developed on the sample surface.

After 200 h of photo-exposure, there is onset of chemi-crystallization processes. Chemi-crystallization processes start from amorphous phase where the entangled polymer chains are present. Photo-oxidation prevails in amorphous phase and causes extensive chain scission. Cleaved chains are free from entanglements and tend to crystallize. This phenomenon is known as chemi-crystallization. *Figure 4.7 (a)* shows the nucleation of new morphology. Formation of irregular structures was also observed after 200 h of photo-exposure [*Figure 4.7 (b)*]. Extensive surface swelling (*Figure 4.8*) was observed after 300 h. Cracks formation becomes more intense at this stage. *Figure 4.9 (a)* shows that surface-swelling has become more and more intense with exposure time. After 400 h of photo-exposure, white needle like structures are visible [*Figure 4.9 (b)*], which are due to formation new surface morphology as a result of chemi-crystallization. *Figure 4.9 (c)* shows a spherulitic structure emerged from the surface, which is resulted from chain folding processes eventuated on an existing spherulite.

After 530 h of photo-exposure [*Figure 4.10 (a)*], sample surface is densely populated with needle like structures. Distinct micro-fibrillar networks were observed at some places [*Figure 4.10 (b)*]. Aggregations of entanglement-free chains of adjacent sites give rise to such kind of micro-fibrillar structures. We did not observe any more reoccurrence of this kind of structures. However, somewhat similar structures were observed [*Figure 4.10 (c)*]. The fractal formation was also observed [*Fig 4.10 (d)*] at this stage of photo-oxidation. Fractals are resulted from well-defined chemi-crystallization processes. This is a rather common phenomenon observed on the surface of degraded polymers^{18, 19}. After 600 h of photo-exposure a bunch of fractals was observed on the surface indicating the reorganization of polymer chains in amorphous phase (*Figure 4.11*), however, there was no uniform distribution of fractals on the surface and also the fractals were different in size and shape. Mirzadeh *et al.*³³ observed the formation of fractals during CO₂ pulsed laser induced grafting of acrylamide onto EPR surface. Fractal formation was attributed to the combination of pulsing laser and the linear aggregative nature of polyacrylamide chains. Grafted chains associate via H -bonding to form large aggregates^{34, 35}. Similarly, in case of nylon 66 photo-oxidation, entanglement free chains formed in amorphous phase can crystallize under the influence of H -bonding and give rise to the fractal formation.

4.4 Conclusions

Photo-oxidation in nylon 66 shows chemi-crystallization of cleaved chain in amorphous region. DSC results show loss in existing crystalline morphology, which is not indicated by XRD results. There could be a possibility of chain-reorganization in crystalline morphology upon heating of sample during DSC analysis. Whereas XRD studies were carried out at room temperature and hence show the actual morphology existing in the sample at room temperature. SEM results show that photo-oxidative processes are localized to some portion of the surface during the initial period of photo-exposure and later on it spread out to entire surface. Prevalence of photo-oxidative processes in amorphous phase is also indicated. Chemi-crystallization was one the important phenomenon observed during the photo-exposure, which gave rise to formation of distinct morphologies on the polymer surface.

4.5 References

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CHAPTER V

THERMAL OXIDATIVE DEGRADATION OF NYLON 66

5.1 Introduction

Nylon 66 is one of the most important engineering thermoplastics often used in adverse environment. Being an engineering thermoplastic, nylon 66 is also used at relatively higher temperature. It is well known for most polymers that thermal degradation in the presence of air is mainly thermal oxidative degradation phenomenon. Thermal oxidative degradation is widely studied by many researchers¹⁻¹⁸. Chemical processes associated with thermal oxidative degradation are studied by the formation of various macro-radicals¹⁻⁵, changes in end-group population⁶⁻⁸, formation of peroxides^{9, 10}, aldehyde and other carbonyl species^{11, 12}. Moreover, formation of luminating species¹³⁻¹⁸ was also postulated during thermal oxidative degradation of nylon 66 and other polyamides.

Some researchers¹⁹⁻²³ have also studied the formation of UV/visible active structures during thermal oxidative degradation of nylon 6 and nylon 66. Study identifying of precise structure and mechanism involved in formation of such structures is very much important, as these chromophoric structures are known to decrease photostability of polyamides. Mainly, luminescence spectroscopy has been employed to study the chemistry of these chromophoric structures. It has been found that these are, mainly, α , β -unsaturated carbonyl species and unsaturated cyclopentanones^{11, 18, 24-26}. Formation of conjugated aldehydes with two to three carbon-carbon double bonds was also observed in the thermally oxidized polyamides²⁷. These, conjugated aldehydes, and other carbonyl species are reported to undergo aldol condensation with primary amines and form azomethine species^{19,20}.

However, there are only a few reports^{28,29} on the characterization of thermal oxidative degradation by FT-IR spectroscopy. Therefore, in the present study, we have tried to look at the formation of unsaturated carbonyl species during thermal oxidative degradation of nylon 66 at three different temperatures. FT-IR spectroscopy was used to study the formation of unsaturated carbonyl species and it was also supported by UV spectroscopic data.

5.2 Experimental

5.2.1 Materials

Nylon 66 samples were received from M/s du Pont de Nemours, USA, and used without further purification.

5.2.2 Sample preparation

Thin films of thickness about 50 μm were prepared as described in Section 3.2.2 of chapter III.

5.2.3 Thermal aging

All the samples were thermally treated in a forced air circulation oven at three different temperatures: 120, 160 and 190°C for various periods.

5.3 Analysis

5.3.1 FT-IR analysis

The principle method employed for studying the thermal oxidative degradation was FT-IR spectroscopy. FT-IR experiments were performed on a Perkin Elmer 16 PC spectrometer.

5.3.2 UV absorption analysis

The ultra-violet absorption measurement for thin films ($\sim 50 \mu\text{m}$) were carried out on Hewlett Packard 8452A Diode Array Spectrophotometer.

5.4 Results and Discussion

5.4.1 Change in hydroxyl regions

Hydroxy and hydroperoxy group absorption ($3350\text{-}2700\text{cm}^{-1}$) appeared as broad peak (*Figure. 5.1.a, b and c*). During initial period of thermal aging, for all the three aging temperatures, there was significant decrease in absorption in this region. After initial decrease, absorption varies inconsistently with aging time (*Figure 5.2*). This suggests that hydroxy and hydroperoxy groups are the unstable intermediate of final thermo-oxidative products, which are being formed and vanished continuously during the thermal treatment. Hydroperoxy groups in aliphatic polyamides are reported³⁰ to undergo decomposition at about 60°C. We also observed³¹ the similar behavior of hydroperoxides during photo-oxidation of nylon 66.

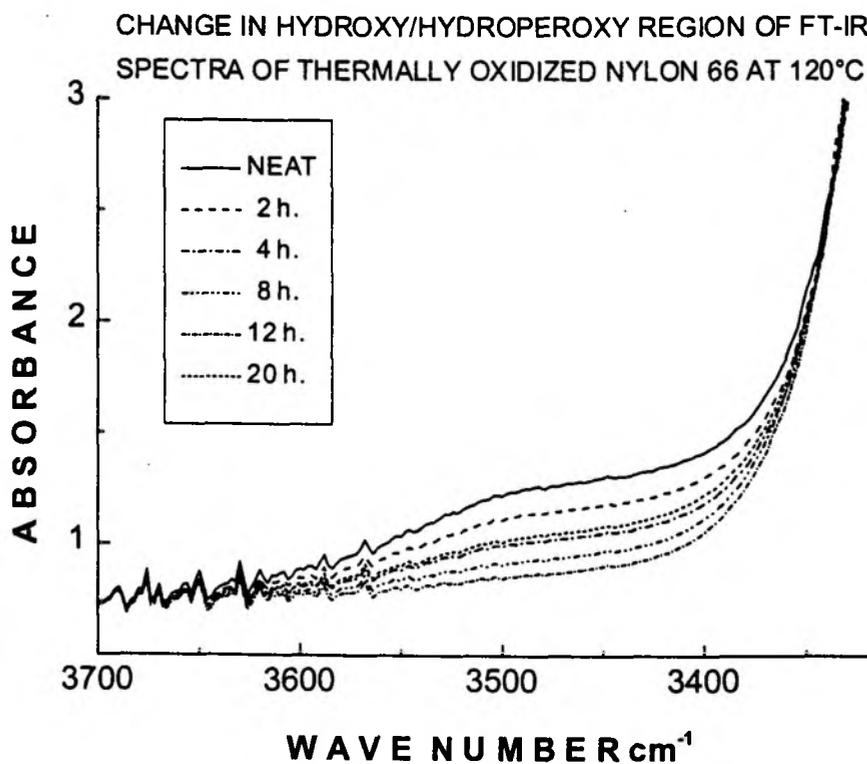


Figure 5.1.a Change in hydroxyl region of IR spectra of nylon 66 during thermal aging at 120°C

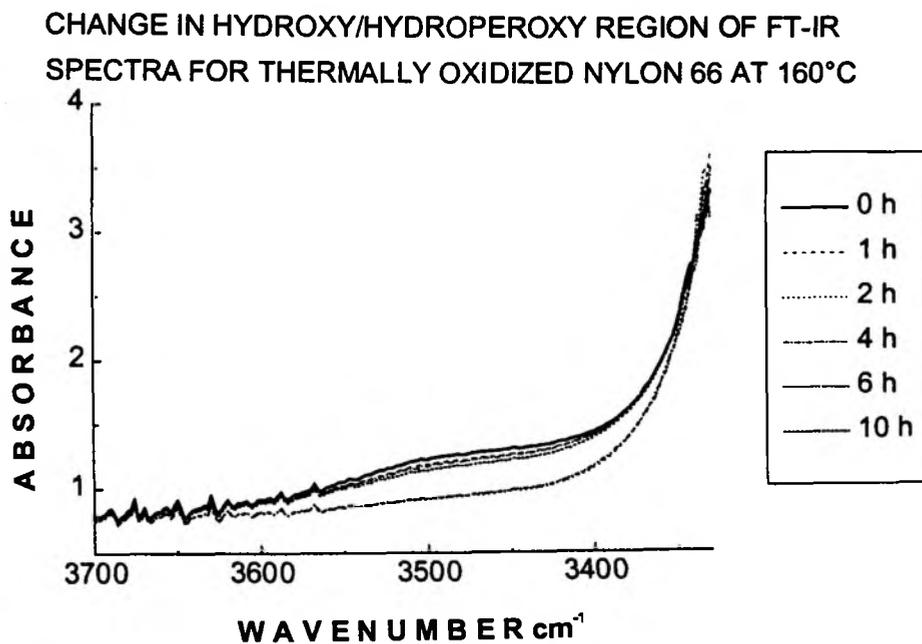


Figure 5.1.b Change in hydroxyl region of IR spectra of nylon 66 during thermal aging at 160°C

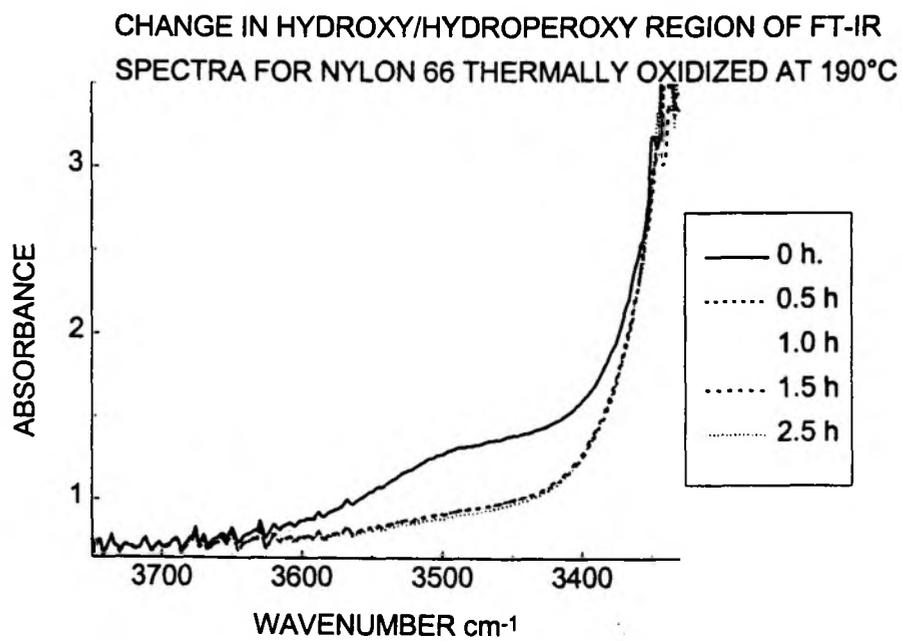


Figure 5.1.c Change in hydroxyl region of IR spectra of nylon 66 during thermal aging at 190°C

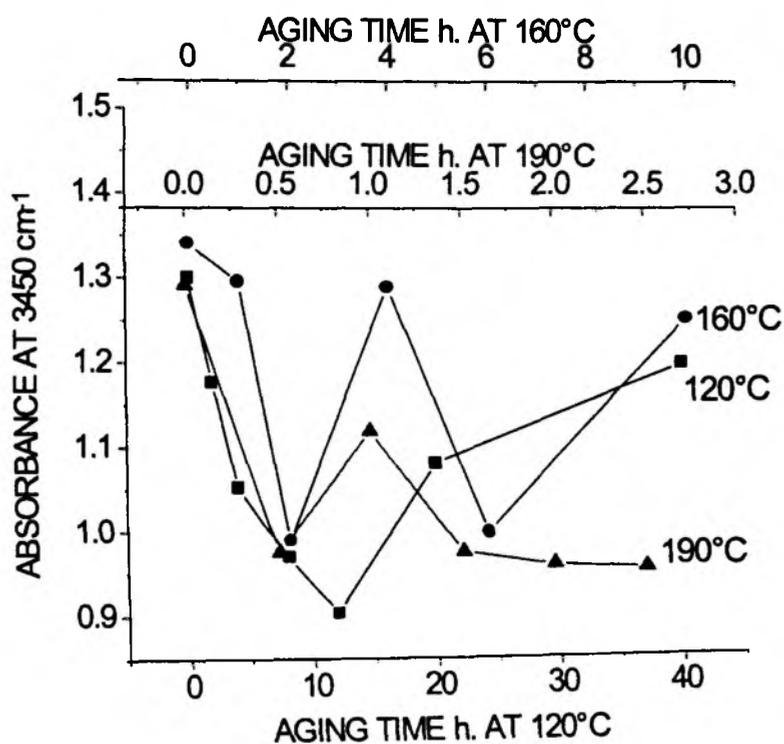


Figure 5.2. Change in hydroxyl peak absorption of nylon 66 with aging time at 120, 160 and 190°C

5.4.2 Change in carbonyl regions

The carbonyl region ($1780 - 1690 \text{ cm}^{-1}$) showed several overlapping bands (*Figure 5.3.a, b and c*). This region is narrow at lower aging temperature and gets broader as the aging temperature is increased. Carbonyl species are formed mainly of imides, aldehydes and other unsaturated carbonyl groups²⁸. Carbonyl absorption is continuously increased with aging time. Moreover, the rate of carbonyl groups formation was found to be increased with increasing aging temperature (*Figure 5.4*).

Increase in carbonyl absorption was found almost similar in a sample aged at 120°C for 40 hours and another sample aged at 160°C for 10 hours. However, the broadening of spectra was quite higher in later one, which indicates that at higher aging temperature, a variety of carbonyl species are formed. The shape of carbonyl absorption bands of the sample aged at 120°C is similar to the of carbonyl band formed in photo-oxidized nylon 66 (*Figure 2.3*). Thus, the carbonyl species, formed during thermal oxidation at 120°C , consists mainly imide groups.

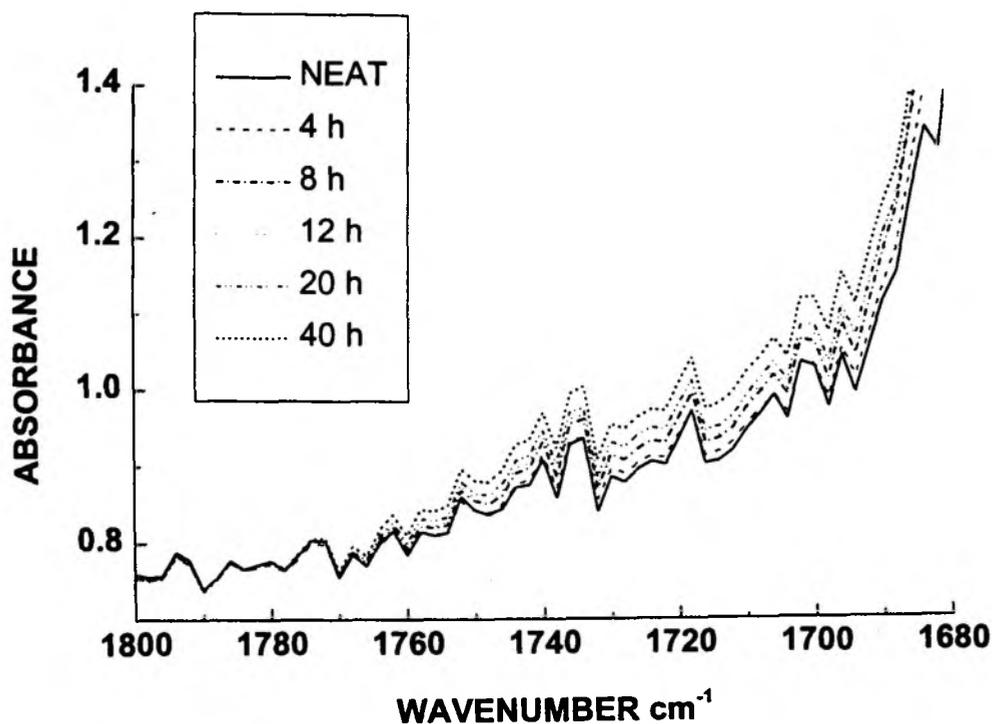


Figure 5.3.a Change in carbonyl region of IR spectra of nylon 66 during thermal aging at 120°C

CHANGE IN CARBONYL REGION OF FT-IR SPECTRA
FOR THERMALLY OXIDIZED NYLON 66 AT 160°C

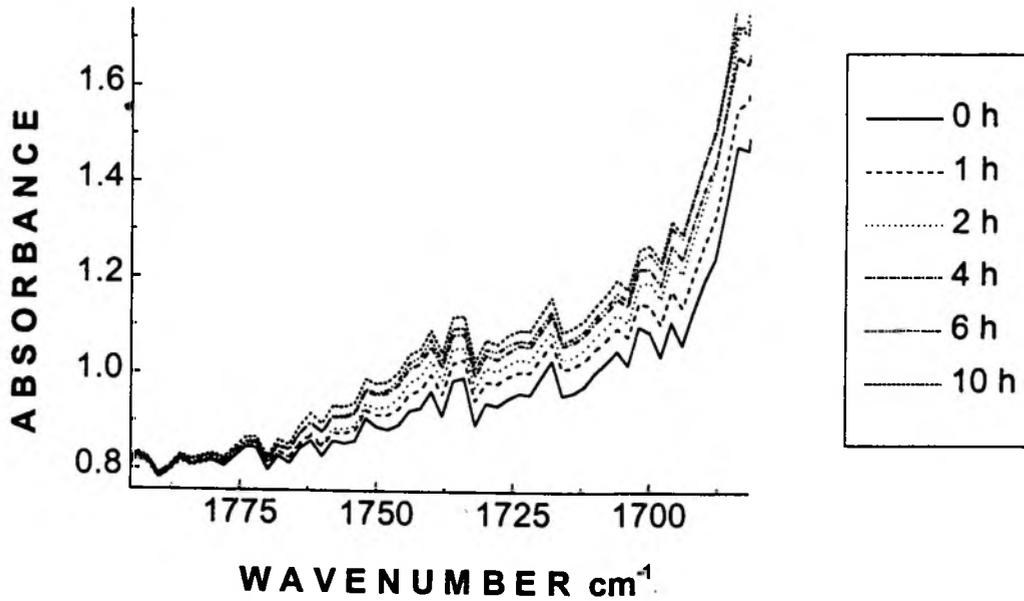


Figure 5.3.b Change in carbonyl region of IR spectra of nylon 66 during thermal aging at 160°C

CHANGE IN CARBONYL REGION OF FT-IR SPECTRA
FOR NYLON 66 THERMALLY OXIDIZED AT 190°C

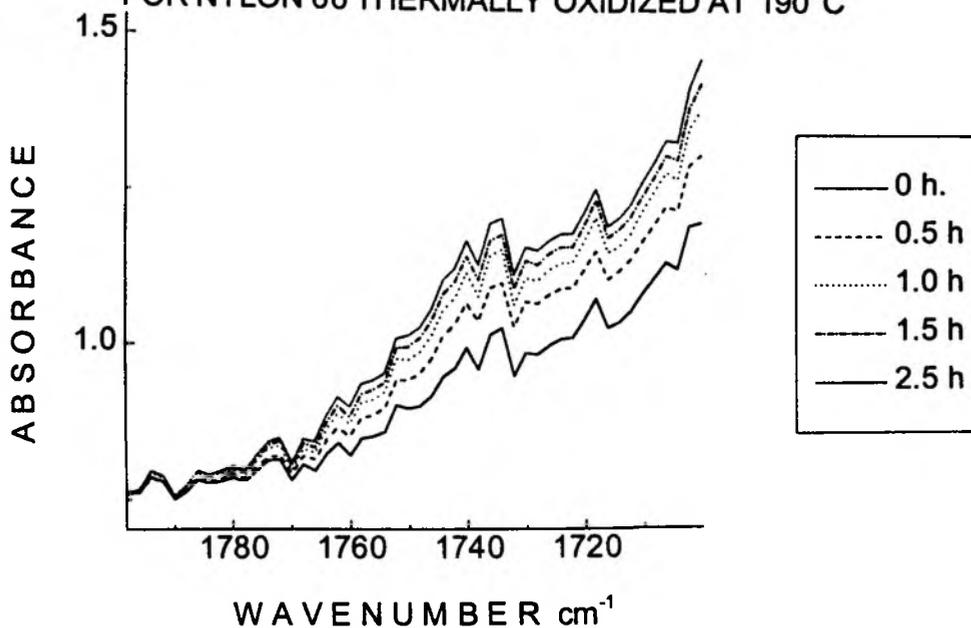


Figure 5.3.c Change in carbonyl region of IR spectra of nylon 66 during thermal aging at 190°C

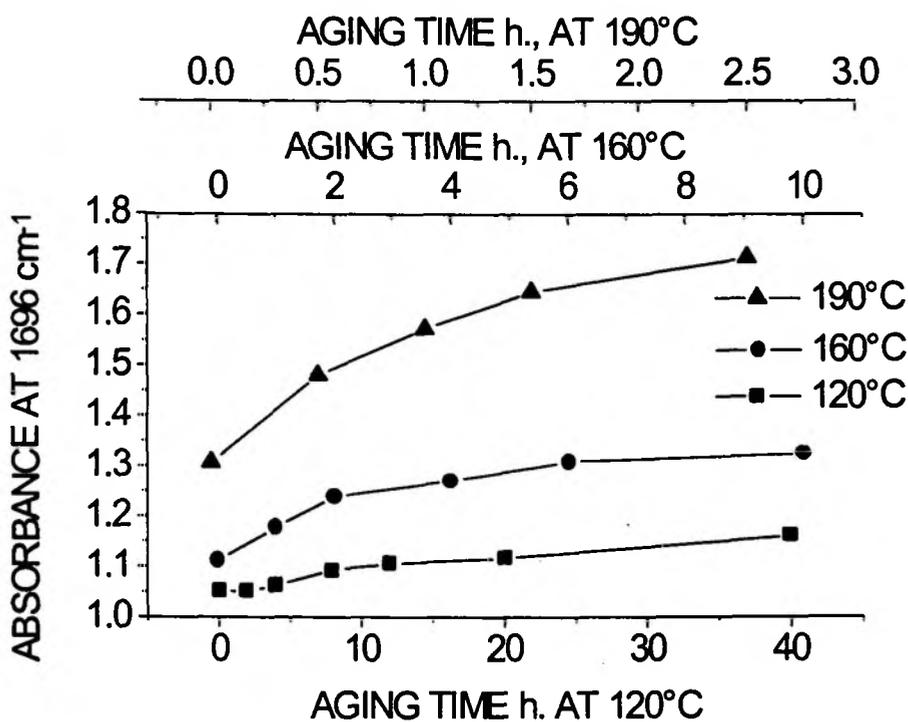


Figure 5.4 Change in carbonyl peak absorption of nylon 66 with aging time at 120, 160 and 190°C

5.4.3 Change in absorption due to formation of unsaturated species

Formation of unsaturated species during thermal oxidative degradation is widely studied but FT-IR spectroscopy is not used for such studies the later can be a very good tool for monitoring the formation of such kind of functional groups with aging time. *Figure 5.5.a and b* show FT-IR spectra of nylon 66 thermally oxidized at 160 and 190°C, respectively. Emergence of a new peak at $\sim 1580 \text{ cm}^{-1}$, which is coincided with a peak due to amide II absorption of nylon 66, was observed in the case of samples aged at 160 and 190°C. However, this was not observed in case of samples oxidized at 120°C (*Figure 5.5.c*). This peak corresponds to conjugated double bonds, which includes C=C and C=N.

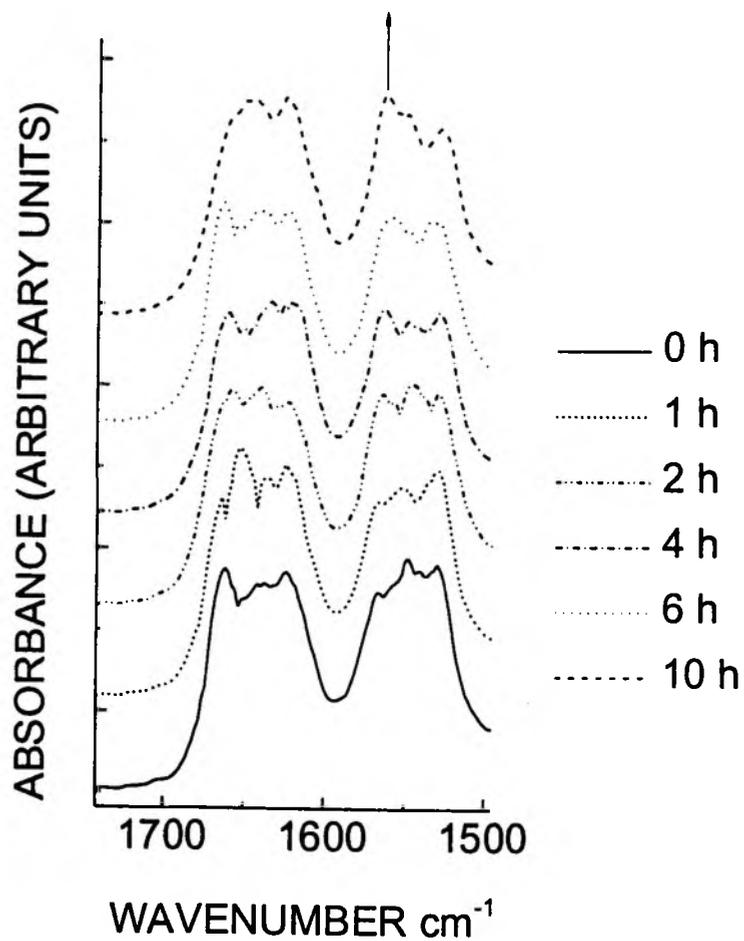


Figure 5.5.a Change in IR spectra of nylon 66 due to formation of conjugated species during thermal aging at 160°C

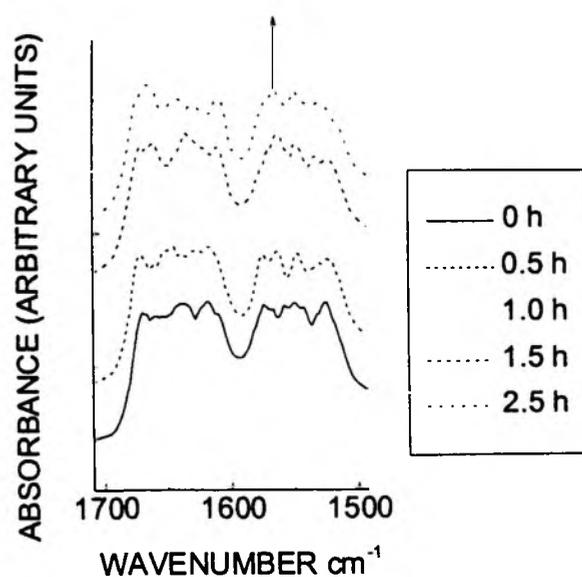


Figure 5.5.b Change in IR spectra of nylon 66 due to formation of conjugated species during thermal aging at 190°C

IR absorption studies³² carried out on a series of conjugated azomethines and aldehydes derivatives show that conjugated double bonds give a strong absorption at 1600-1580 cm^{-1} . Therefore, the peak emerged at 1580 cm^{-1} is a clear indication for the formation of conjugated double bonds. Thus, there is formation of conjugated double bonds in sample aged at 160 and 190°C but not in the samples aged at 120°C.

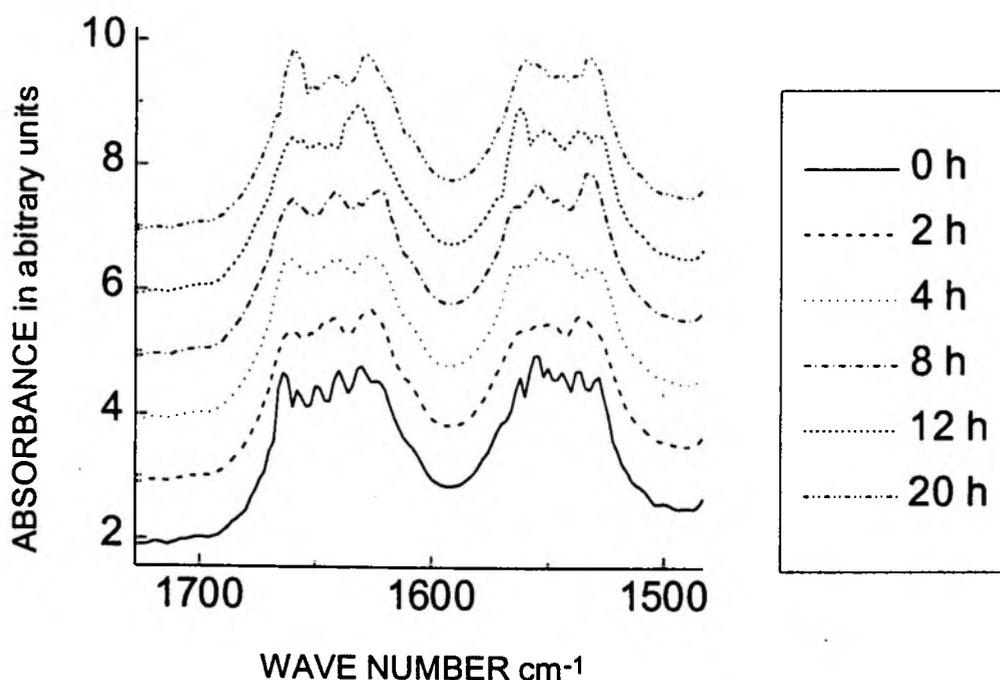
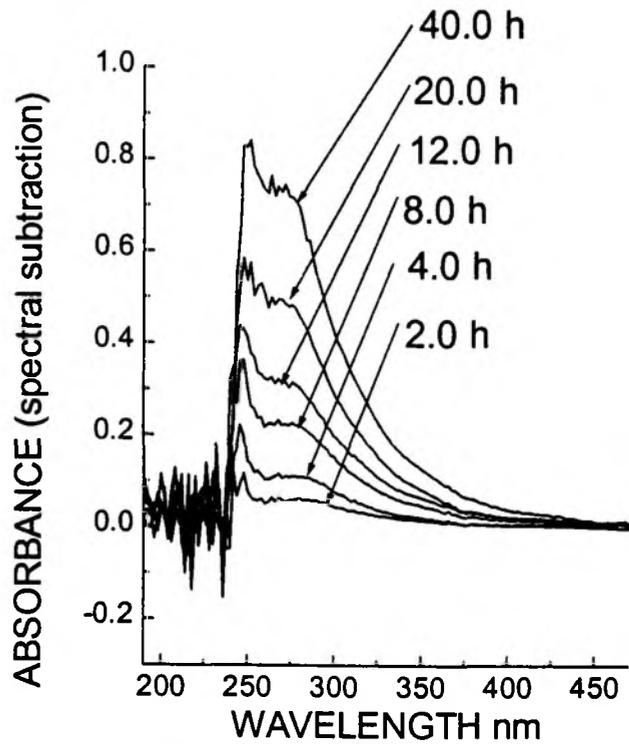


Figure 5.5.a Change in IR spectra of nylon 66 due to formation of conjugated species during thermal aging at 120°C

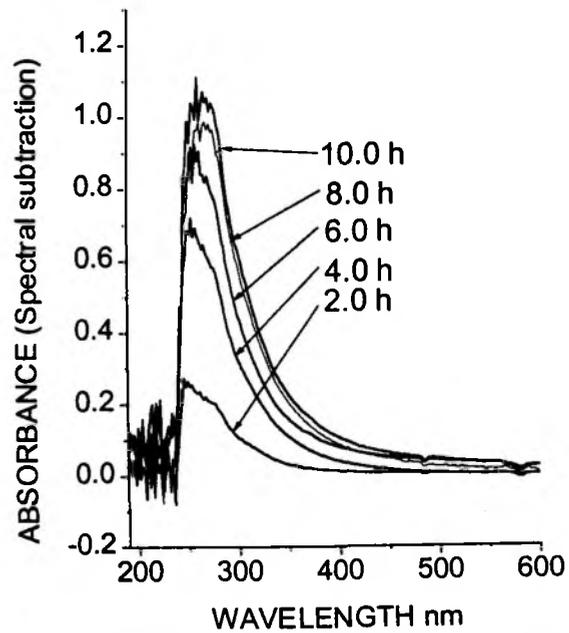
5.5 UV absorption studies

UV absorption (230-380 nm) was found to increase with thermal aging of nylon 66. However, the characteristics of absorption are different at different aging temperatures. *Fig. 5.6.a, b and c* correspond to increase in UV absorption with thermal aging of nylon 66 at three different temperatures. Broad peak is observed with maxima at ~ 246 nm and a shoulder at ~ 278 nm. This peak is intensified and also gets broadened with exposure time. It is clear from *Fig. 5.6.b and c* that at



CHANGE IN UV ABSORPTION WITH TIME FOR THERMALLY AGED NYLON 66 FILM AT 120°C

Figure 5.6.a Change in UV-visible absorption of nylon 66 during thermal aging at 120°C



CHANGE IN UV ABSORPTION WITH TIME FOR THERMALLY AGED NYLON 66 FILM AT 160 °C

Figure 5.6.b Change in UV-visible absorption of nylon 66 during thermal aging at 160°C

higher aging temperatures, there is much more broadening in absorption peak and it is extended even in visible range.

Absorption band emerged at ~ 246 nm is due to the formation of imide groups³³. UV absorption studies³⁴ carried out on conjugated azomethines and aldehydes show that a peak at ~ 280 nm corresponds to conjugation. Moreover, this peak is broadened towards higher wavelength as length of conjugation is increased. Thus, this is again an evidence for the formation of unsaturation during thermal oxidative degradation at higher aging temperatures.

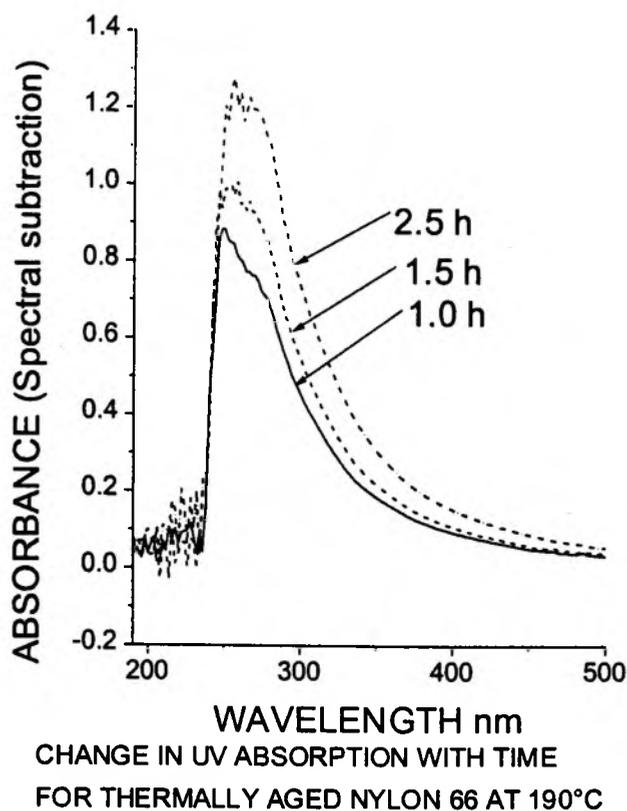
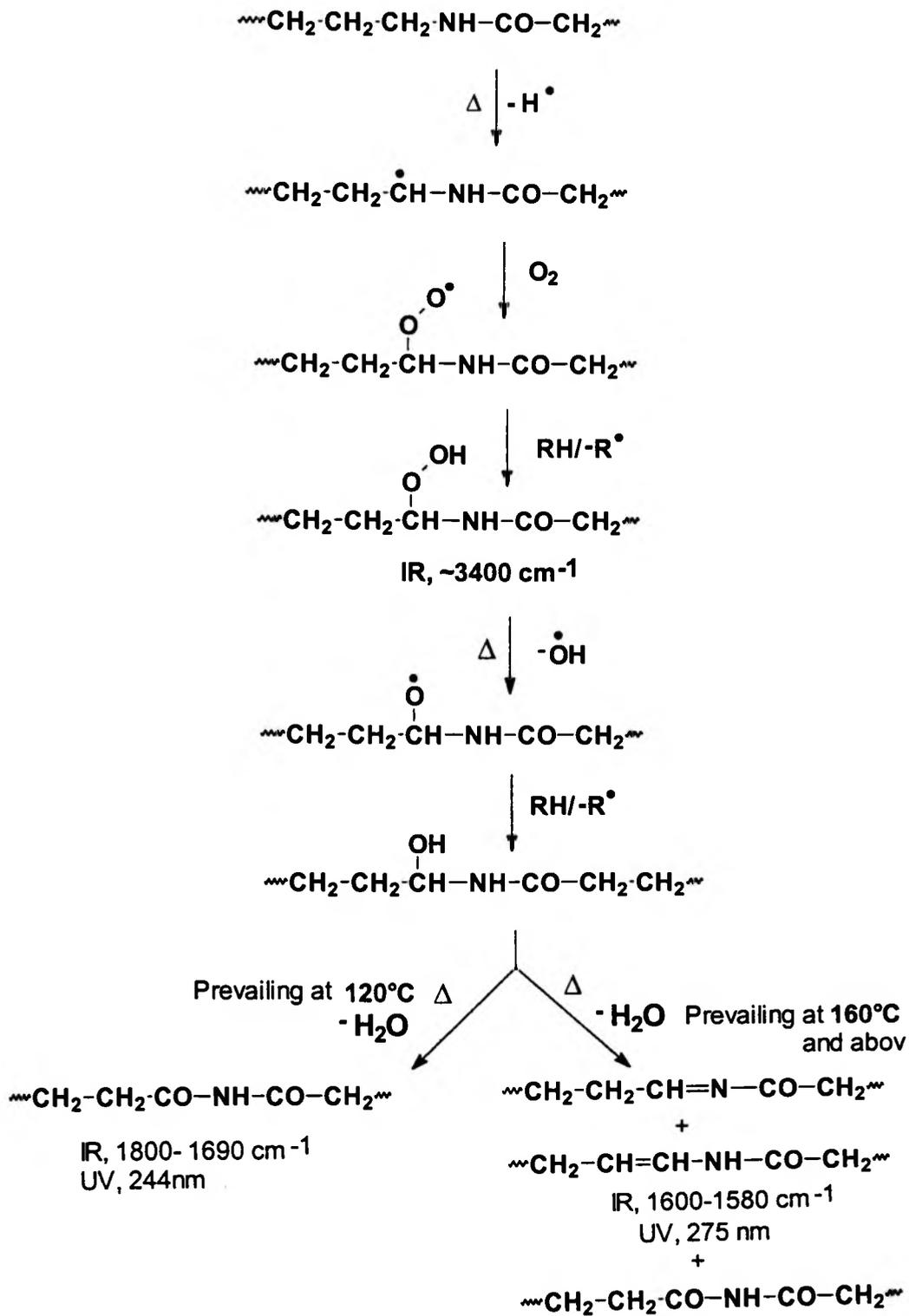


Figure 5.6.c Change in UV-visible absorption of nylon 66 during thermal aging at 190°C

It is now very much clear that depending on aging temperature, two different oxidation mechanisms are prevailing during thermal oxidative degradation. Mechanism for thermal oxidative degradation, which is driven by aging temperature, is suggested as follows:



5.6 Conclusions

FT-IR and UV spectroscopy are identified as very good techniques to characterize and monitor thermal oxidative degradation in nylon 66. Thermal oxidative degradation in nylon 66 was increased with increasing aging time and temperature. We observed that thermal oxidative degradation in nylon 66 follows two different oxidative mechanism depending on aging temperature. At lower aging temperature the oxidation products are mainly imide species, while at higher aging temperature along with formation of imide species, formation of unsaturated species was also observed.

5.7 References

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CHAPTER VI

EFFECT OF DYEBATH pH ON PHOTOSTABILITY OF DYED

NYLON 66

6.1 Introduction

The photo-oxidative degradation in polyamides is well studied. Mechanistic aspects of photo-oxidative degradation of neat polyamides are well reported. Photo-oxidation of polyamides in the presence of oxygen, impurities, dyes, pigments and delustrants is well reported. However, mechanistic aspects of dye sensitized photo-oxidative degradation of polyamides are always remained an important area of research for textile chemists and polymer scientists⁶⁻¹⁰.

Nylon polymers are one of the most important materials used for fiber application and clothing. For this particular application the photostability of polymer in presence of dye is very much important. Anthraquinone acid dyes are one of the important class of dyes used for polyamides, especially for blue and other related shades.

Koenig and Roberts¹ investigated a ground state complex formation between the dye and the polyamide using photoluminescence technique. They observed that the energy level of electronic states of this complex favoured triplet-triplet energy transfer from the nylon to the complex. They also observed an additional energy transfer, which occurred between the excited free-dye and the complex by either a singlet-triplet or a triplet-triplet mechanism. However, they could not identify the exact chemical nature of the dye-nylon complex and the free-dye. The dye-nylon complex acted as an energy trap and sensitized the photochemical oxidation of nylon 66.

Freeman *et al.*⁹ studied the photo-oxidation mechanism of anthraquinone dyes in a model amide (dimethyl formamide) and also in a polyamide (nylon 66). They observed that anthraquinone dyes were faded via photoreduction mechanism. According to them the fading of dye proceeds by hydrogen atom abstraction from the solvent and polymer.

Allen *et al.*¹¹ studied the influence of various dyeing parameters like pH, leveling agents, fiber setting and reducing agents on photostability of dyed nylon 66. They observed significant effect of dyeing-pH for all the three dyes; Tectilon Red 2B, Tectilon Yellow 3R and Tectilon Blue 4 RS in their studies. Fading of these dyes considerably reduced when dyeing pH was increased from 3 to 5, further increase in pH up to 7 did not show any significant change in lightfastness properties of the dyes. The optimum pH for better light stability of red and blue dyes nylon 66 was found to be 7. They also observed that the population of phosphorescent species was reduced

when dyebath pH was increased from 2 to 6. The presence of phosphorescent species is known to reduce the light stability of polymer and photofastness of dyes.

In the present study we have examined the photochemical behavior of an anthraquinone acid blue dye for a range of pH from 2 to 7. This is the pH range where the dyeing of polyamides is performed. We observed a peculiar behavior of this dye, which is solely controlled by dyeing pH. This particular pH dependent behavior of anthraquinone class of dyes is discussed with an appropriate hypothesis in present report.

6.2 Experimental

6.2.1 Materials

Nylon 66 (Zytel 101 L NC 10) was received from M/s E. I. du Pont de Nemours, USA, and used without further purification. C. I. Acid Blue 25 [1-amino-4-(aminophenyl)-2-anthraquinone sodium sulfonate] was purchased from Aldrich Chemical Company and purified by acetone extraction followed by recrystallization from ethanol.

6.2.2 Sample preparation

Thin films of nylon 66 (thickness $45 \pm 5 \mu\text{m}$) were prepared by pressing the polymer between two preheated platens in a hydraulic press at 270°C under $\sim 14 \text{ kg/cm}^2$ pressure for 2 minutes. The films were quench cooled rapidly in the press.

6.2.3 Dye uptake measurement

First of all, calibration (standard concentration versus UV absorption) curve (*Figure 6.1*) for aqueous dye solution was made by measuring absorbance at 604 nm (λ_{max}) for a series of dye-concentrations (4.5×10^{-5} to 2.4×10^{-4}) in water. Nylon 66 films ($\sim 130 \text{ mg}$) were deep in the 100 mL of dye solution with dye concentration $\sim 2 \times 10^{-4} \text{ mol/L}$ and stirred for different time intervals. Initial dye concentration was measured with the help of standard calibration curve. Dye uptake was monitored, time to time, by measuring the decrease in the dye concentration of solution. Dye concentration went on decreasing as dye was absorbed onto the nylon 66 films. Loss in dye concentration was then correlated to the amount of dye absorbed onto the films. Finally the percentage dyeing was calculated by using the following method:

$$(1) \quad \text{Amount of dye in the dyebath (Volume, } x \text{ Liter) before dyeing} = \\ [\text{Concentration (mol/L)}] \times [\text{Molecular weight (g/mol)}] \times [x \text{ (L)}] = y \text{ g}$$

- (2) Amount of dye in the dyebath after dyeing = z g
 (3) Amount of dye absorbed by p g of nylon 66 films = $(y - z)$ g = a g
 (4) % dyeing = $a/p \times 100$

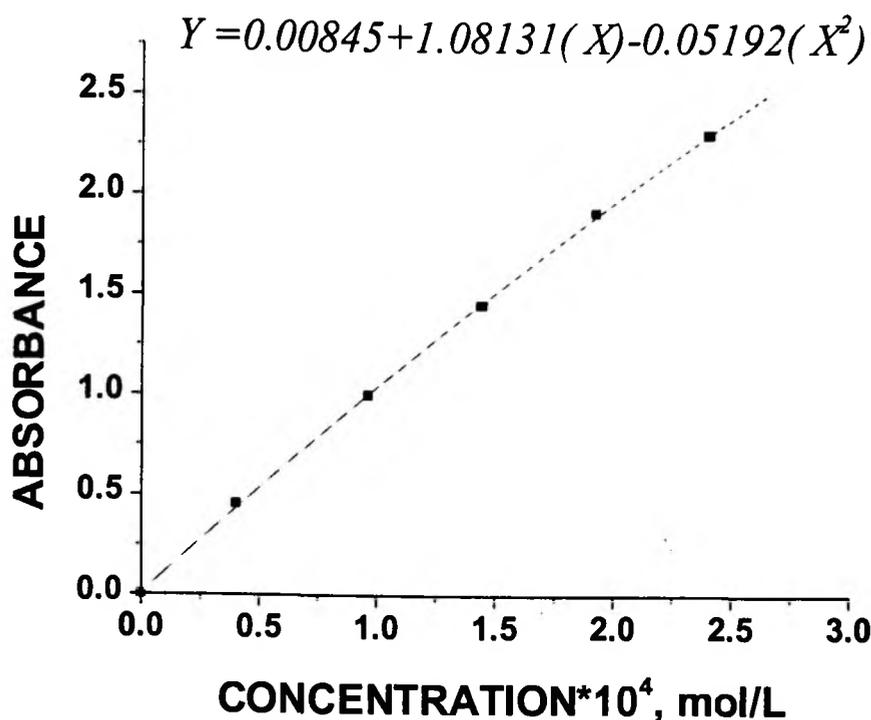


Figure 6.1 Standard concentration against UV-visible absorption ($\lambda_{\max} = 604$ nm) calibration curve for the aqueous solutions of C. I. Acid Blue 25.

Dyebath pHs were set with hydrochloric acid and dyeing was carried out at room temperature. All the samples dyed to the same dye content 0.7% w/w. Dyed samples were dried in vacuum oven at 35°C.

6.2.4 Photo-irradiation and characterization of photo-oxidation and photofading

All the samples were irradiated in SEPAP 12/24 (an accelerated photo-irradiation chamber $\lambda \geq 290$ nm) at 60°C for different time intervals. The detail of this equipment is given elsewhere¹². Extent of photo-oxidation was monitored by FT-IR spectroscopy whereas the fading of dye was monitored by UV absorption spectroscopy. These instruments are described in Chapter III, 3.2.

6.3 Results and Discussion

Photo-oxidation of (all the samples dyed to 0.7% w/w dye content) nylon 66 was characterized by measuring the increase in the partial area in IR spectrum from 1800

to 1690 cm^{-1} using baseline from 1820 to 972 cm^{-1} . This increase is mainly due to the formation of imide species and some other carbonyl products.¹⁰ Percentage increase in partial area under the peak was considered as extent of photo-oxidation.

Figure 6.2 shows effect of pH on photo-oxidation of nylon 66 with exposure time. Samples dyed at pH 3.0 to 7.0 show the same extent of photo-oxidation. Neat samples showed more photo-oxidation than those of dyed above pH 3.0. This indicates the photostabilizing effect of dye on photo-oxidative degradation of nylon 66. Koenig *et al.*¹ also observed the similar fact. They found that samples containing 0.52% and 0.83% dye (C. I. Acid Blue 40) degraded much lesser than the undyed nylon. However, the nylon containing 0.25% dye was observed to degrade more rapidly than control sample. They explained this particular concentration effect of dye in terms of dye-nylon photophysical energetics. At a higher dye concentration, most of the incident energy is absorbed by the dye, exciting the dye to its second excited singlet state. Excited free dye can dissipate this energy by radiationless decay to the ground state. This process was believed to serve as a mechanism to protect polyamide substrate from the photo-oxidative degradation whereas at low dye concentration, most of the incident energy is absorbed by the dye-nylon complex. This dye-nylon complex can act as energy trap and hence sensitizes the photo-oxidative degradation in nylon 66.

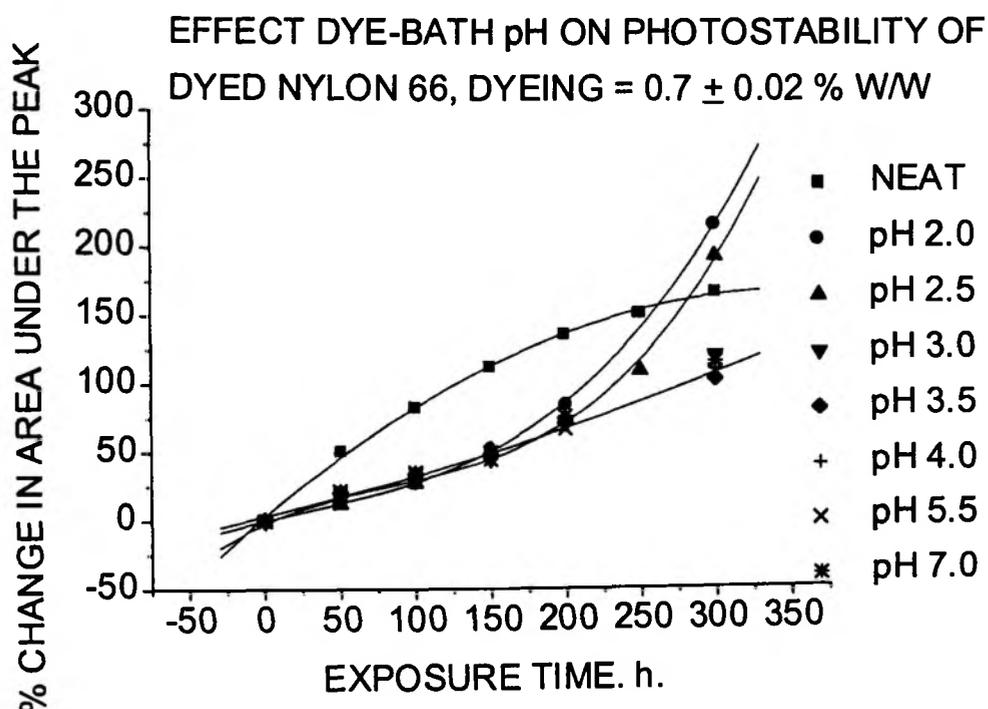
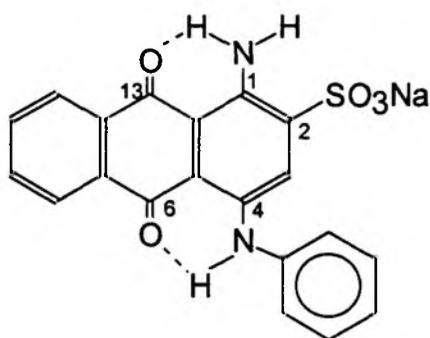


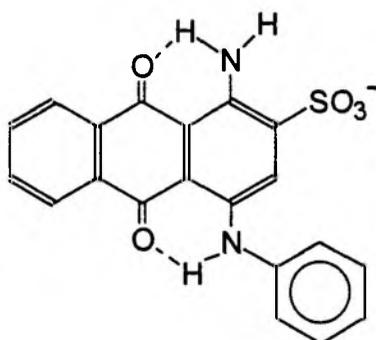
Figure 6.2 Effect of dye-bath pH on photo-oxidation of nylon 66 with exposure time.

The samples dyed at pH less than 3.0 shows more steep increase in photo-oxidation in comparison to neat samples. This peculiar effect of pH on photochemical behavior of dye can be explained by looking at the chemical structure of dye molecule.

Dye molecule has got primary amine functional group in its 1-position and secondary amine group in its 4-position. Protons bonded with nitrogen in 1- and 4-position are also associated with carbonyl oxygen in 13- and 6-positions, respectively, via intramolecular hydrogen bonding. Due to such kind of hydrogen bonding, the dye molecule can absorb ultra-violet radiation transforming it into vibrational energy and/or heat through efficient radiationless deactivation pathways⁴.

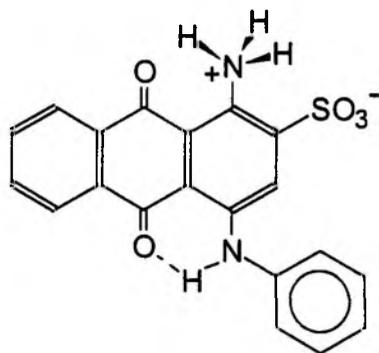


Upon dyeing at pH > 3.0, the following dye species may exist in the dyebath:

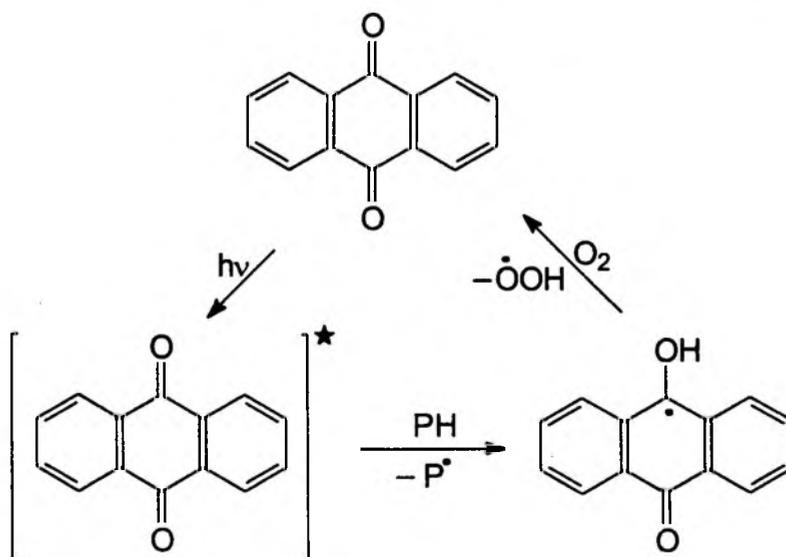


where the intramolecular hydrogen bonding exists and these species can act as photostabilizer for nylon substrate.

At much lower pH (pH < 3.0) there is no existence of free primary amine moiety instead of that there will be existence of quaternary ammonium salt in dyebath:



In quaternary ammonium salt all protons are not in same plane and also they lose co-planarity with atoms involved in cyclic intramolecular hydrogen bonding. Hence, the criterion for cyclic intramolecular hydrogen bonding, co-planarity of all atoms involved in it, is not fulfilled which leads to disruption of intramolecular hydrogen bonding. In dye molecule, anthraquinone moiety without intramolecular hydrogen bonding can act as photosensitizer^{15, 16}. Mainly, it sensitizes photo-oxidation via photoinduced hydrogen abstraction and singlet oxygen formation⁵. The mechanism they have suggested for photoinduced hydrogen abstraction is as follows:



Thus, the photochemical processes involved with anthraquinone chromophore produces the polymeric free radicals and other peroxy-radicals, which in turn enhance the photochemical oxidation of the substrate.

6.3.1 Effect of dyebath pH on photofading of dyed nylon 66

Effect of dyebath pH on photofading behavior of dyes has paid significant importance^{11, 17-20} to these days. In the present study we have made an attempt to examine the effect of dyebath pH on photofading behavior of nylon 66 when they are dyed with C. I. Acid Blue 25. Photoirradiation of dyed samples caused fading of dye and was characterized by measuring UV-visible absorption at 600 nm. *Figure 6.3* shows that absorbance, in the range of 500-700 nm, continuously decreases with exposure time.

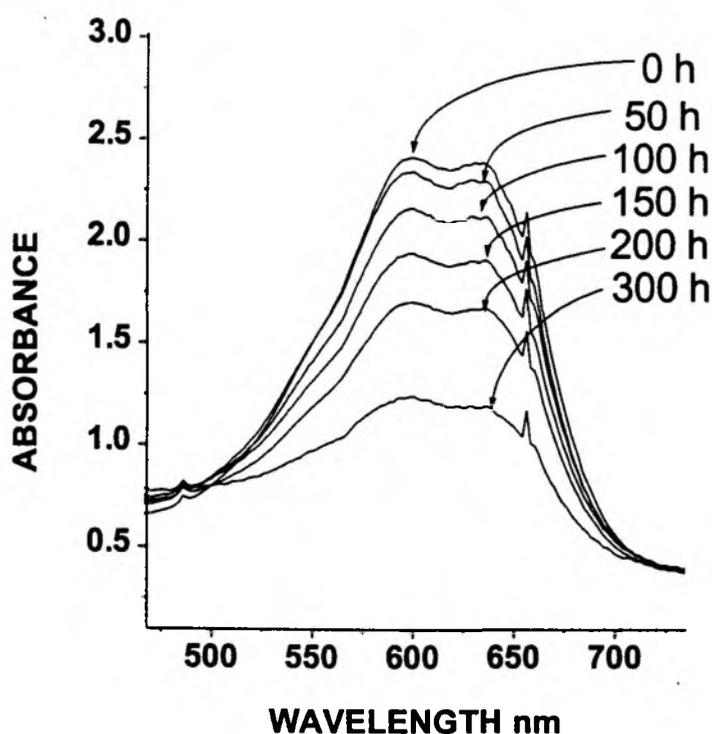


Figure 6.3 Change in UV-visible absorption in nylon 66, dyed with C. I. Acid Blue 25 at pH 2.0, with exposure time.

Figure 6.4 shows fading of samples dyed at four different pH. It is clear from the figure that lower dyebath pH has adverse effect on lightfastness of dyed polymer. Allen *et al.* also studied the fading of dyed nylon 66 for a range of pH. They observed that lower and higher dyebath pH has detrimental effect on dyed polymers. This particular effect of dyebath pH was explained with the ionic strength of the dye solution. At higher and lower dyebath pH, the ionic strength of the dye solution will be higher. Thus, at lower pH, excited dye molecule can easily abstract the proton and

undergo photoreduction whereas at higher pH the electron abstraction by excited dye molecule is more facile.

Similar phenomenon seems to be prevailing in our case also. Nylon 66 dyed at pH 2.0 showed more fading and is decreased as pH is increased. Further increase in pH from 4.0 to 7.0 did not show any more improvement in fading behavior of dyed polymer.

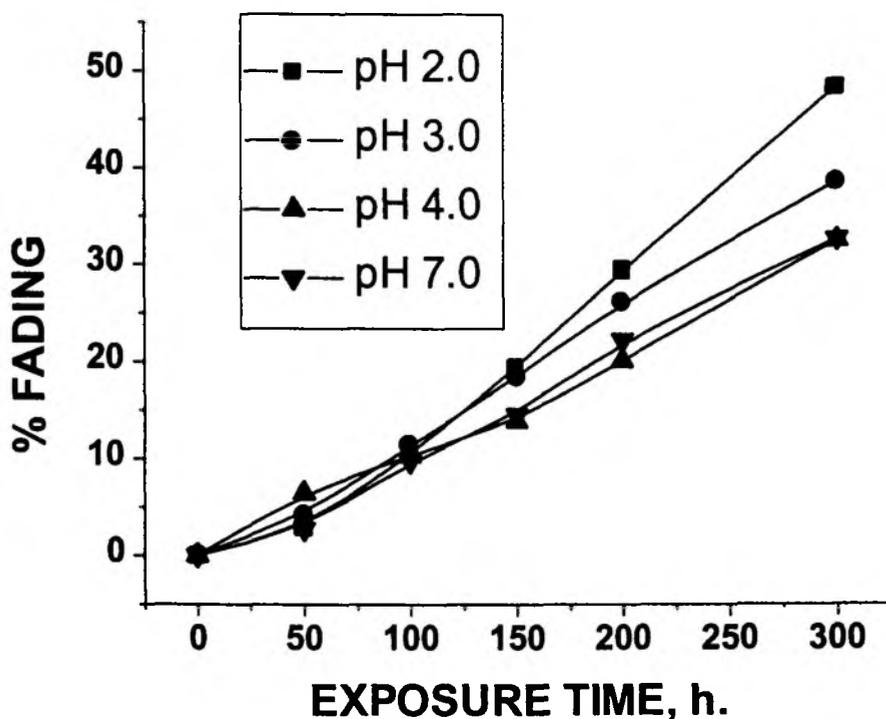


Figure 6.4 Fading of nylon 66 dyed (0.7% w/w) with C. I. Acid Blue 25 at different pH.

There is significant concentration of hydronium ions at pH 2 and 3 (0.01 M and 0.001 M respectively) and these concentrations are sufficiently higher and can also diffuse into polyamide and provide the hydronium ions during the photoinduced hydrogen abstraction process initiated by excited dye molecules. On the other hand, at pH 4 and onwards (up to 7) the hydronium ions concentration is too low to diffuse into the polyamide and affect the fading behavior of dye. Thus, the increase in pH above 4 up to 7 does not have any practical significance on hydronium ions and subsequently on the fading characteristics of the dye.

6.4 Conclusions

We observed a peculiar effect of dyebath pH on the photostability of dyed nylon 66. Much lower dyebath pH has adverse effect on the photostability of dyed nylon 66. Dyed samples were more stable when dyed at pH 3 and above that (up to 7) whereas the samples dyed at pH < 3.0 showed sensitized photo-oxidative degradation in nylon 66.

Formation of quaternary ammonium salt on dye-chromophore was considered responsible for the pH-controlled behavior of anthraquinone acid dyes. Proposed hypothesis for the photosensitizing behavior of anthraquinone acid dyes at lower dyebath pH can be affirmed by studying the excitation behavior of nylon 66 samples dyed at different pH.

Photofading behavior of dyed samples showed significant effect of dyeing pH. Effect of dyebath pH, on photofading of dyed samples, is more pronounced at lower dyeing pH and prevails upto pH 4. Hydronium ions concentration was considered to be responsible for the enhanced fading of dye for the samples dyed at the lower pH.

6.5 References

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CHAPTER VII
PHOTOSTABILIZATION OF NYLON 66 IN PRESENCE OF
DYES

7.1 Introduction

Nylon 66 is one of the important polymers used in fiber applications. For this particular application, the photostability is one of the important criteria polymer should meet. Photostability of the nylon polymers is often determined by the presence of trace amount of impurities present in the polymer¹⁻⁶. These impurities are reported⁷ to be formed during melt processing or thermal oxidative degradation of nylon 66. Moreover, these impurities slowly get vanished as photo-oxidative degradation progresses. These impurities are, mainly, α , β -unsaturated carbonyl species and unsaturated cyclopentanone⁸⁻¹² derivatives.

In our previous study (Chapter III), we observed a significant amount of hydroxy/hydroperoxy groups present in unexposed samples. Photo-oxidative degradation was found more rapid during the initial period of photoexposure, which was due to the rapid decomposition of the hydroxy/hydroperoxy groups present in the samples. Polymer morphology is another important factor, which considerably controls the kinetics of oxidative degradation¹³⁻¹⁶.

Since early 60's efforts are being made to improve the photostability of polyamide thermoplastics and fibers but many of the photostabilizers reported¹⁷⁻²³ are not conventional stabilizers normally used for plastic materials, viz. manganese salts, alkali metal salts, titanium dioxide, metalized dyes, thiophines, etc. Efficiency of these class of photostabilizers is directly related to their ability to quench the excitation of impurities present in polyamides. There are also some reports²⁴⁻²⁸ on photostabilization of polyamides using conventional photostabilizers like UV absorbers and HALS.

For a fiber material, the dyeing ability and oxidative stability of substrate is much more important. The presence of the dye is often crucial in determining the nature of photoreactions, which occur and these, in turn, will influence the stability of the polymer itself²⁹⁻³¹. Photo-oxidative degradation of synthetic and natural polymers is very important area of research from scientific as well as industrial point of view. However, a lot of fundamental work has been done to study the photo-oxidative behavior of synthetic polymers in presence of dyes³²⁻³⁹.

Much of efforts have been made to stabilize nylons and many other polymers in presence of dyes using a variety of photostabilizers^{31, 40-54}. Among these stabilizers, the UV absorbers are widely used stabilizers for enhanced stabilization of dyed polymers. Dye-bound UV absorbers were synthesized and applied on different

substrates⁴⁰⁻⁴³. Certain tailored UV absorbers have been prepared for applications to fibers during or after dyeing⁵²⁻⁵⁴. HALS have been used for various dyes and substrate for enhanced lightfastness and substrate stability as well^{42, 43, 55}.

In the present study, we have followed an empirical approach to study the photostability of nylon 66 and lightfastness of anthraquinone acid blue dyes in the presence of various concentrations of UV absorber and HALS. This study provides useful data on stabilizing efficiencies and self-stability of these additives in nylon 66. We have also studied the relative fading behavior and photostabilizing efficiencies of three different anthraquinone acid blue dyes. Several facts concerning the photostability and the self-association of additives are perceived in this study.

7.2 Experimental

7.2.1 Materials

Nylon 66 samples were received from M/s du Pont de Nemours, USA and used as received. C. I. Acid Blue 25, C. I. Acid Blue 40, C. I. Acid Blue 129 and 2, 2, 6, 6-tetramethylpiperidin-4-ol were received from Aldrich Chemical Company. All the dyes were purified by solvent extraction using acetone as solvent. Solvent extracted dyes were recrystallized from ethanol. 2, 2, 6, 6-Tetramethylpiperidin-4-ol was used as received. 2(2'-Hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole (Tinuvin 326) was received from Ciba-Geigy, Switzerland. Tinuvin 326 was recrystallized from chloroform.

7.2.2 Sample preparation

All the additives were mixed with nylon 66 in different proportions by melt mixing at 270°C using small-scale melt mixing unit. Films out of these additive-mixed polymers were prepared as method discussed in 3.2.2.

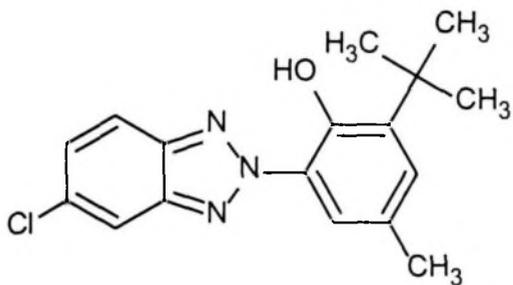
7.2.3 Photo-irradiation

All the samples were photoirradiated in SEPAP 12/24 for different time intervals up to 300 h.

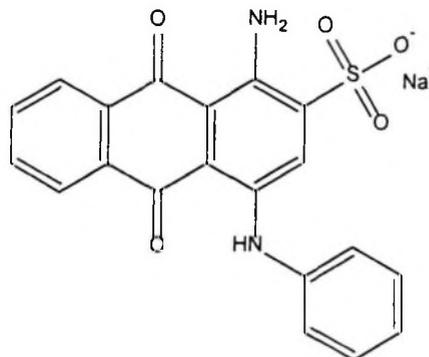
7.2.4 Analysis

All the samples photoirradiated for different time intervals were characterized using FT-IR and UV spectroscopy. These instruments are described in Chapter III, 3.2.

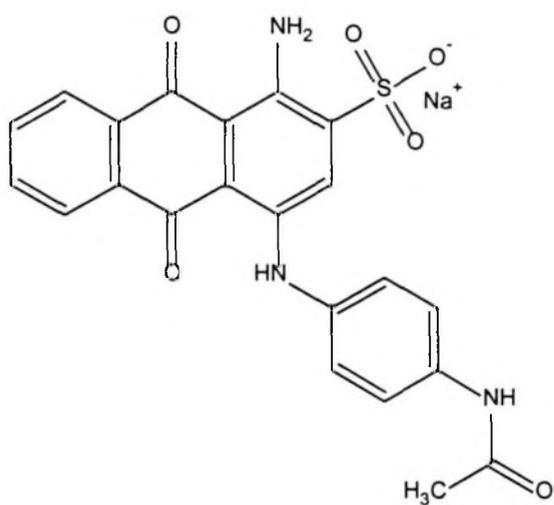




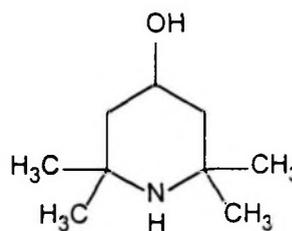
2-(2-Hydroxy-3-t-butyl-5-methyl-phenyl)-
5-chloro-benzotriazole (Tinuvin 326)



C. I. Acid Blue 25

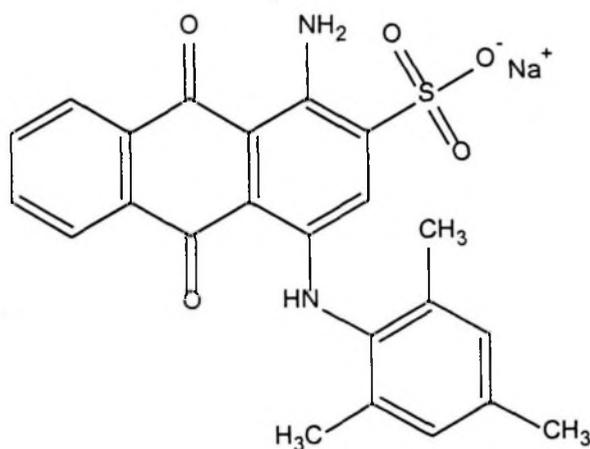


C. I. Acid Blue 40



2, 2, 6, 6-Tetramethylpiperidin-4-ol

Th 8690



C. I. Acid Blue 129

7.3 Results and Discussion

7.3.1. Photo-oxidation of nylon 66 in presence of Tinuvin 326

An effect of UV absorber (Tinuvin 326) concentration on the photostability of nylon 66 was studied with the help of IR spectroscopy. Tinuvin 326 was mixed with nylon 66 in three different concentrations; 0.2, 0.5 and 1.0 % w/w. *Figure 7.1* shows

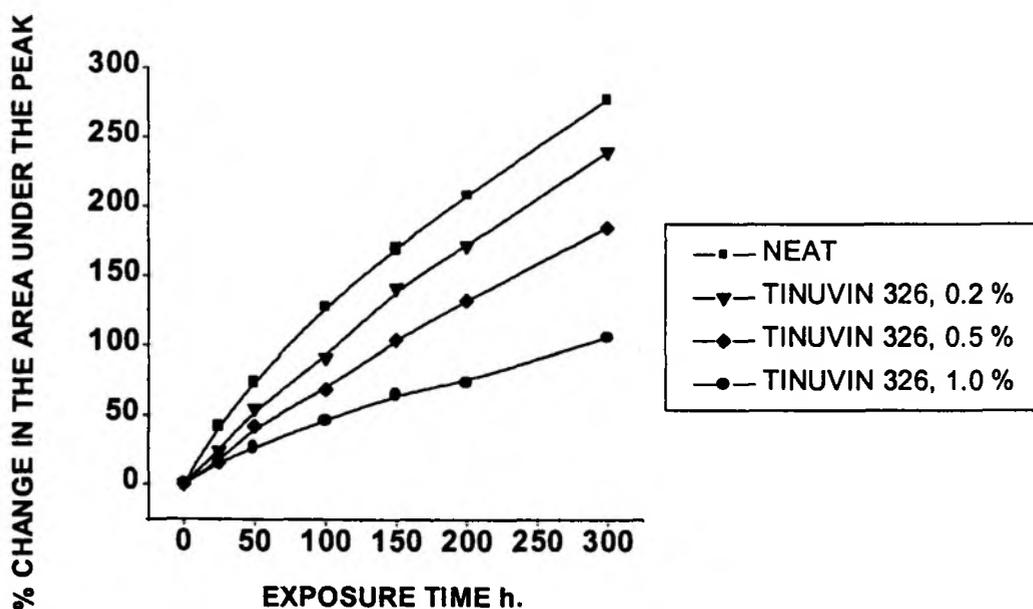


Figure 7.1 Photo-oxidation of nylon 66 in presence of UV absorber [2(2'-Hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole] present in three different concentrations.

percentage change in area under the carbonyl peak with exposure time. With increasing UV absorber concentration the photo-oxidation was found to be decreased. Maximum UV absorber concentration used was 1.0% w/w and at this particular concentration after 300 h of exposure, the photo-oxidation was found to be reduced by more than two times as compared to neat samples. However, there was also marginal reduction in photo-oxidation even when 0.2 % w/w of UV absorber was added. Initially, the rate of photo-oxidation was fast and it was slightly reduced after 100 hr. of exposure. This is true for control sample as well as the samples with all the three concentration of UV absorber.

7.3.2 Photo-oxidation of nylon 66 in presence of 2, 2, 6, 6-tetramethylpiperidin-4-ol

Hindered amine light stabilizers are reported²⁷ to be very efficient stabilizers for nylon 66 against photo-oxidative degradation. 2, 2, 6, 6-Tetramethylpiperidin-4-ol was also found an effective light stabilizer for nylon 66. However, the effect of its concentration on photostability of nylon 66 is not well reported. In present study, we have used three different concentrations; 0.2, 0.5, and 1.0 % of 2, 2, 6, 6-tetramethylpiperidin-4-ol (HALS) and their effect on photostability on nylon 66 was studied. Figure 7.2 shows the effect of HALS concentration for photostability of

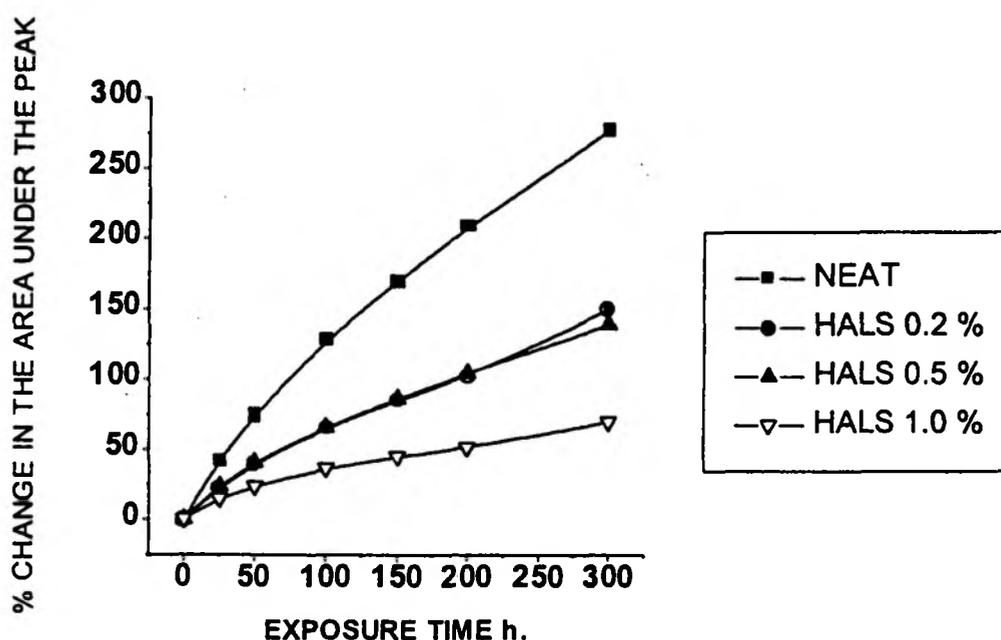


Figure 7.2 Photo-oxidation of nylon 66 in presence of HALS (2, 2, 6, 6-tetramethylpiperidin-4-ol) present in three different concentrations.

nylon 66. Unlike UV absorbers, HALS shows very peculiar effect on photostability of nylon 66. Amongst there different concentrations of HALS, the 0.2 and 0.5 % HALS containing samples exhibited almost similar stability. However, the samples containing 1.0 % HALS showed enhanced photostability, i.e. five times more than control sample.

7.3.3 Photo-oxidation of nylon 66 in presence of C. I. Acid Blue 25

C. I. Acid Blue 25 is found to stabilize nylon 66 at neutral pH (Chapter 6). However, the effect of different dye concentration on photostability of nylon 66 is not studied.

C. I. Acid Blue 25 was melt blended with nylon 66 in three different concentrations; 0.1, 0.2 and 0.5 % w/w. Dye concentration has very peculiar effect on the photostability of nylon 66. *Figure 7.3* shows that by increasing dye concentration

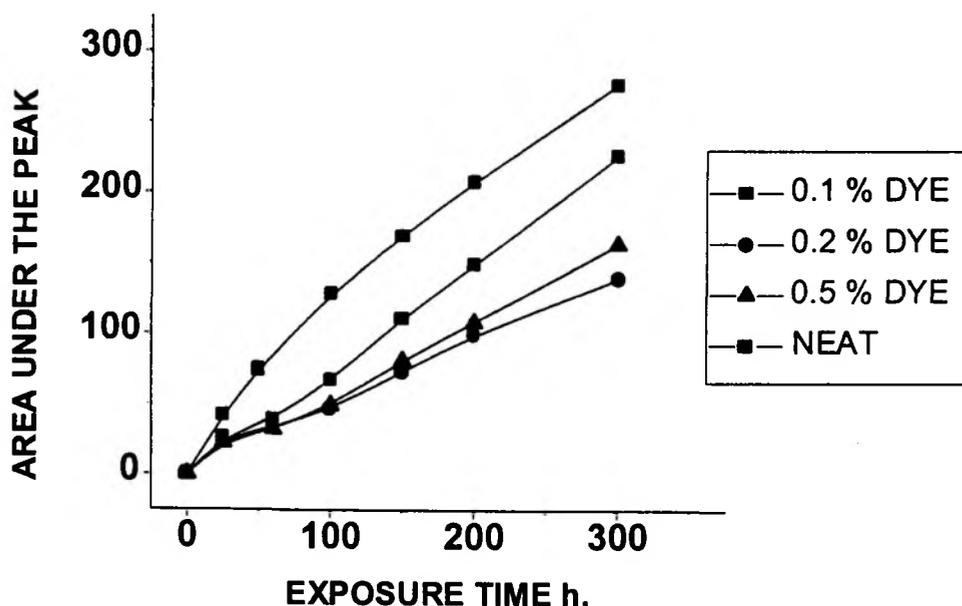


Figure 7.3 Photo-oxidation of nylon 66 in presence of dye (C. I. Acid Blue 25) present in three different concentrations.

from 0.1 to 0.2 % w/w the change in area under the peak was reduced by 100 % after 300 h of photoirradiation. Increase in dye concentration from 0.2 % to 0.5 % was found to decrease the photostability of nylon 66. Hence, the 0.2 % dye concentration is the optimum concentration for better photostability of nylon 66. In case of control sample, the rate of photo-oxidation was slightly reduced after the 100 h of photoexposure. However, the dyed sample showed the reverse trend. As it is shown in *Figure 7.3*, the rate of photo-oxidation was low during initial period of photo-oxidation and was increased continuously with increasing exposure time.

7.3.4 Photo-oxidation of nylon 66 in presence of dye and UV absorber

Many authors have studied⁵⁶⁻⁶³ the effect of UV absorbers during photoirradiation of dyed polymers. However, these reports are mainly concentrated to lightfastness of dye and not to the substrate stability. In our study, the nylon 66 samples with three difference dye concentration and a constant UV absorber concentration (0.5 % w/w)

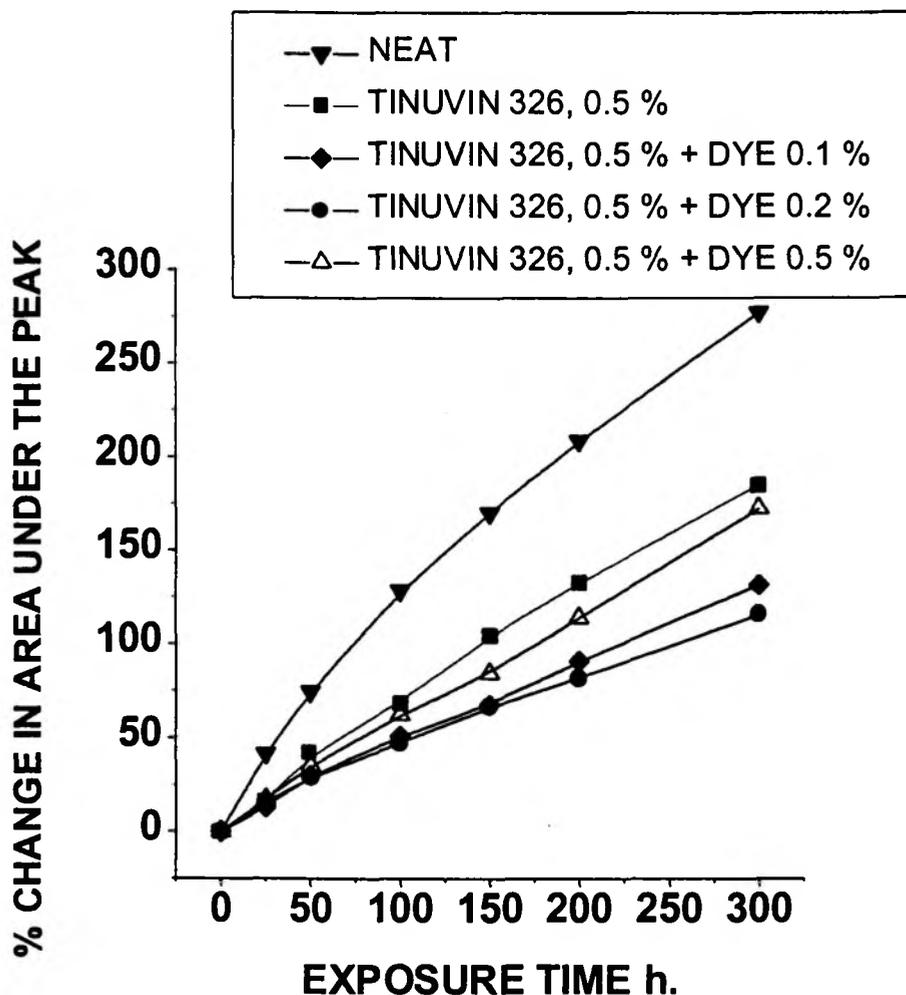


Figure 7.4 Photo-oxidation of nylon 66 in presence of dye (C. I. Acid Blue 25) present in three different concentrations and a constant concentration of UV absorber [2(2'-Hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole].

were photoirradiated for 300 h. As it is shown in *Figure 7.4* all the samples were found more photostable than control sample. Mixture of dye and UV absorber is a synergistic mixture and gives an enhanced stability to the substrate. However, the optimum dye concentration is 0.2 % as was observed when only dye was added where the maximum stability to the nylon 66 substrate was observed.

7.3.5. Photo-oxidation of nylon 66 in presence of dye and HALS

Hindered amine light stabilizers are not commonly used stabilizers in dyed polymers. However, there are number of reports^{55, 64-68} indicating the improvement in

photochemical stability of dyed polymer. *Figure 7.5* shows that dye is still showing the stability in presence of hindered amine light stabilizers (0.5 % w/w). This indicates that the mixture of dye and HALS is a synergistic mixture. A concentration of 0.2 % dye is the optimum dye concentration, which imparts the maximum photostability to the nylon 66. Samples with combination of 0.5 % HALS and 0.2 % dye exhibited five times higher stability as compared to control one.

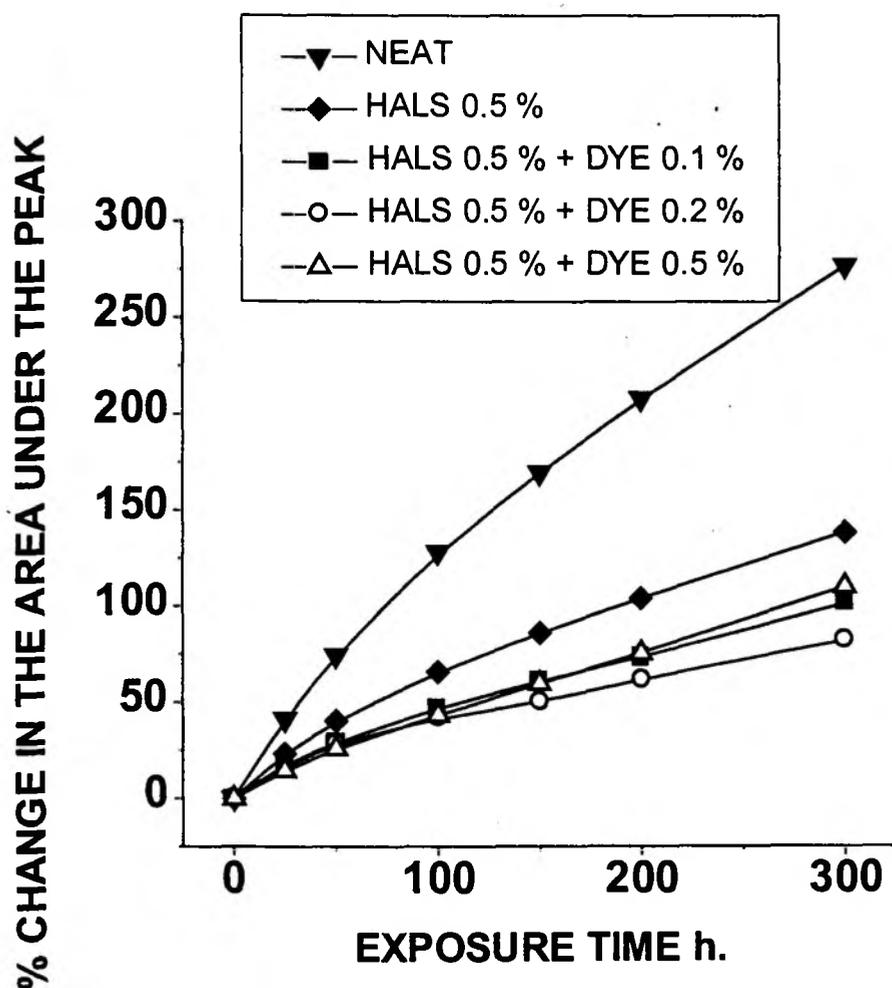


Figure 7.5 Photo-oxidation of nylon 66 in presence of dye (C. I. Acid Blue 25) present in three different concentrations and a constant concentration of HALS (2, 2, 6, 6-tetramethylpiperidin-4-ol).

7.3.6. Photofading of dye in nylon 66

Fading characteristic was checked for three different dye-concentrations; 0.1, 0.2 and 0.5 % w/w. *Figure 7.6* shows that with increasing dye concentration the fading was increased. After 200 h of photoirradiation, samples with 0.5 % w/w dye content, showed two times higher fading as compared to samples containing 0.2 % dye. Results indicate that when the dye molecules are well dispersed in the system, they are more stable. The 0.1 % and 0.2 % concentrations are fairly low and dye molecules are well-dispersed in nylon 66 matrix whereas 0.5 % is high enough to make molecular aggregates in the system. However, this again depends on the relative stability of the aggregates and dispersed molecules. There are certain reports^{69, 70}, which show that dye aggregates are having more lightfastness. It was also observed²⁷ that dyes in more amorphous polymers tend to display a higher lightfastness than when they are present in a crystalline polymer. Thus, for C. I. Acid Blue 25, the dye-polymer interaction is observed to impart greater stability to dye whereas dye-dye interaction is found to be harmful for dye stability.

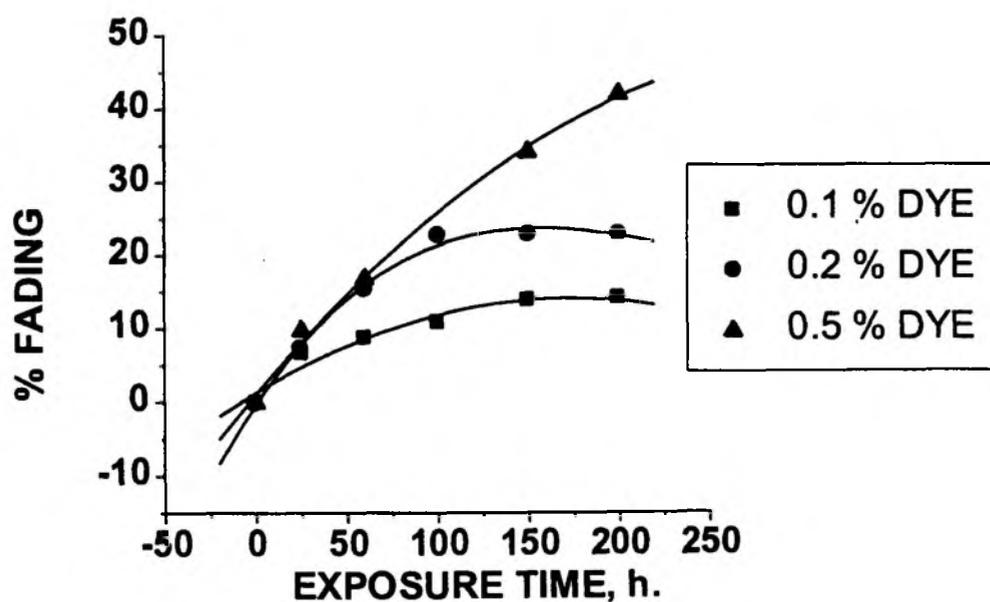


Figure 7.6 Photofading of nylon 66 with three different concentrations of a dye (C. I. Acid Blue 25)

7.3.7. Photofading of dye in presence of UV absorber

UV absorbers are most commonly used additives for colour stability of textile materials. In the present study, we kept a constant concentration of UV absorber (0.5 %) and dye concentration was varied from 0.1 to 0.5 %. Fading behavior (*Figure 7.7*) of dye is same as it is shown in *Figure 7.6* but its rate of fading was retarded considerably.

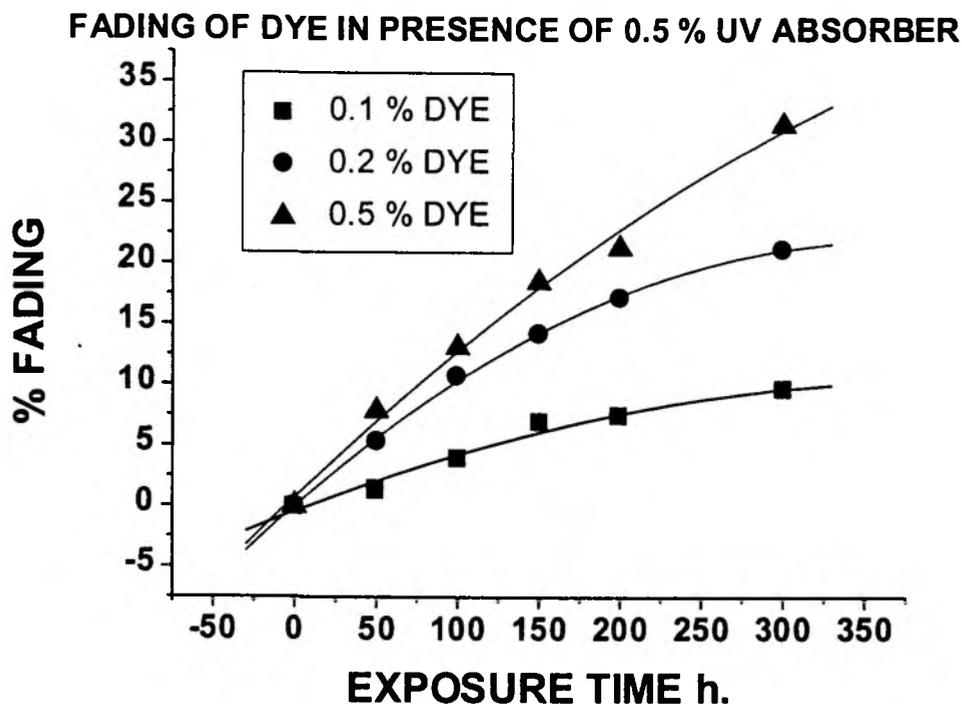


Figure 7.7 Photofading of nylon 66 with three different concentrations of a dye (C. I. Acid Blue 25) and constant concentration of UV absorber [2(2'-Hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole]

Thus, the UV absorber imparts stability to substrate as well as to colour. However, the efficiency of UV absorbers as colour stabilizer is remained a matter of debate. Some researchers^{56, 62} found little reduction of fading of direct dyes on cotton and observed increased fading on modified polyester dyed with methylene blue as a result of application of substantive UV absorbers. Woepfel⁶³ found no significant reduction in fading of acid blue dyed nylon when three hydroxy benzophenone absorbers were applied by immersion treatment.

Polymer-dye-UV absorber is seems to be a complex system and many times behaves very unpredictably. However, the results obtained in present study are as per expectation and indicated the simplicity of the system.

7.3.8 Photofading of dye in presence of HALS

HALS are gaining much more importance in improving colour stability of textile materials^{42, 43, 55}. In the present study, an effect of a constant concentration of HALS is examined for a series of dyes (*Figure 7.8*) concentrations. HALS is found to stabilize the colour in nylon 66. In this system also, the behavior of dye fading remains the same. Samples with higher extent of dye had shown the maximum fading.

Figure 7.9 shows the relative effect of UV absorber and HALS individually on photofading characteristics of dye. It is quite clear from the figure that UV absorber imparts greater colour stability as compared to HALS. Addition of 0.5 % UV absorber showed two times higher photostability after 200 h of exposure as compared to sample with dye only.

FADING OF DYE (C. I. ACID BLUE 25) IN PRESENCE OF 0.5 % HALS

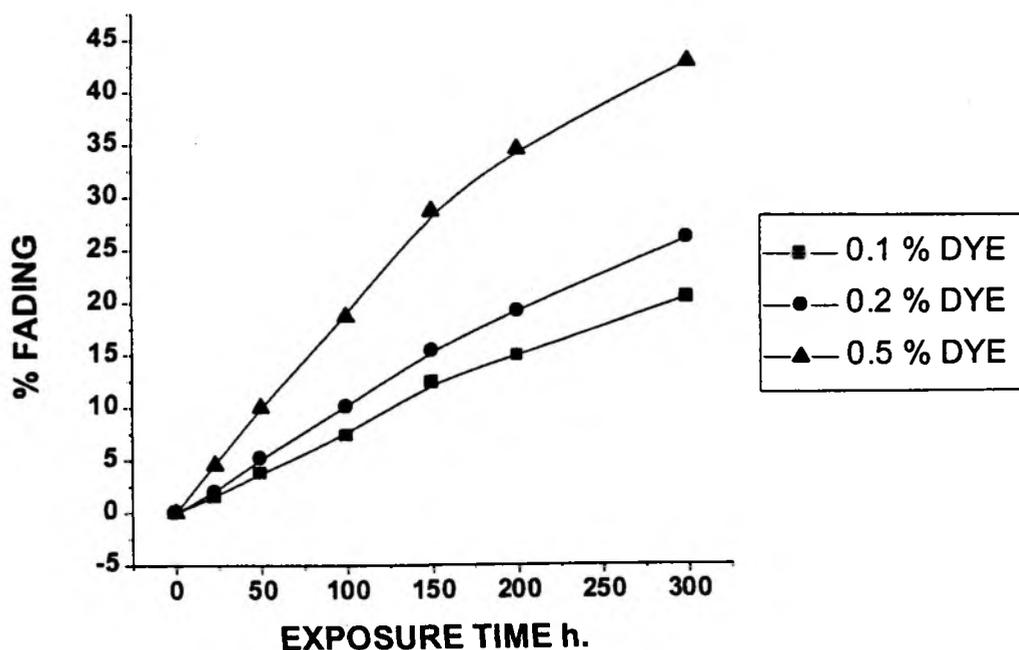


Figure 7.8 Photofading of nylon 66 with three different concentrations of a dye (C. I. Acid Blue 25) and constant concentration of HALS (2, 2, 6, 6-tetramethylpiperidin-4-ol).

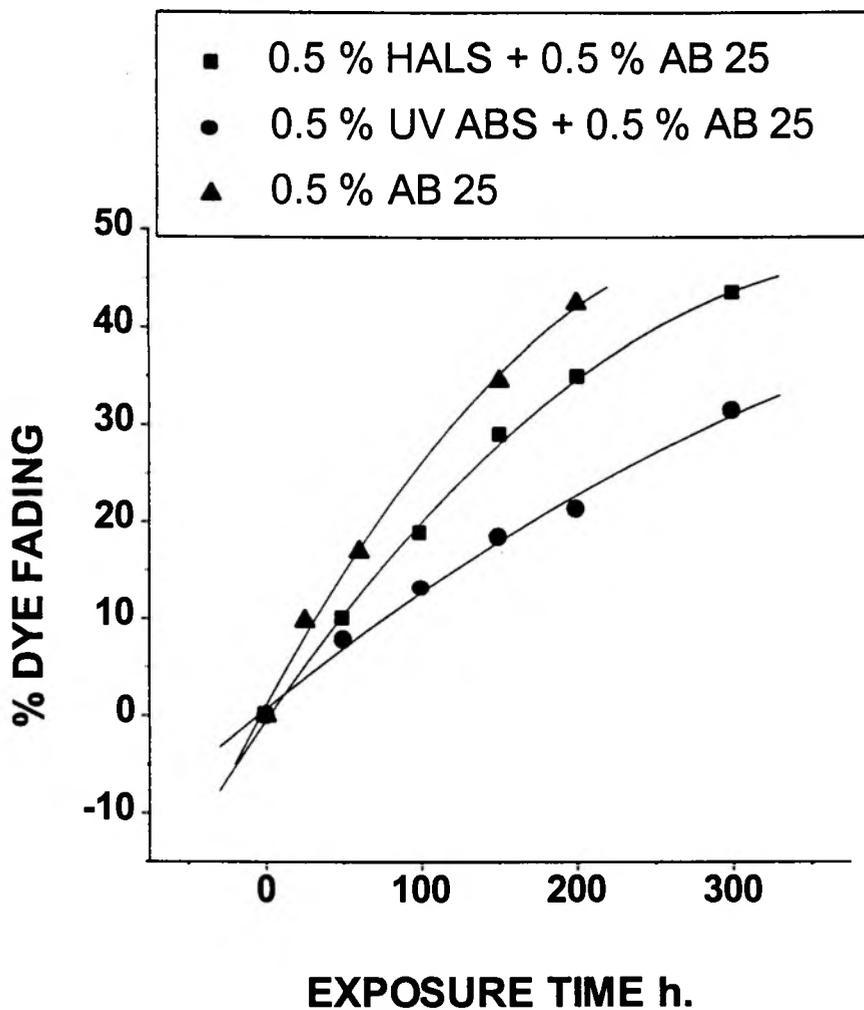


Figure 7.9 Photofading of dye (C. I. Acid Blue 25) in presence of HALS (2, 2, 6, 6-tetramethylpiperidin-4-ol) and UV absorber (2(2'-Hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole) in nylon 66.

7.3.9 Decomposition of UV absorber

Nylon 66 containing UV absorber shows distinct UV absorption from 275 to 400 nm. We found that UV absorber also gets decomposed with exposure time. *Figure 7.10* shows continuous decrease in UV absorption at 356 nm as photoirradiation progresses. *Figure 7.11* is in the form of spectral subtraction of unexposed sample spectrum from each spectrum of sample exposed for different time intervals. This spectral subtraction shows net change in UV absorption after different time interval.

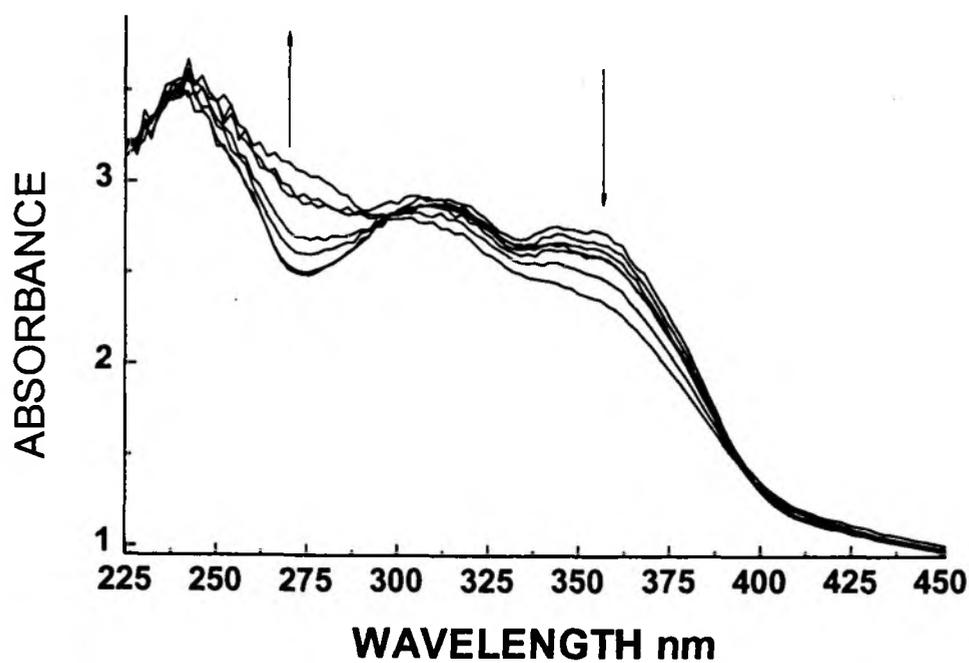


Figure 7.10 Change in UV absorption of nylon 66 with 1.0 % UV absorber [2(2'-Hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole] with photoirradiation.

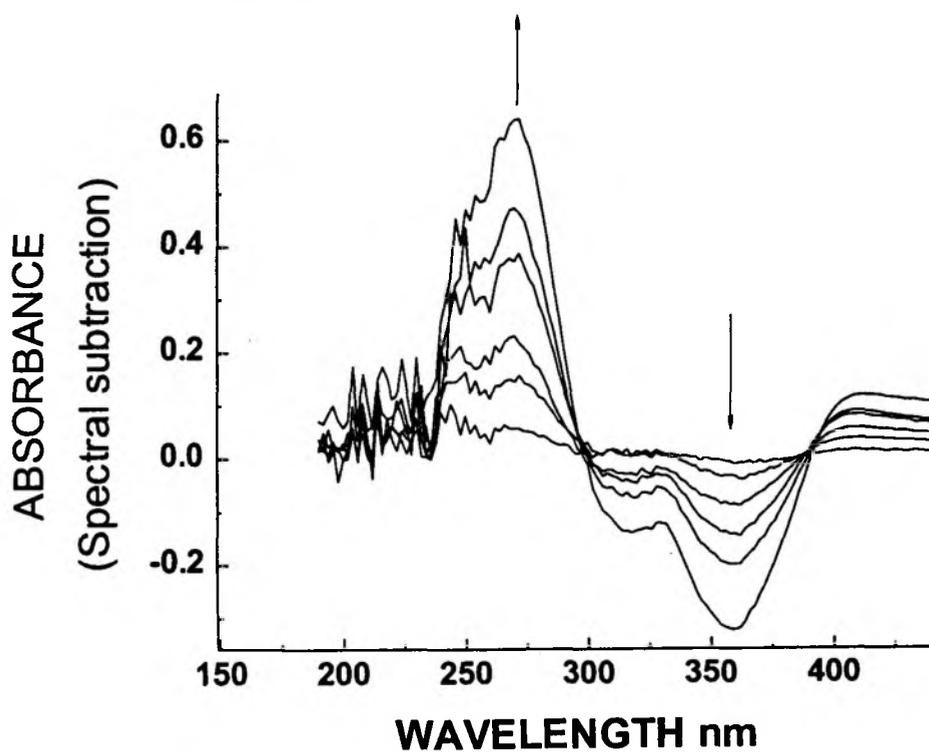


Figure 7.11 Change in UV absorption (in spectral subtraction form, subtraction of spectrum of unexposed sample from each of the spectra of samples exposed for different time intervals) of nylon 66 with 1.0 % UV absorber [2(2'-Hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole] with photoirradiation.

Figure 7.11 shows that when absorption at 356 nm decreases, the absorption at 264 nm starts increasing continuously as exposure goes on. This indicates that the decomposition products of UV absorber absorb at 264 nm and probably inactive to show further stability to the substrate.

Figure 7.12 shows the relative rate of UV absorber decomposition with exposure time. For a series of UV absorber concentrations, the percentage decomposition does not change significantly. Nevertheless, there is a difference in decomposition with concentration and samples with less amount of UV absorber showed the maximum fading of UV absorber. This behavior could be due to the enhancement in stability as the aggregation is increased. Samples with 1.0 % UV absorber would have more aggregates and in turn the stability of UV absorber in aggregates was enhanced.

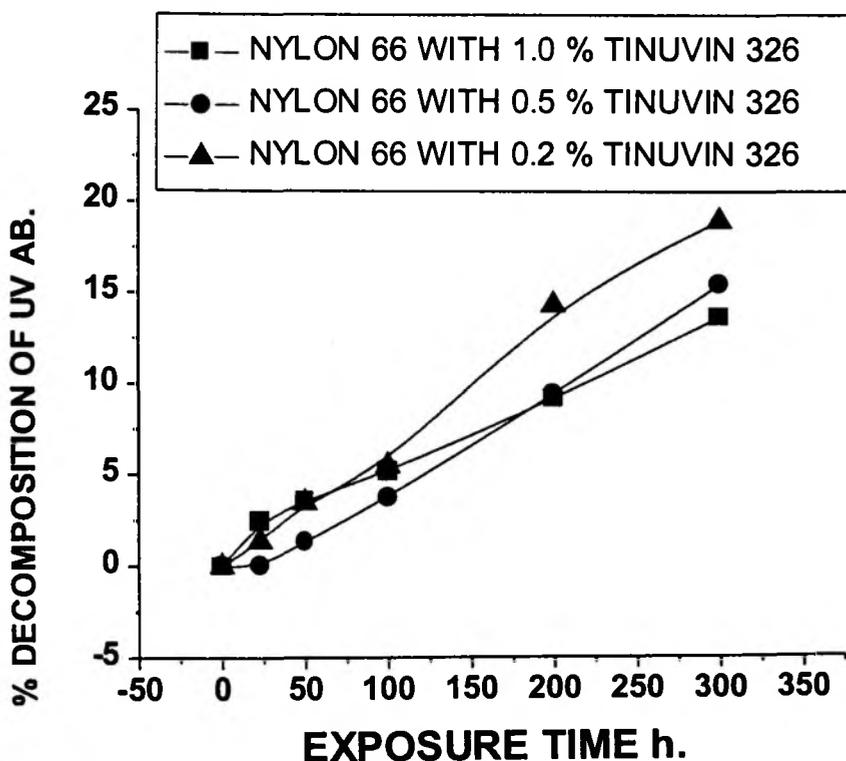


Figure 7.12 Loss of UV absorber in nylon 66 with exposure time.

7.3.10 Photo-oxidation of nylon 66 in presence of three different dyes

Photo-oxidative stability of nylon 66 in presence of three different dyes (C. I. Acid Blue 25, C. I. Acid Blue 40 and C. I. Acid Blue 129, 0.5 % each) is shown in Figure

7.13. All the three dyes are anthraquinone dyes with different substituents. Figure shows that all the three dyes impart the same photostability that is quite higher than control sample. Results indicate that the substitutions on the pendant phenyl ring (outside the anthraquinone moiety) do not have any significant effect of photostabilizing property of dyes. However, the substitution on anthraquinone moiety has significant effect on photostabilizing properties and photofading behavior of dyes²⁷.

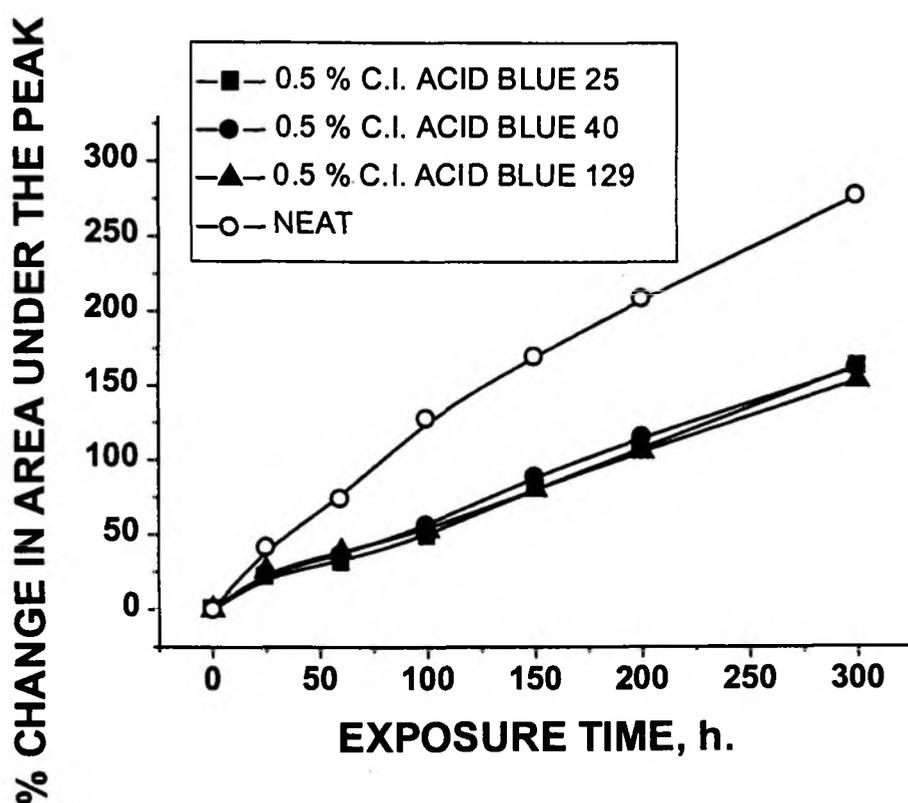


Figure 7.13 Photo-oxidation of nylon 66 in presence of three dyes; C. I. Acid Blue 25, C. I. Acid Blue 40 and C. I. Acid Blue 129 each one in 0.5 % w/w.

Fading behavior of these three dyes was studied and as it is shown in Figure 7.14 the two dyes C. I. Acid Blue 25 and C. I. Acid Blue 129 faded fast as compared to C. I. Acid Blue 40. C. I. Acid Blue 40 is having a polar substituent on pendant

phenyl ring that can help dye to disperse in polar polyamide matrix. Thus, the perfectly dispersed dye has more lightfastness as compared to aggregated one.

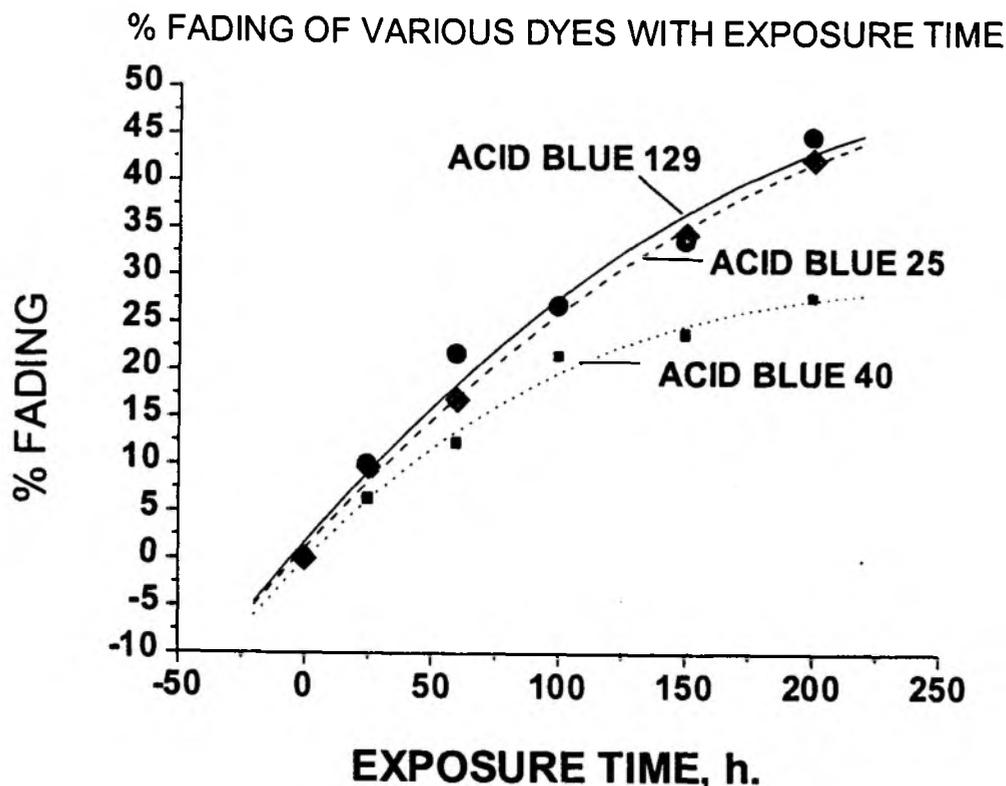


Figure 7.13 Photofading of three different dyes; C. I. Acid Blue 25, C. I. Acid Blue 40 and C. I. Acid Blue 129 each one in 0.5 % w/w in nylon 66.

7.4 Conclusions

Dye, UV absorber and HALS are observed to impart photostability to nylon 66. UV absorber and HALS showed the greater photostability at higher loading whereas in case of C. I. Acid Blue 25, the 0.2 % is the optimum concentration and beyond that its photostabilizing efficiency is deteriorated. Fading of dye is increased with increasing dye concentration and this is due to the poor lightfastness of dye aggregates in nylon 66. UV absorber imparts higher lightfastness to the dye as compared to HALS. UV absorber also gets vanished with exposure time. Decomposition of UV absorber is fast when it is added in a smaller quantity. Thus, the UV absorber itself is more stable when it is in an aggregated form.

Substitution on pendant phenyl ring of anthraquinone acid blue dyes has no effect on photostabilizing of efficiency of these dyes. However, if the dye is made

compatible and more dispersed in nylon 66 by placing some polar substituents on pendant phenyl ring, the lightfastness of the dye can be improved.

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CHAPTER VIII

**SYNTHESIS AND PROPERTY EVALUATION OF WATER-
SOLUBLE UV ABSORBERS IN NYLON 66**

8.1 Introduction

Protection of polymer against thermal and photo-oxidative degradation is achieved by blending the polymer with appropriate stabilizers which ensure the desirable polymer properties throughout its service life. During the past decade, the chemistry of synthesis of stabilizers and their mechanism of action has been extensively studied. The interaction between polymer and the stabilizer at molecular level has been elucidated¹.

The photostabilization of polymers involve retardation or elimination of destructive photochemical processes in polymers. UV absorbers are widely used stabilizers to prevent photodegradation in varieties of polymers. The most efficient UV absorbers include *o*-hydroxy phenyl benzotriazoles and *o*-hydroxy phenyl-*s*-triazines. This class of stabilizers bear intramolecularly hydrogen bonded phenol moiety, which helps in converting incident UV-energy into less harmful form of heat.

Basic understanding of these energy conversion processes is always remained an important area of research for polymer researchers and Physical chemists. In last few years, a lot of work has been done towards the understanding of fundamental aspects of functioning of UV absorbers²⁻⁷. It was observed that intramolecular hydrogen bond in benzotriazole based stabilizers can be disrupted in polar solvents. Other factors influencing the photostabilizing efficiency of this class of stabilizers are the planarity of the molecule, bulky substituents adjacent of hydroxy group, electronegativity of the substituents, pH and the polarity of the substrates.

UV absorbers are commonly used stabilizers for textile materials. They are found to impart good light stability to the substrate as well as color stability to the dyes⁶⁻¹⁷. Maerov and Kobsa¹⁶ observed improvements in lightfastness of dyes in the range of 200 to 300% when 2, 2'-dihydroxy-4, 4'-dimethoxybenzophenone was applied in the dyebath. Coleman and Peacock¹² observed 24- 86 % improvement in the lightfastness of disperse dyes on acetate and reduced the degradation of nylon when 2, 2'-dihydroxy-4, 4'-dimethoxybenzophenone was applied in dyebath. Gantz and Sumner¹⁵ also found that substituted benzophenone absorber markedly improve the lightfastness of the dyes. Reinert and Thommen¹⁷ observed improvement in the fastness of the pale shades of dyed nylon when UV absorber was applied during dyeing.

However, some researchers found UV absorbers to be ineffective or detrimental in reducing the dye fading. Cegarra and Ribe¹⁸ found only slight

improvement in lightfastness of acid dyed wool treated with 2, 4-dihydroxy benzophenone-2-ammonium sulfonate applied in a dye bath. Crews and Reagan¹⁴ observed increase in fading of some dyes on wool when treated with selected hydroxybenzophenones. Some researchers¹⁶⁻¹⁹ also found little reduction in fading of direct dyes on cotton and increased fading on modified polyesters dyed with methylene blue as a result of application of an UV absorber. Rich and Crews²⁰ evaluated efficiency of seven UV absorbers to reduce the fading of nylon dyed with nine synthetic acid dyes. They found only limited beneficial effects of these UV absorbers. Some of these UV absorbers have shown detrimental effects on all the dyes. According to them further testing is needed to determine the effects of specific absorbers on specific dyes.

Water-soluble or water dispersible UV absorbers are new class of UV absorbers, which are gaining importance these days²¹⁻²⁹. They are particularly useful for textile materials. This class of UV absorbers can be easily applied onto polymers by treating polymers in the aqueous solution of these UV absorbers.

In the present study, we have synthesized two novel water-soluble UV absorbers from an existing commercial UV absorber. We herewith report a new route for functionalization of existing benzotriazole UV absorbers, which can lead to the synthesis of many more tailor-made UV absorbers. One of the two water-soluble UV absorbers was applied onto the nylon 66 and its property evaluation was carried out for dyed and undyed nylon 66.

8.2 Experimental

8.2.1 Materials

Nylon 66 sample received from M/s du Pont de Nemours and used as received. 2-(2H-Benzotriazole-2-yl)-4-methylphenol (Tinuvin P) was received from Ciba-Geigy, Switzerland. C. I. Acid Blue 25, 4-aminobenzoic acid and 4-aminobenzene sulfonic acid were received from Aldrich Chemical Company. C. I. Acid Blue 25 was purified by acetone extraction followed by recrystallization from ethanol.

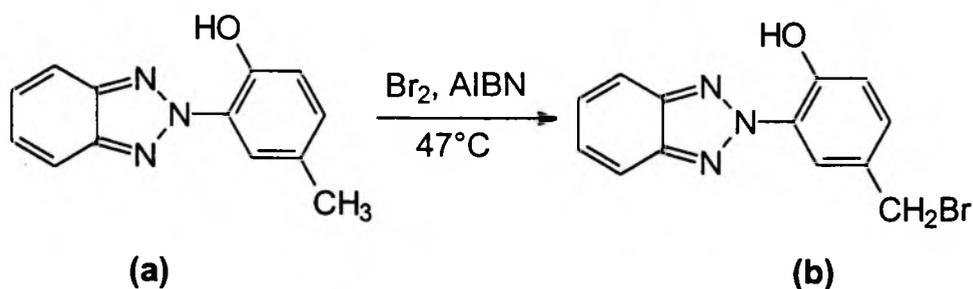
8.2.2 Analysis

FT-IR analyses were carried out in Perkin-Elmer 16 PC FT-IR instrument. UV absorption analyses were performed on Hewlett Packard model 5911-Diode array UV spectrometer. NMR spectra were recorded on Bruker AC200 Spectrometer using TMS as an internal standard.

8.2.3 Synthesis of water-soluble UV absorbers

8.2.3.1 Synthesis of 2-(2H-Benzotriazole-2-yl)-4-bromomethylphenol

2-(2H-Benzotriazole-2-yl)-4-bromomethylphenol was prepared from the bromination of 2-(2H-Benzotriazole-2-yl)-4-methylphenol using AIBN as initiator.



In a 500 ml three-necked round bottomed flask, 5 g (0.0223 mol) of 2-(2H-Benzotriazole-2-yl)-4-methylphenol (**a**) and 100 mg of AIBN were taken and dissolved in 150 ml of dry carbon tetrachloride. In a separate conical flask 4.18 g (1.5 ml, 0.03 mol) of bromine was dissolved in 75 ml of dry carbon tetrachloride and solution was transferred to a cylindrical funnel with pressure equalizing tube. Three-necked round-bottomed flask containing solution of (**a**) was kept in oil-bath with temperature 47°C. Nitrogen was bubbled through the solution for creating inert atmosphere. Cylindrical funnel containing bromine solution was mounted on the three-necked round-bottomed flask. Solution was continuously stirred with the help of magnetic stirrer. Bromine solution was added, drop-by-drop, from funnel to the flask for a span of 4-5 hours till all the solution was poured out. After that heating was stopped and the final reaction mixture was allowed to cool at room temperature. Product was separated by solvent evaporation. Finally the product was purified by recrystallization from acetone. The yield of (**b**) was 5.5 g (80%) m.p. 169-171°C.

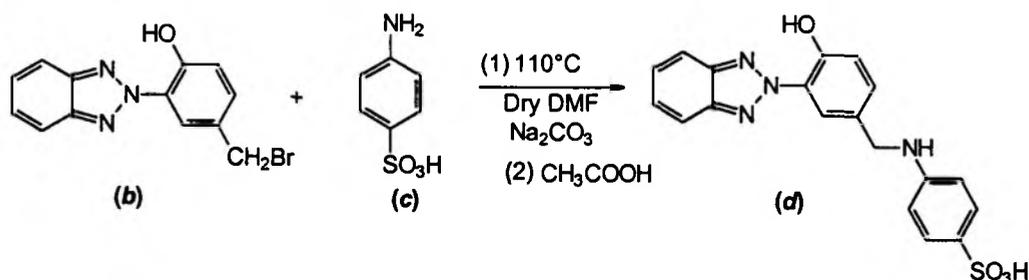
¹H-NMR, δ : 4.5-4.7 (s, 2H), 7.15-7.25 (d, 1H), 7.35-7.45 (d, 1H),
(200 MHz, CDCl₃) : 7.45-7.60 (q, 2H), 7.90-8.05 (q, 2H), 8.45-8.53 (d, 1H),
(Figure 8.1.a and b) : 11.45-11.55 (s, 1H)

IR (KBr, cm⁻¹) : 3300, -O-H stretching
(Figure 8.2) : 1222, C-O stretching
: 1258, -CH₂- wagging
: 684, C-Br stretching

Microanalysis :	Theoretical (%)	Observed (%)
C	51.13	51.40
H	03.28	03.24
N	13.18	13.95
O	05.26	05.77
Br	26.30	25.64

MS, m/z (% Relative intensity): 303 (M^+ , 25), 167 (20), 120 (15), 105 (10), 90 (15), 78 (20), 65 (23), 51 (50), 39 (40), 28 (25), 18 (100).

8.2.3.2 Synthesis of 4'-[3-(2H-Benzotriazole-2-yl)-4-hydroxybenzyl]aminophenyl sulfonic acid



2-(2H-Benzotriazole-2-yl)-4-bromomethylphenol (**b**) (3.0 g, 0.01 mol) 4-aminosulfonic acid (2.6 g, 0.015 mol), 3.0 g sodium carbonate and 200 ml of dry DMF were magnetically stirred in a 500 ml round bottomed flask for 12 hours in an oil-bath at 110°C. The solvent was then removed on a rotary evaporator and residue was dissolved in 50 ml of methanol and acidified with a little amount of acetic acid. Acidified solution was absorbed on 25 g of silica gel (60-120 mesh) and all the components were separated using column chromatography. 1.5:8.5 methanol:chloroform mixture was used as an eluting solvent. Purified 4'-[3-(2H-Benzotriazole-2-yl)-4-hydroxybenzyl]aminophenyl sulfonic acid (**d**) is slightly yellow powder, m. p. 313-315°C (decomposes at melting temperature), yield 700 mg (17%).

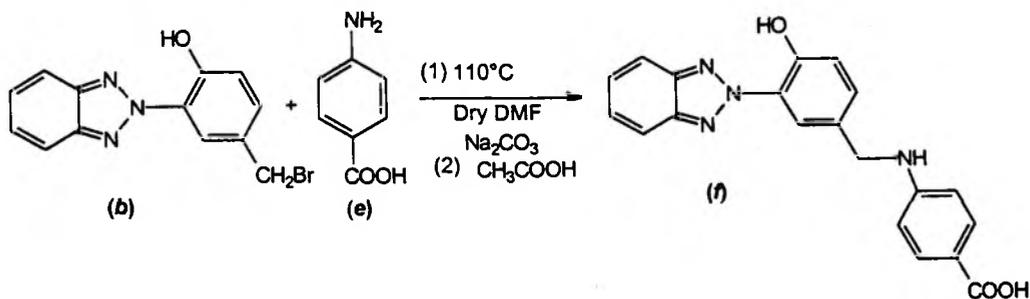
$^1\text{H-NMR}$, δ : 4.20-4.27 (d, 2H), 4.65-4.75 (broad s, 1H), 6.46-6.60 (200 MHz, DMSO- d_6) (d, 2H), 7.0-7.15 (d, 1H), 7.2- 7.33 (d, 2H). 7.33-7.40 (Figure 8.3) (d, 1H), 7.45-7.65 (q, 2H), 7.70-7.80 (d, 1H), 7.9-8.15 (q, 2H)

Phenolic proton in benzotriazole based UV absorbers is reported⁶ to form complex with DMSO and may not show signal at 11.5 δ in NMR spectrum, compound used for NMR was a sodium salt of 4'-[3-(2*H*-Benzotriazole-2-yl)-4-hydroxybenzyl]aminophenyl sulfonic acid.

IR (KBr, cm^{-1}) : 3380, -N-H (Ar-NH-R), stretching
(Figure 8.4) 1256, -CH₂- wagging
1180, C-O stretching for phenol
1128, S-O vibrations
1036, S-Ph vibrations
890, S-O stretching

Microanalysis :	Theoretical (%)	Observed (%)
C	57.57	57.40
H	04.04	04.10
N	14.14	14.17
S	08.08	08.12

8.2.3.3 Synthesis of 4'-[3-(2*H*-Benzotriazole-2-yl)-4-hydroxybenzyl]aminobenzoic acid



3.0 g (0.010 mol) of 2-(2*H*-Benzotriazole-2-yl)-4-bromomethylphenol (b), 2.0 g (0.015 mol) of 4-aminobenzoic acid, 3 g of sodium carbonate and 200 ml of dry DMF were magnetically stirred in a 500 ml round bottomed flask. Rest of the procedure was

followed same as described in 8.2.3.2. Here the eluting solvent used for column chromatography was a 1:9 mixture of methanol and chloroform. 4'-[3-(2H-Benzotriazole-2-yl)-4-hydroxybenzyl]aminobenzoic acid (*f*) is slightly yellow coloured powder with m. p. 249-252°C, yield 1.0 g (28%).

¹H-NMR, δ : 4.25-4.50 (d, 2H), 6.50-6.70 (d, 2H), 7.10-7.25 (d, 1H), 7.35-7.45 (d, 1H), 7.45-7.60 (q, 2H), 7.60- 7.75 (d, 2H), 7.75-7.90 (d, 1H), 7.9-8.2 (q, 2H), 10.40-10.60 (s, 1H).
(200 MHz, DMSO-d⁶)
(Figure 8.5)

IR (KBr, cm⁻¹) : 3356 -N-H, (Ar-NH-R) stretching
(Figure 8.6) 3000 (broad) -O-H, stretching in Ar-COOH.
1780 -C=O stretching in Ar-COOH
1312 C-O stretch
1260 -CH₂- wagging
1176 C-O stretch (phenol)
742 Ar-CH₂ stretching

Microanalysis :	Theoretical (%)	Observed (%)
C	66.66	66.13
H	04.44	04.14
N	15.55	14.96

8.2.4 Sample preparations

Film samples of nylon 66 were prepared as per method described in 3.2.2

8.2.5 Dye and UV absorber uptake measurements

Dye and UV absorber uptakes were measure as per the method described in Chapter VI, section 6.2.3. One of the water-soluble UV absorber with carboxylic acid moiety {4'-[3-(2H-Benzotriazole-2-yl)-4-hydroxybenzyl]aminobenzoic acid} needed in higher concentration (40 mg/dl) to be applied onto nylon 66 films.

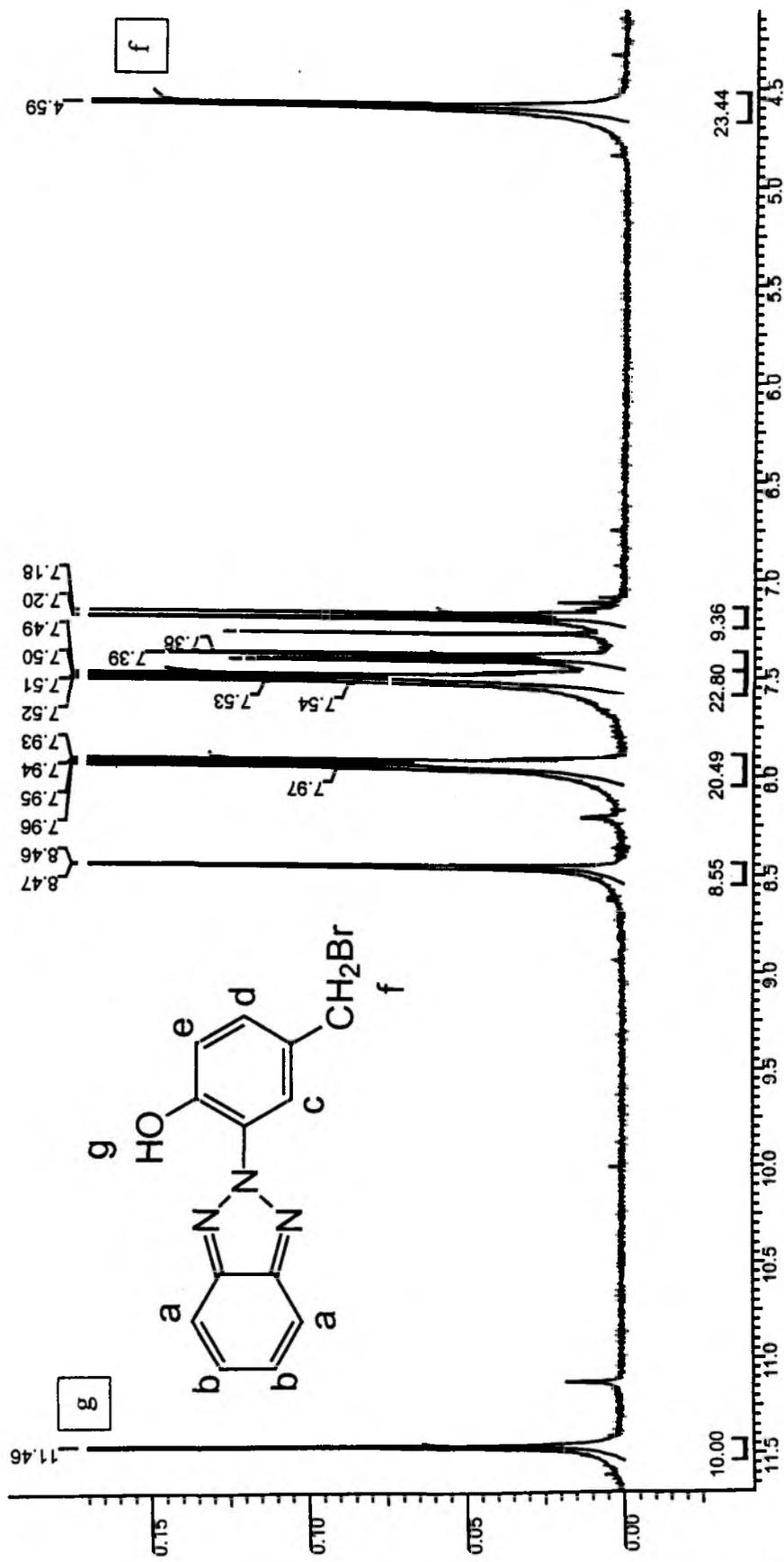


Figure 8.1.a ¹H-NMR spectrum of 2-(2H-Benzotriazole-2-yl)-4-bromomethylphenol

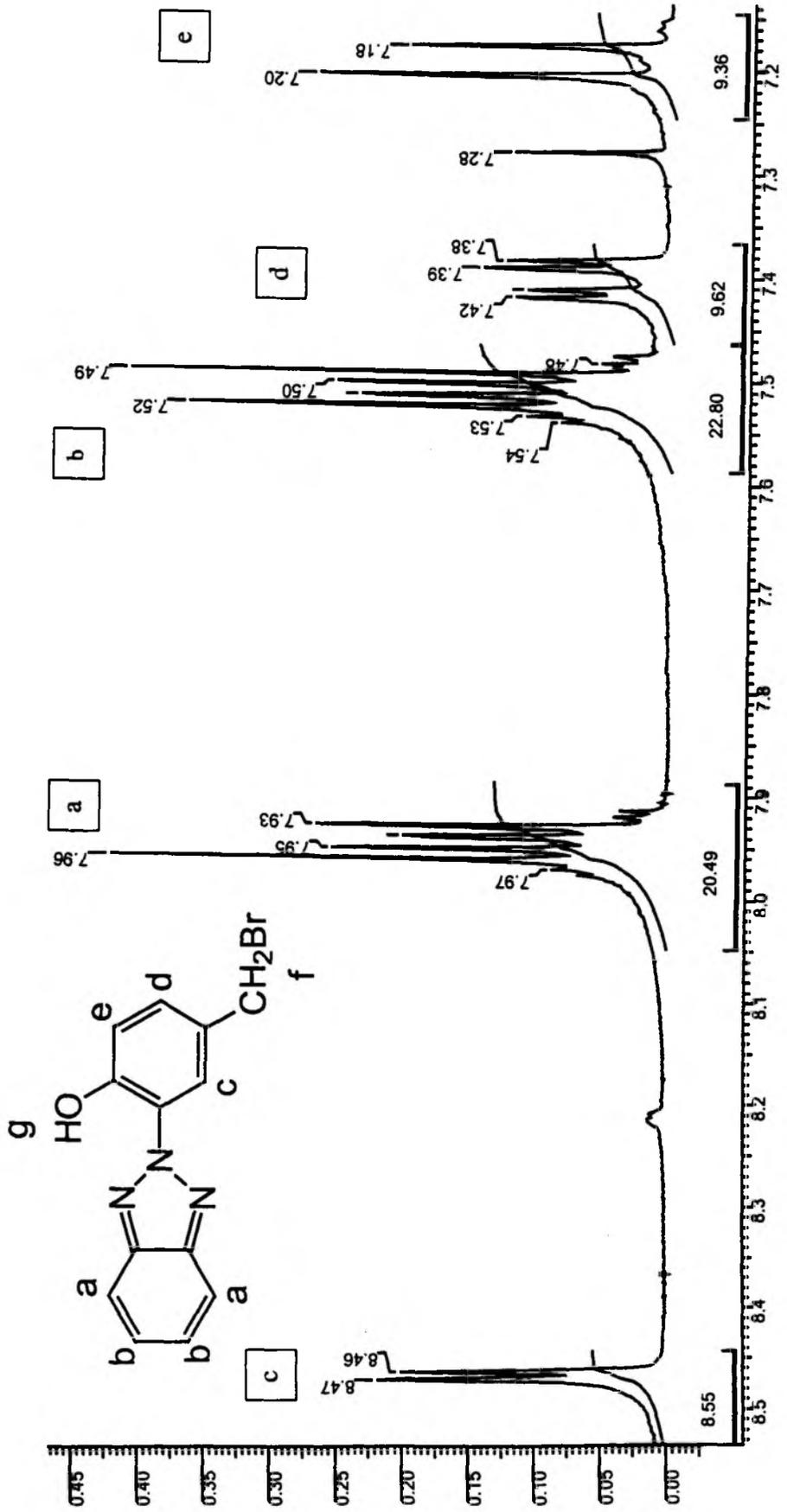


Figure 8.1.b ¹H-NMR spectrum of 2-(2H-Benzotriazole-2-yl)-4-bromomethylphenol (expanded arom. Region)

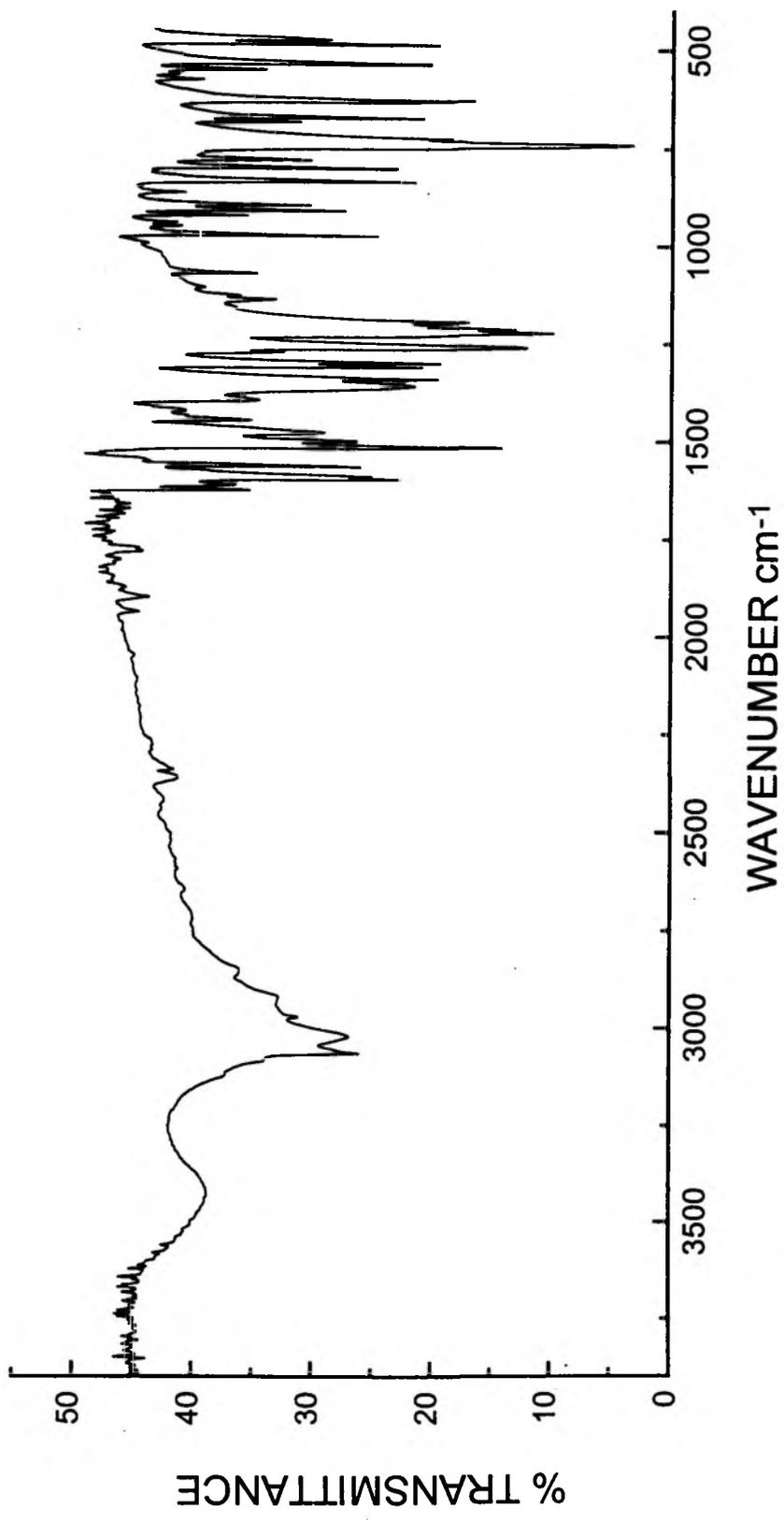


Figure 8.2 FT-IR spectrum of 2-(2H-Benzotriazole-2-yl)-4-bromomethylphenol

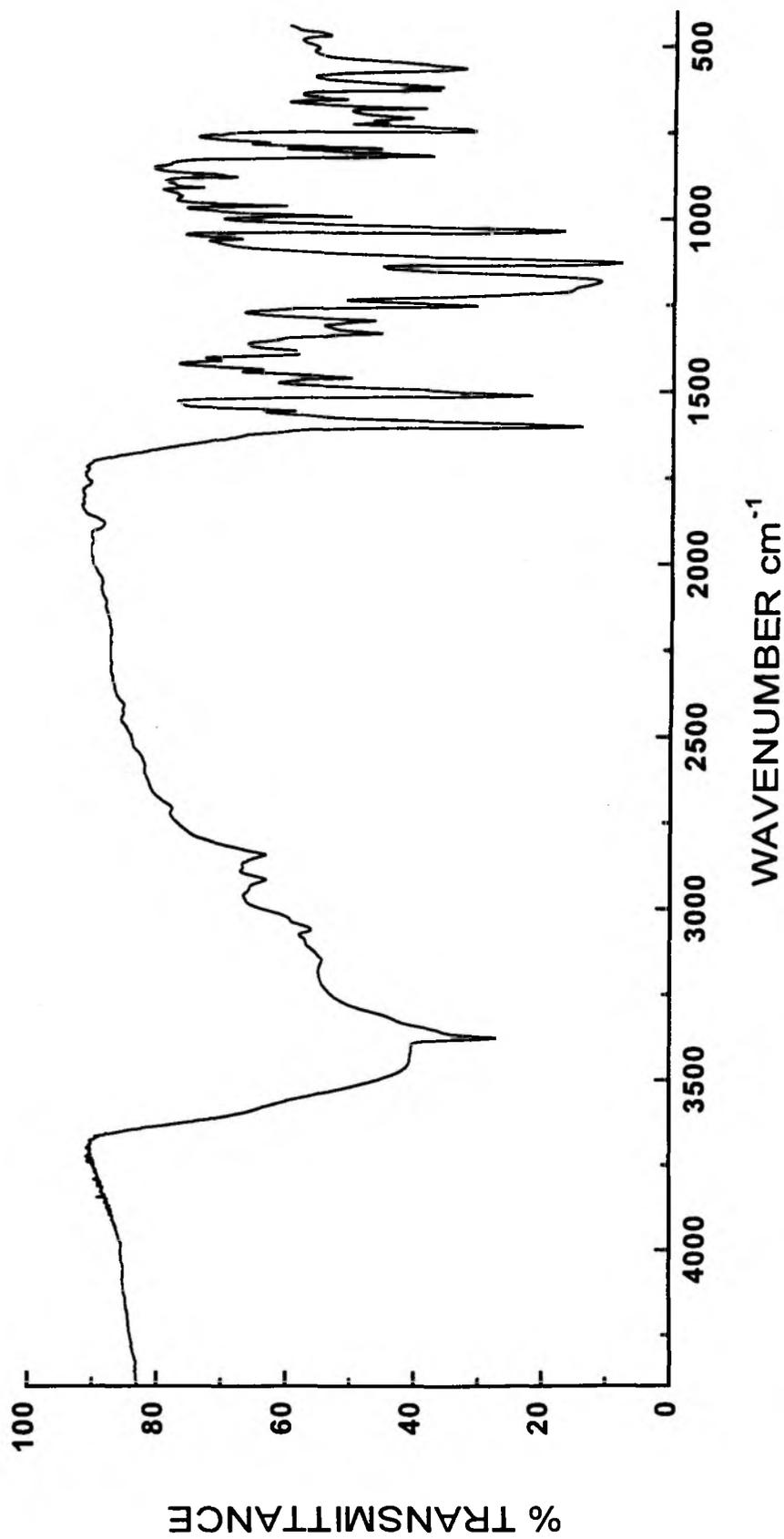


Figure 8.4 FT-IR spectrum of 4'-[3-(2H-Benzotriazole-2-yl)-4-hydroxybenzyl]aminophenyl sulfonic acid

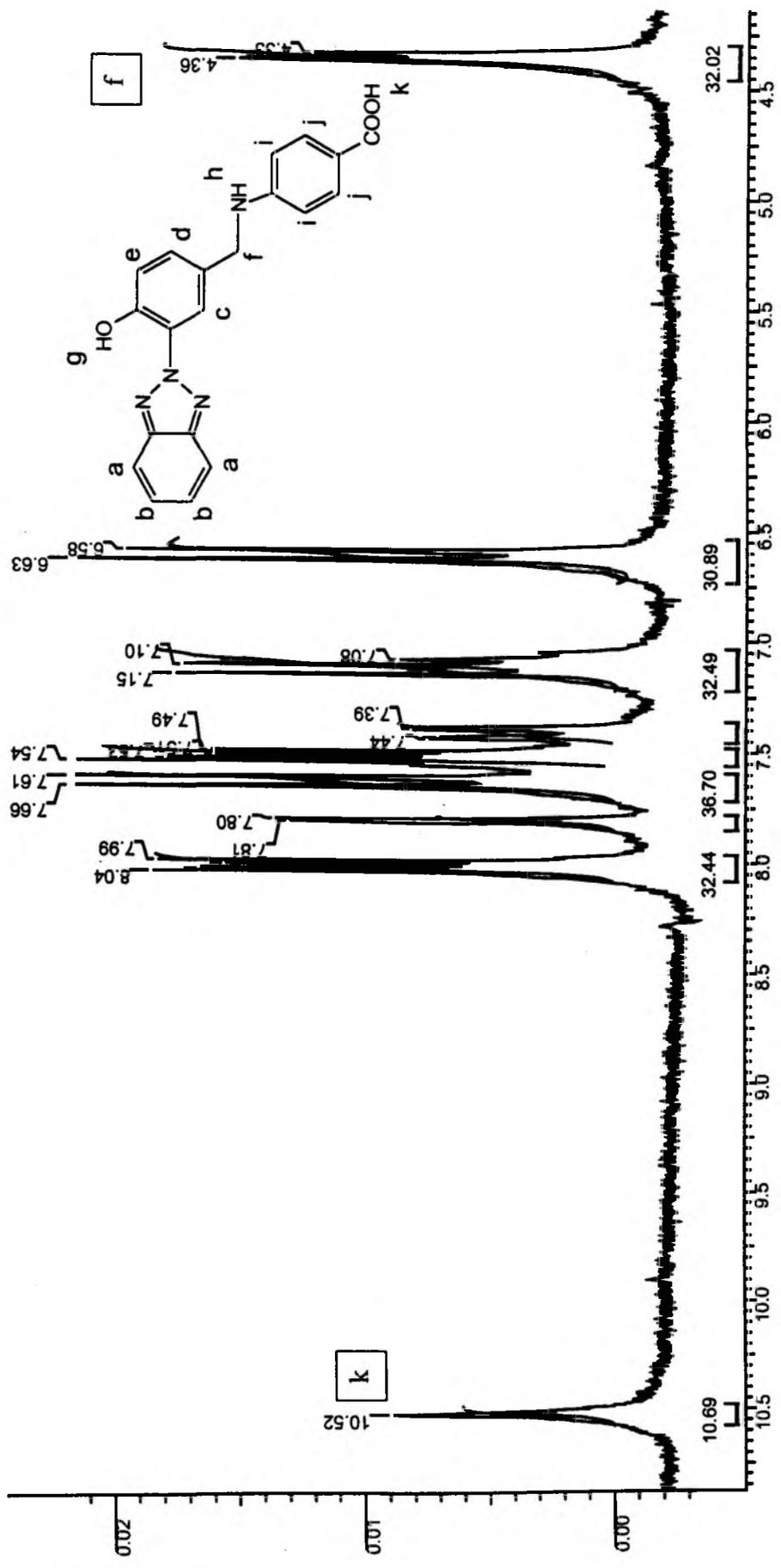


Figure 8.5.a ¹H-NMR spectrum of 4'-[3-(2H-Benzotriazole-2-yl)-4-hydroxybenzyl]aminobenzoic acid

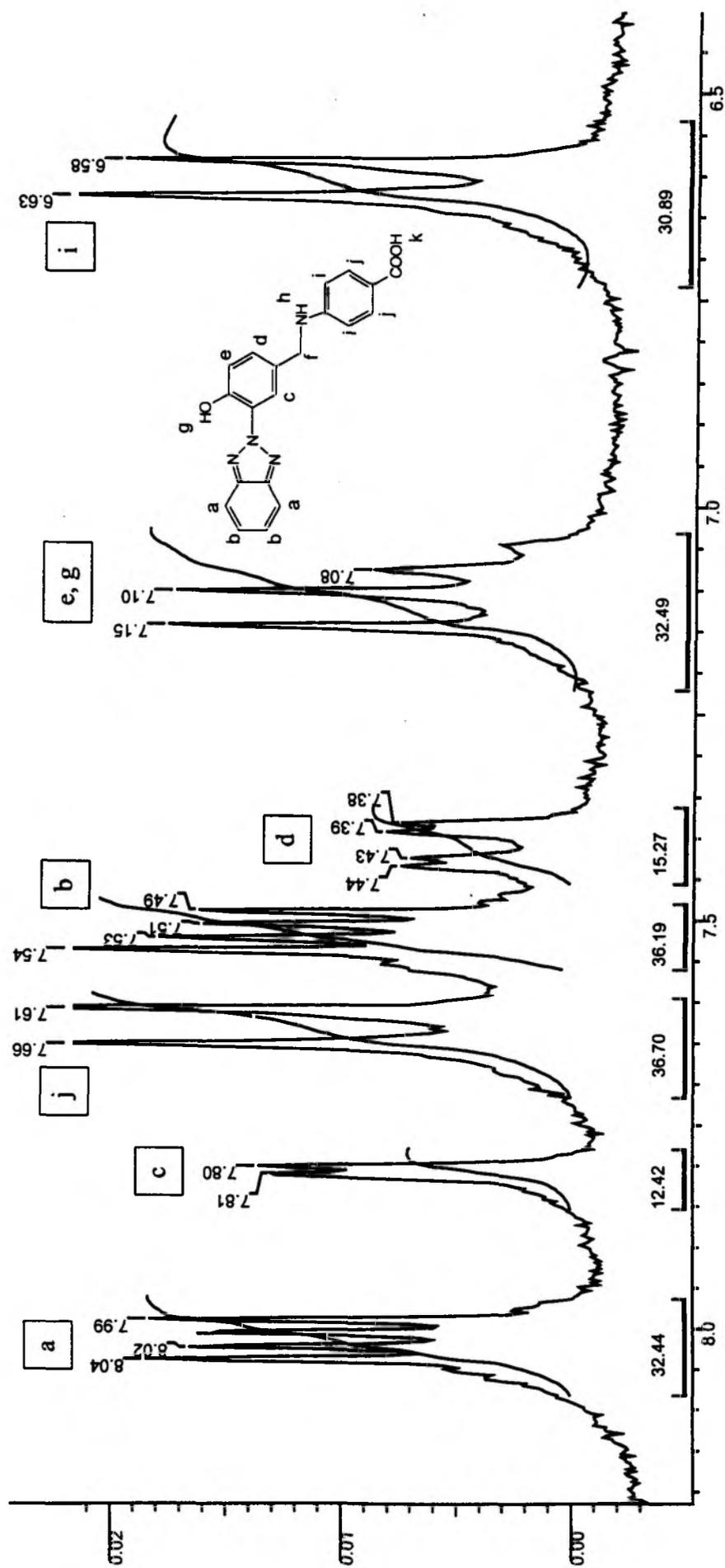


Figure 8.5.b ¹H-NMR spectrum of 4'-[3-(2H-Benzotriazole-2-yl)-4-hydroxybenzyl]aminobenzoic acid (expanded arom. region)

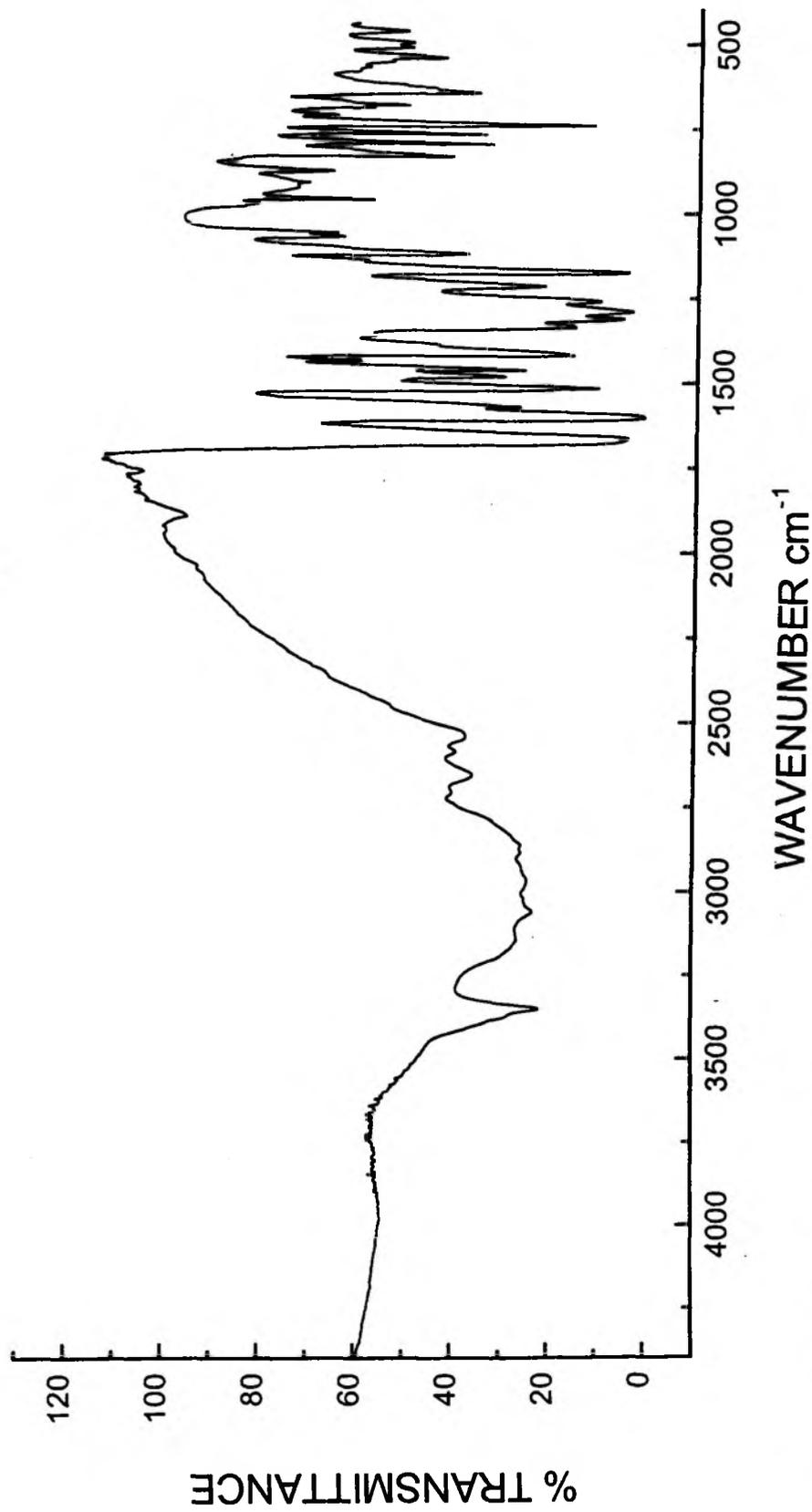


Figure 8.6 FT-IR spectrum of 4'-[3-(2H-Benzotriazole-2-yl)-4-hydroxybenzyl]aminobenzoic acid

At this concentration, it does not follow the Lambert-beer's law and calibration curve of standard concentration versus absorption could not be made hence the data for uptake measurements could not be obtained. Thus, in the present report we have evaluated the stabilizing effect of only 4'-[3-(2*H*-Benzotriazole-2-yl)-4-hydroxybenzyl]aminophenyl sulfonic acid.

4'-[3-(2*H*-Benzotriazole-2-yl)-4-hydroxybenzyl]aminophenyl sulfonic acid uptake for samples **A** and **B** was 1.7% w/w and 1.3% w/w, respectively. Samples with and without UV absorber were dyed separately and dye uptake for all the samples was 0.43% w/w.

8.3 Results and Discussion

8.3.1 Effect of water-soluble UV absorber on photostability of nylon 66

In present study, we have used two different water-soluble UV absorber concentrations in nylon 66; 1.7% (**A**) and 1.3% (**B**) and their effectiveness as photostabilizers was evaluated. *Figure 8.7* shows that with increasing UV absorber concentration the photostability of nylon 66 was improved. After 213 h of

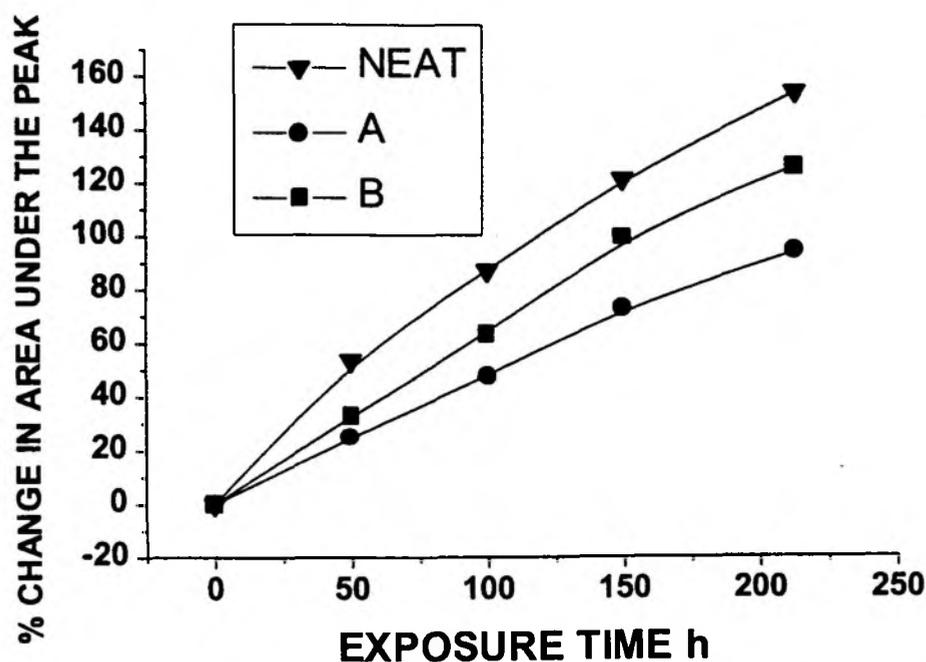


Figure 8.7 Effect of water-soluble UV absorber on photostability of nylon 66

Photoirradiation, the sample A showed increased stability by factor 1.6 and sample B showed the increase in photostability by factor 1.2 as compared to the neat samples. These factors are in correlation with the concentrations of UV absorber present in the polymer.

8.3.2 Photostabilization of dyed nylon 66 with water-soluble UV absorber

Nylon 66 containing 1.7% w/w water-soluble UV absorber was dyed with 0.43% w/w and the photostability of these samples was studied. Samples containing dye as well as UV absorber were found more stable as compared to samples containing only UV absorber (Figure 8.8). Samples with dye and UV absorber gave the stability with factor 2 whereas the samples with only UV absorber gave stability with factor 1.6 as compared to the neat samples.

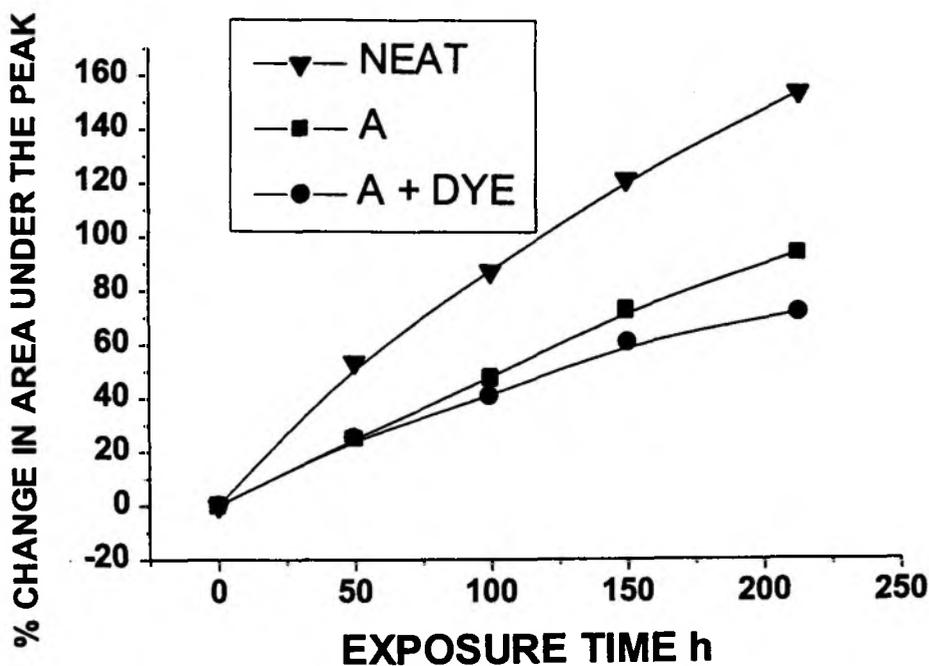


Figure 8.8 Effect of dye on photostabilizing effect of water-soluble UV absorber

Figure 8.9 shows the photostabilization of nylon 66 in presence of two different concentrations A (1.7% w/w) and B (1.3% w/w) of UV absorber and a constant concentration of dye 0.43% w/w. Here in this case also the samples with 1.7% w/w UV absorber concentration showed the maximum stability. Samples with 0.43% w/w dye and 1.7% w/w UV absorber showed the improvement in the photostability with factor 2 whereas the samples with 0.43% w/w dye and 1.3% w/w UV absorber showed the improvement in photostability with factor 1.6.

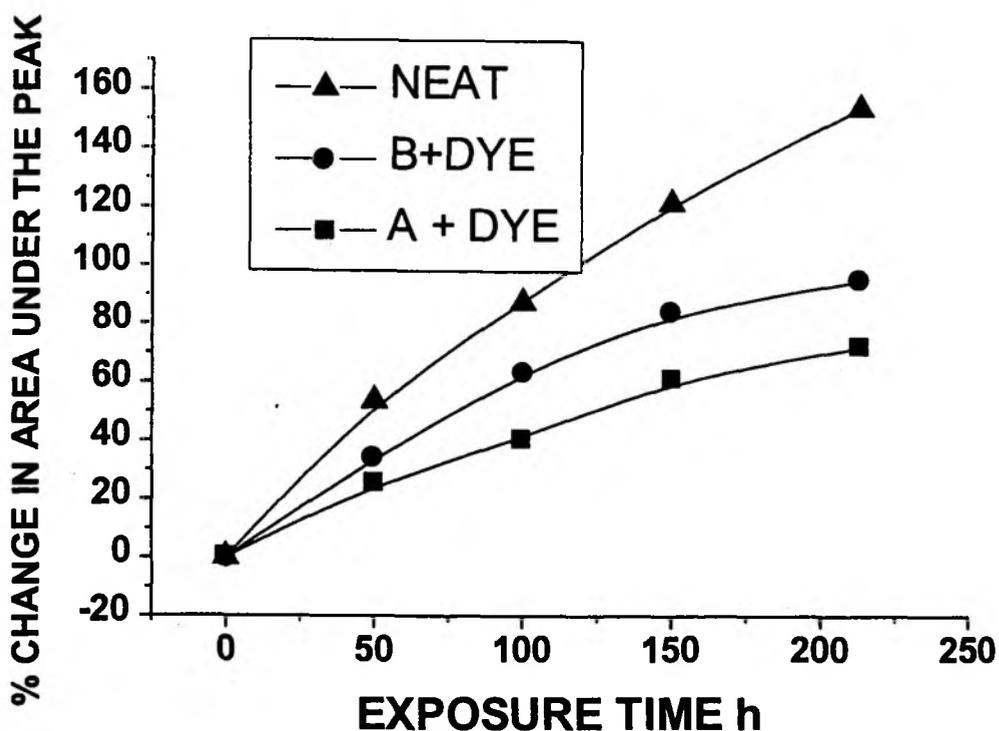


Figure 8.9 Photostabilization of nylon 66 with water-soluble UV absorber in presence of dye

8.3.3 Fading of the dye in the presence of water-soluble UV absorber

Water-soluble UV absorber was absorbed by the nylon 66 in two different concentration 1.7% w/w and 1.3% w/w after that these samples were treated with the aqueous solution of dye. Amount of dye absorbed onto the nylon 66 was calculated to be the 0.43% w/w.

Fading of dye was determined by monitoring the loss in UV-visible absorption at different time intervals during the photoirradiation. Figure 8.10.a and b show the decrease in UV-visible absorption with irradiation time for the samples with dye and

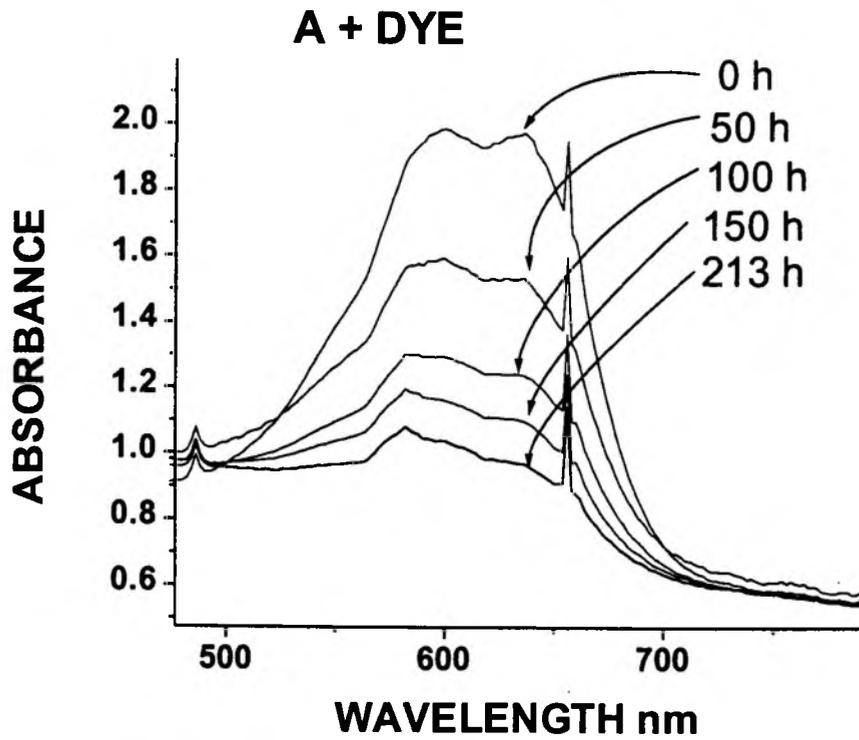


Figure 8.10.a Change in UV-visible absorption spectra with irradiation time for the samples containing 1.7% w/w water-soluble UV absorber and 0.43% w/w dye.

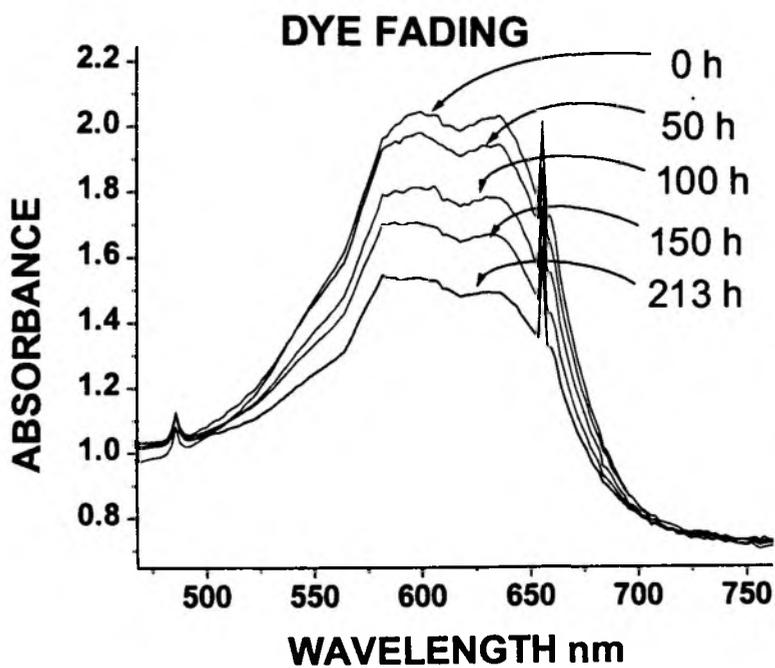


Figure 8.10.b Change in UV-visible absorption spectra of nylon 66 dyed with 0.43% w/w dye

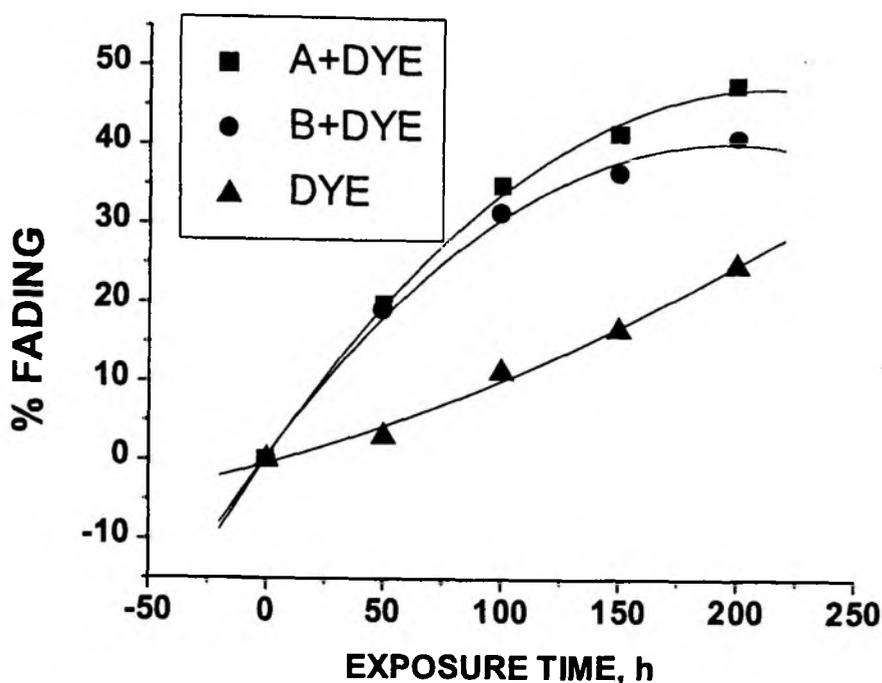


Figure 8.11 Effect of water-soluble UV absorber on fading behavior of dye in nylon 66

UV absorber and samples containing only dye. *Figure 8.11* shows the fading behavior of these samples; samples containing 1.7% w/w UV absorber and 0.43% w/w dye (A + dye), samples containing 1.3% w/w of UV absorber and 0.43% w/w of dye (B + dye) and samples with only 0.43% w/w of dye. This figure also shows that the samples containing UV absorber exhibited enhanced fading. As the concentration of UV absorber is increased the fading also gets increased. Samples with 1.7% w/w UV absorber and 0.43% w/w dye showed the enhancement in fading with factor 2 whereas the samples with 1.3% w/w UV absorber and 0.43% w/w dye with factor 1.7 as compared to samples containing only 0.43% w/w dye.

This clearly indicates that water-soluble UV absorber shows the antagonistic effect on lightfastness of anthraquinone acid blue dyes. Rich and Crews²⁰ also observed the similar effect for nylon 66 dyed with various anthraquinone acid dyes and treated the dye samples with a number of water-soluble/dispersible UV absorbers. The same authors also observed that almost all the UV absorbers had detrimental effect on lightfastness of all dye/shades combinations. However, some UV absorber-dye/shade combinations gave beneficial effects. Thus, the general recommendation can not be made regarding the UV absorber used for preventing the photofading of

dye polymers. Some of the water-soluble UV absorbers are more effective on reducing/fading on lighter shades than on darker shades. Our results also indicate that after certain degree of fading the dyed samples containing water-soluble UV absorber showed no significant fading on further photoirradiation after 150 h. Samples containing only dye showed that the fading was less during the initial period of photoirradiation but it increased more rapidly as photoirradiation progressed.

Although the samples containing UV absorber showed the enhanced photofading after 213 h of photoirradiation, the further photoirradiation should have been carried out to see the fading when the dyes would have been in lighter shades.

Ghiggino *et al.*³⁰ examined the photophysical behavior of a water-soluble UV absorber 2-(2'-hydroxy-5'-methylphenyl)benzotriazole sulfonate. They observed that excitation is due to nonplanar form of UV absorber in acetonitrile whereas in aqueous solution UV absorber was found to be in the planar form. The absorption and emission behavior of this water-soluble UV absorber molecule in hydrogen bonding polymer substrates was also studied. A significant proportion of the molecules adopted a nonplanar conformation in which excited state intramolecular proton transfer (ESIPT) did not occur. ESIPT is the process by which the excited and UV absorber molecules dissipate the harmful incident UV energy into less harmful IR energy.

Similarly, in our case also the hydrogen bonding nature of substrate could be responsible for the ineffectiveness of water-soluble UV absorber in preventing the fading of dye molecule. Water-soluble UV absorbers were absorbed in nylon 66 matrix by diffusion processes. In such kind of case, polymer-UV absorber interaction will be considerably higher and this interaction could be responsible for the inefficient ESIPT. In case of nonpolar UV absorber, the UV absorbers may exist in the form of small aggregates even in polar polymers like nylon 66. In such cases the UV absorber molecules on the surface of aggregates are only available for hydrogen bonding with the substrate. Rest of the molecules can effectively participate in converting high energy UV radiation into less harmful forms of energy.

8.4 Conclusions

Water-soluble UV absorber with sulfonic acid moiety is water-soluble even at neutral pH and can be easily applied into the polyamide substrate. However, the UV absorber with carboxylic acid group is having limited diffusivity in polyamide substrate and is water insoluble in its acid form.

UV absorber with sulfonic acid group showed the considerable photostabilizing effect on the nylon 66 substrate. However, the effect is not comparable with nonpolar UV absorbers applied by melt mixing to the polymers. Polyamide containing water-soluble UV absorber showed poor lightfastness when they are dyed with anthraquinone acid blue dyes. This could be due to the increase interaction of UV absorber with polar polyamide substrate. Thus the more dispersed form of UV absorber is having detrimental effect on its efficiency to photostabilize the polymer and colour.

In the present study, we could develop a new route for the functionalization of existing UV absorbers, which can be used to make many other tailor-made UV absorbers. Although, the UV absorbers are synthesized in present work did not show convincing properties on dyed polyamide they can be proved better on aqueous emulsions of nonpolar polymers.

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CHAPTER IX

SUMMARY AND CONCLUSIONS

Degradation studies of nylon 66

Photo-oxidation of nylon 66 was found to be controlled by processing history and morphology of the samples. The presence of hydroxy/hydroperoxide groups in melt processed film was detected in quite a higher concentration and according to us that is the main driving force for the higher rate of photo-oxidation during the initial period of exposure. The continuous increase in carbonyl group concentration concludes the existence of a single photo-oxidation mechanism through out the oxidation process. We also confirmed that primary photo-oxidation process in polyamide is the oxidation of methylene group in the vicinity of the $-NH-$ group. FT-IR assisted us to study the physical changes in polymer matrix like disappearance of amorphous phase with exposure time which is the main evidence for effectiveness of photo-oxidation in amorphous phase. This preliminary observation led us to study, in more details, the change in the polymer morphology. UV absorption study suggested that the increase in UV absorption at ~ 244 nm is due to the imide formation.

Morphological changes in photodegraded nylon 66 are rather complicated. DSC results showed loss in existing crystalline morphology, which was not indicated by XRD results. We assume a possibility of reorganization of crystalline morphology while heating of sample during DSC analysis, whereas XRD studies were carried out at room temperature and hence show the actual morphology existing in sample. This fact is to be confirmed by more detailed study. Higher temperature XRD studies may help to prove this particular phenomenon. SEM results showed that photo-oxidative processes were localized to some portion at the surface during the initial period of photo-exposure and later on it spread out to entire surface. Prevalence of photo-oxidative processes in amorphous phase was also indicated. Chemi-crystallization was one of the important phenomena observed during the photo-exposure, which gave rise to the formation of distinct morphologies at the polymer surface.

Thermal oxidative degradation study is also equally important for detailed understanding of photo-oxidative mechanism in nylon 66 as it influences the oxidation mechanism during the photoirradiation of nylon 66. FT-IR and UV spectroscopy are identified very good techniques to characterize and monitor the thermal oxidative degradation in nylon 66. Thermal oxidative degradation in nylon 66 was increased with increasing aging time and temperature. We observed that thermal oxidative degradation in nylon 66 followed two different oxidative mechanisms depending on aging temperature. At lower aging temperature oxidation products are mainly imide

species while at higher aging temperature along with the formation of imide species, formation of unsaturated species was observed.

The prime objective of the present study was to examine the photochemical behavior of anthraquinone acid blue dyes on nylon 66. We could accomplish our goal by giving the fundamental understanding of the photochemical processes prevailing during the photoirradiation of nylon dyed at a series of pH. We observed a peculiar effect of dyebath pH on the photostability of dyed nylon 66. Much lower dyebath pH has adverse effect on the photostability of dyed nylon 66. Dyed samples were more stable when they are dyed at or above pH 3 (up to 7) whereas, the samples dyed at pH < 3.0 showed sensitized photo-oxidative degradation in nylon 66. Formation of quaternary ammonium salt on dye-chromophore was considered as responsible for the pH-controlled behavior of anthraquinone acid dyes. Proposed hypothesis for the photosensitizing behavior of anthraquinone acid dyes at lower dyebath pH can be affirmed by studying the excitation behavior of nylon 66 samples dyed at different pH. Photofading behavior of dyed samples showed significant effect of dyeing pH. Effect of dyebath pH, on photofading of dyed samples, is more pronounced at lower dyeing pH and prevails up to pH 4. Hydronium ions concentration was considered to be responsible for the enhanced fading of dye for the samples dyed at the lower pH.

Photostabilization of nylon 66

In an empirical study we examined two different class of photostabilizers on nylon 66 to prevent photo-oxidation of polymer and colour fading of a dye. Dye, UV absorber and HALS are observed to impart photostability to nylon 66. UV absorber and HALS showed the greater photostability at higher loading whereas in case of dye, the 0.2 % was observed as the optimum concentration and beyond that its photostabilizing efficiency is deteriorated. Fading of dye was increased with increasing dye concentration and this might be due to the poor lightfastness of dye aggregates in nylon 66. UV absorber imparted higher lightfastness to the dye as compared to HALS. UV absorber also found to be vanished with exposure time. Decomposition of UV absorber is fast when it is added in a smaller quantity. Thus, the UV absorber itself is more stable when it is in an aggregated form.

Substitution on pendant phenyl ring of anthraquinone acid blue dyes had no effect on photostabilizing of efficiency of these dyes. However, if the dye is made compatible and more dispersed in nylon 66 by placing some polar substituents on pendant phenyl ring, the lightfastness of the dye can be improved.

Finally, we made an attempt to functionalize a commercial UV absorber to make it water-soluble so that it can be easily absorbed by nylon 66 upon treating the nylon samples with the aqueous solution of the UV absorber. We observed that water-soluble UV absorber with sulfonic acid moiety was water-soluble even at neutral pH and could be easily applied onto the polyamide substrate. However, the UV absorber with carboxylic acid group was having limited diffusivity in polyamide substrate and was water insoluble in its acid form. UV absorber with sulfonic acid group showed the considerable photostabilizing effect on the nylon 66 substrate. However, the effect was not comparable with nonpolar UV absorbers applied by melt mixing to the polymers. Polyamide containing water-soluble UV absorber showed poor lightfastness when they were dyed with anthraquinone acid blue dyes. This could be due to the increase interaction of UV absorber with polar polyamide substrate. Thus, the more dispersed form of UV absorber had shown the detrimental effect on its efficiency to photostabilize the polymer and colour.

Scope of the future work

The end of my thesis starts with a great scope for the future work. Although the photo-oxidation in nylon 66 was well characterized in present study, the morphological changes in photoirradiated nylon 66 have to be characterized in depth to affirm the hypothesis we have given.

The effect of dyebath pH on photochemical behavior of anthraquinone acid blue dyes can be examined in details with the help of excitation characteristics at different pH. This can enable us to design many more dyes which will not be sensitive to the dyebath pH.

Our route to synthesize water-soluble UV absorbers gave a vital intermediate, which can be used to synthesize many more tailor-made UV absorbers useful for polymers as well as cosmetics. Detrimental effect of water-soluble UV absorbers on lightfastness of dyed nylon 66 is needed to be understood thoroughly which will help to design and synthesize more efficient UV absorbers.

SYNOPSIS

absorbers were found to be more photostable and also their colour-fastness was increased.

Thus there are lot of opportunities and challenges for photostabilization of coloured polyamides. Many water-soluble UV absorbers are available commercially, but still there is interest in new efficient products.

Objectives of present investigation

The principal objectives of the present investigations are:

1. To characterize photo-oxidation in nylon 66.
2. To study effect of aging temperature on thermal oxidative behavior of nylon 66.
3. To prevent sensitized photo-oxidation in nylon 66 caused by anthraquinone acid blue dyes.
4. To prevent photofading of anthraquinone acid blue dyes in nylon 66 substrate.

Out line of the thesis

CHAPTER I

This introductory chapter deals with a discussion of various kinds of degradation. Thermal and photodegradation in polyamides is discussed in detail. General mechanism for all kinds of photostabilization as well as various types of stabilization for polyamides is also widely discussed.

CHAPTER II

Principal objectives and scopes of present work are discussed in this chapter.

CHAPTER III

This chapter deals with characterization of photo-oxidation in nylon 66. FT-IR and UV spectroscopic techniques were used for characterization. FT-IR spectroscopy gave idea about formation of imide and other carbonyl species. Decrease in the amorphous and methylene (vicinal to -NH-) peak intensities was also studied by FT-IR spectroscopy. UV spectroscopy also showed the formation of imide groups upon photo-oxidation. A mechanism for photo-oxidation is also suggested.

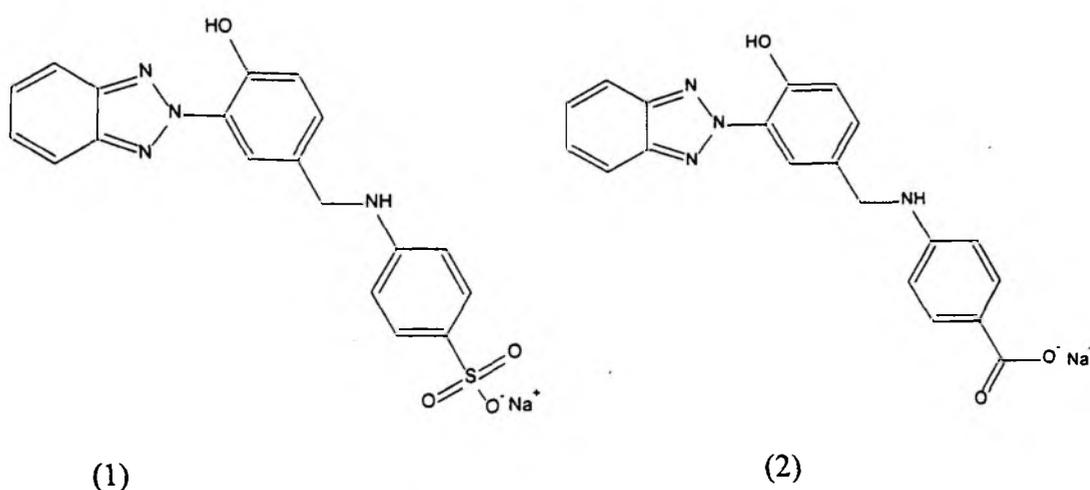
CHAPTER IV

CHAPTER VII

In this chapter, photo-oxidation of nylon 66 was studied in presence of various combination of HALS (Hindered Amine Light Stabilizer), UV absorber and dye. Dye used was C. I. Acid Blue 25, HALS was 2,2,6,6, tetramethyl 4-hydroxy piperidine and Tinuvin 326 [2(2'-Hydroxy-3'-t-butyl-5'-methylphenyl)-5-chorobenzotriazole] All three were melt-blended with nylon 66, individually, dye 0.1, 0.2, 0.5% w/w, HALS 0.2, 0.5, 1.0% w/w and UV absorber 0.2, 0.5, 1.0% w/w. In order to study the photostabilization effect of these two stabilizers in presence of dye, two combinations were made maintaining, HALS and UV absorber concentration constant at 0.5% w/w and varying dye concentration from 0.1 to 0.5% w/w. Photo-oxidation study showed that samples with HALS were more stable than with UV absorber. However, UV absorber imparted more colour stability as compared to HALS. Dye was also found to stabilize substrate against photo-oxidation.

CHAPTER VIII

Synthesis of novel water-soluble UV absorbers and their effectiveness in nylon 66 substrate is described in this chapter. Novel water-soluble UV absorbers with following chemical structures were synthesized and used in the form of aqueous solution.



Nylon samples were treated in a bath containing aqueous solution of these UV absorbers. Their effectiveness as photostabilizer for substrate and dye was studied.

CHAPTER IX

This chapter summarizes the results and describes the remarkable conclusions of the study. Additional scopes for further research are also indicated.

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(To be communicated)
8. P. N. Thanki and R. P. Singh
Thermal Oxidative Degradation of Nylon 66: Effect of Aging Temperature
on Oxidation Mechanism
(Manuscript is under preparation)
9. P. N. Thanki and R. P. Singh
Effect of Dyeing pH on Photochemical Behavior of Anthraquinone Acid
Blue Dye on Nylon 66
(Manuscript is under preparation)