Chapter 7: Photostabilization of nylon 66 in presence acid blue 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 polymer\textsuperscript{1-6}. These impurities are reported\textsuperscript{7} 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, $\alpha$, $\beta$-unsaturated carbonyl species and unsaturated cyclopentanone\textsuperscript{8-12} 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 degradation\textsuperscript{13-16}.

Since early 60’s efforts are being made to improve the photostability of polyamide thermoplastics and fibers but many of the photostabilizers reported\textsuperscript{17-23} 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 reports\textsuperscript{24-28} 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 itself\textsuperscript{29-31}. 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 dyes\textsuperscript{32-39}.

Much of efforts have been made to stabilize nylons and many other polymers in presence of dyes using a variety of photostabilizers\textsuperscript{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
substrates. Certain tailored UV absorbers have been prepared for applications to
fibers during or after dyeing. HALS have been used for various dyes and
substrate for enhanced lightfastness and substrate stability as well.

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 recrystalized 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
recrystalized 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

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

C. I. Acid Blue 40

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 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

![Graph showing percentage change in area under the carbonyl peak with exposure time for different concentrations of Tinuvin 326.](image)

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.
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 reported\textsuperscript{27} 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 nylon 66.

![Figure 7.2](image)

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 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 studied\textsuperscript{56-63} 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) 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.

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].
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\textsuperscript{55, 64-68} indicating the improvement in photochemical stability of dyed polymer. \textit{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.

\textbf{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\textsuperscript{69, 70}, which show that dye aggregates are having more lightfastness. It was also observed\textsuperscript{27} 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)](image-url)
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.

![Fading of dye in presence of 0.5% UV absorber](image)

**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\textsuperscript{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. Woeppel\textsuperscript{63} 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 materials⁴², 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.

*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).

![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).](image-url)
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.

![Graph showing UV absorber decomposition](image)

**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
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 dyes.

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 studies 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.
7.5 References

20. Imperial Chemical Industries Ltd., Fr. 546,069 (1968).
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