

Chapter 2: Thermo-oxidative degradation in 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.

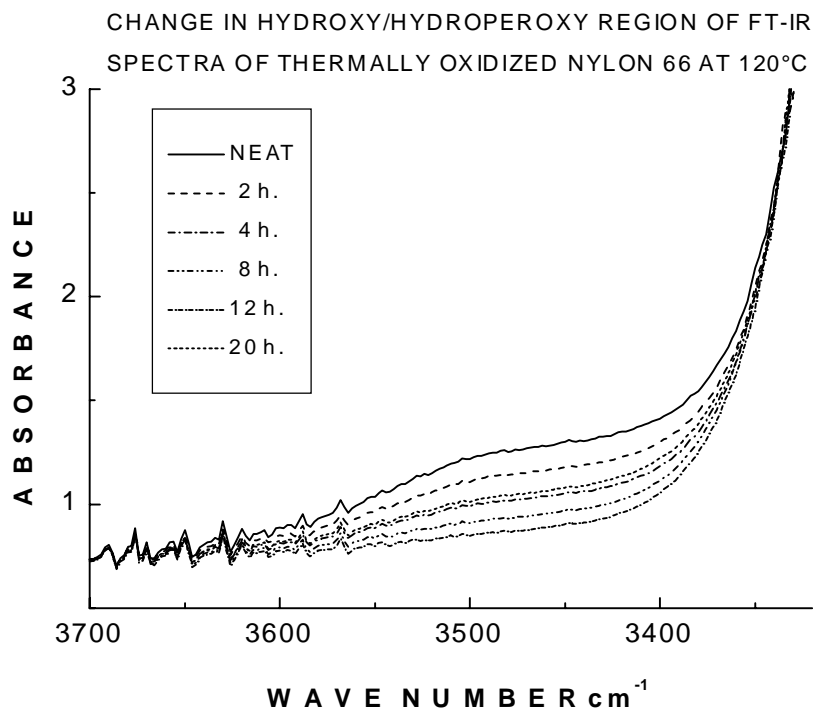


Figure 5.1.a Change in hydroxyl region of IR spectra of nylon 66 during thermal aging at 120°C

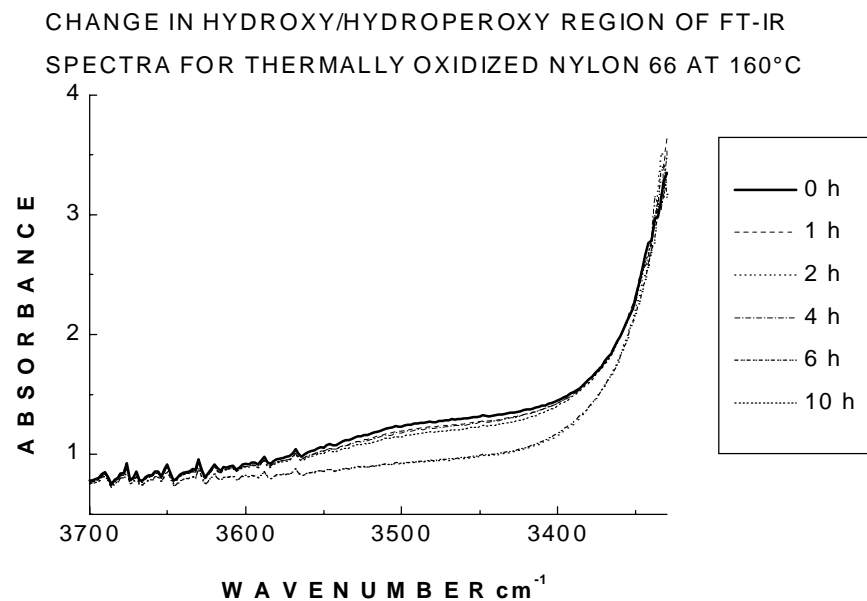


Figure 5.1.b Change in hydroxyl region of IR spectra of nylon 66 during thermal aging at 160°C

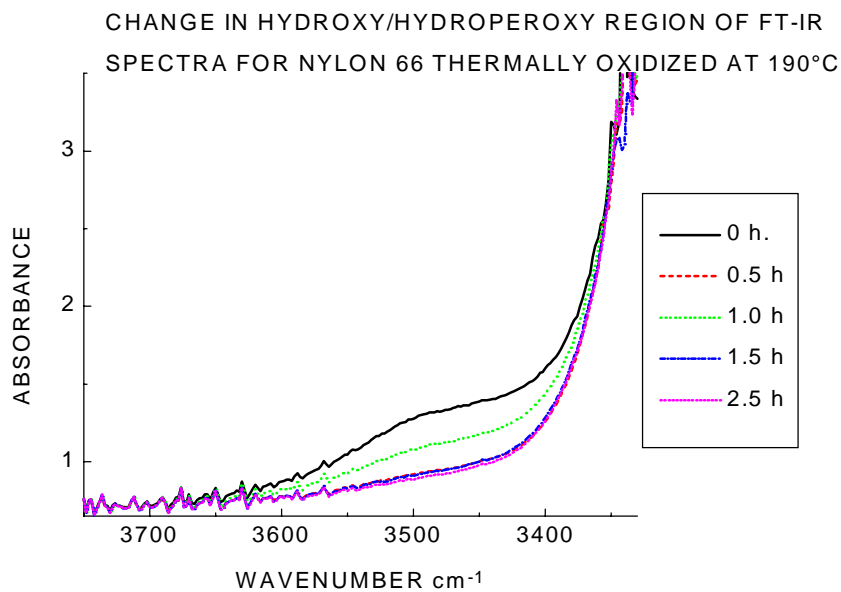


Figure 5.1.c Change in hydroxyl region of IR spectra of nylon 66 during thermal aging at 190°C

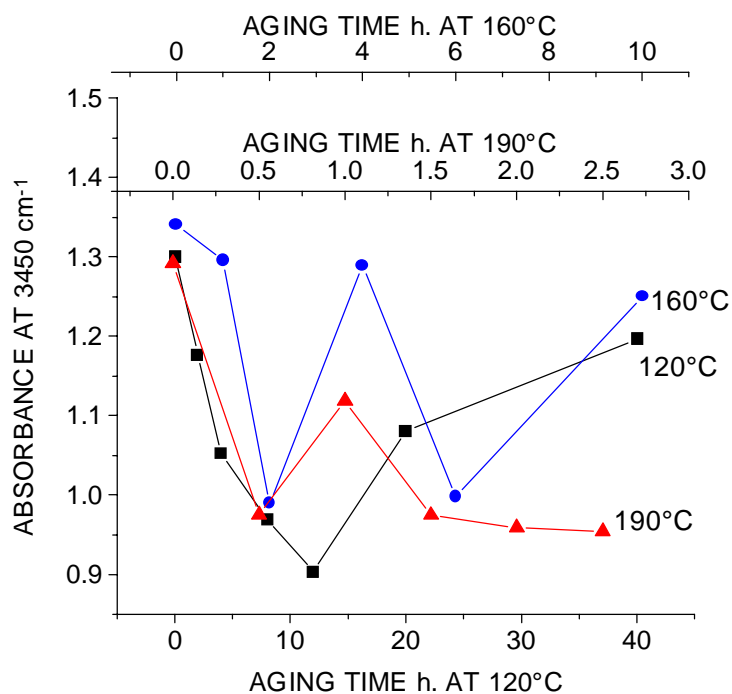


Figure 5.2. Change in hydroxyl peak absorption of nylon 66 with aging time at 120, 160 and 190°C

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 broaden 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.

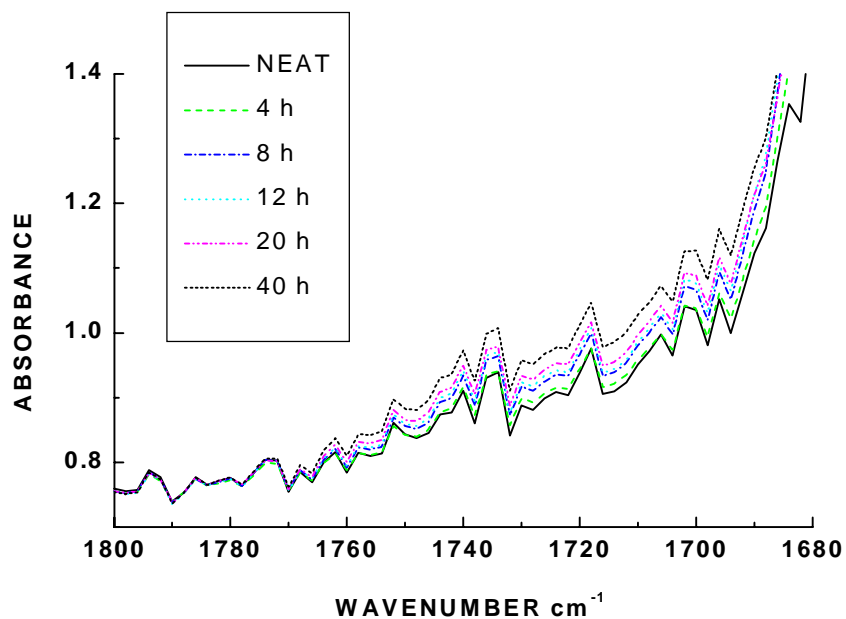


Figure 5.3.a Change in carbonyl region of IR spectra of nylon 66 during thermal aging at 120°C

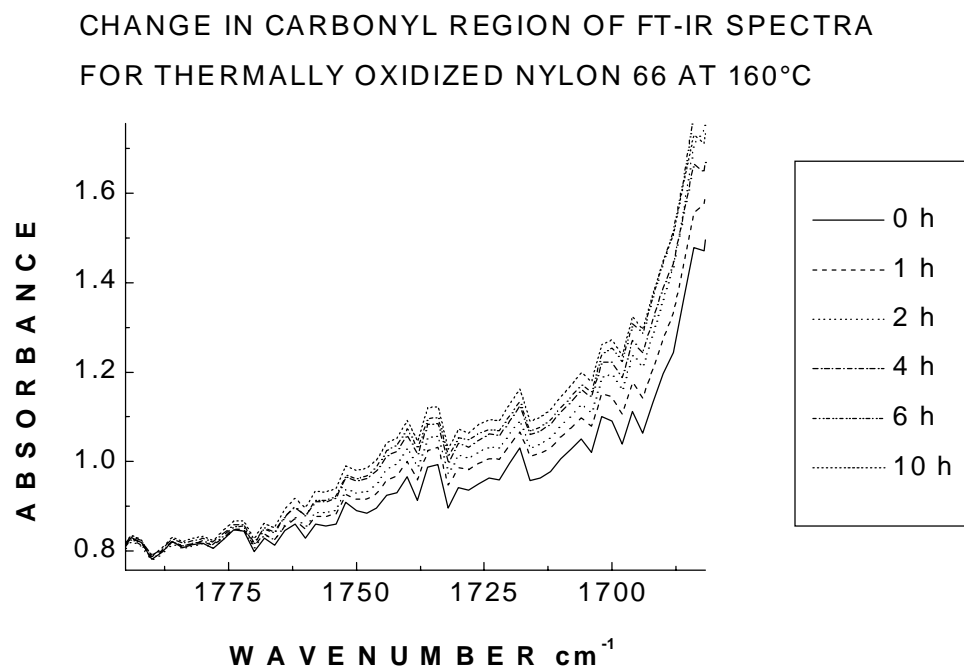


Figure 5.3.b Change in carbonyl region of IR spectra of nylon 66 during thermal aging at 160°C

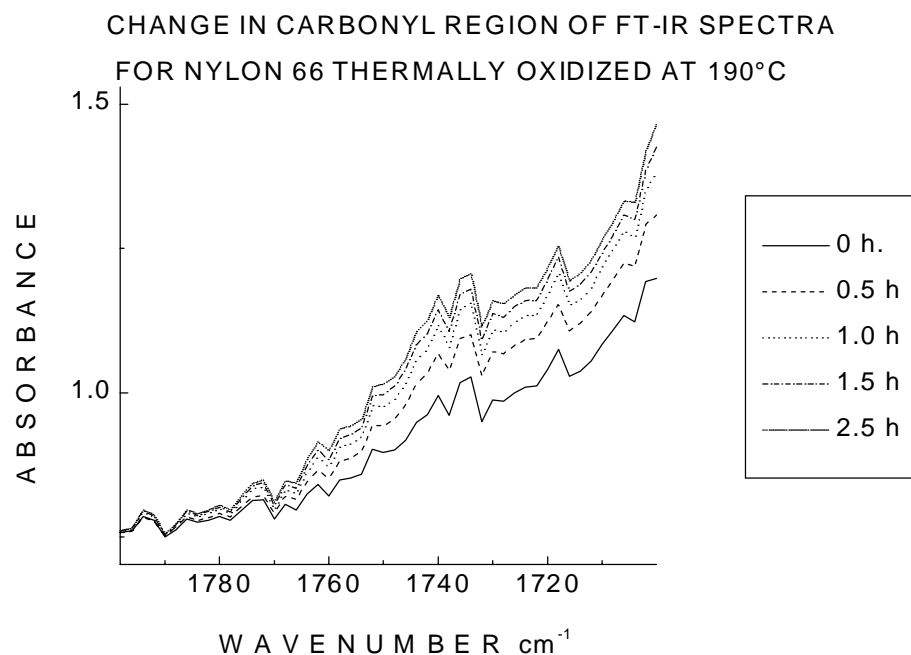


Figure 5.3.c Change in carbonyl region of IR spectra of nylon 66 during thermal aging at 190°C

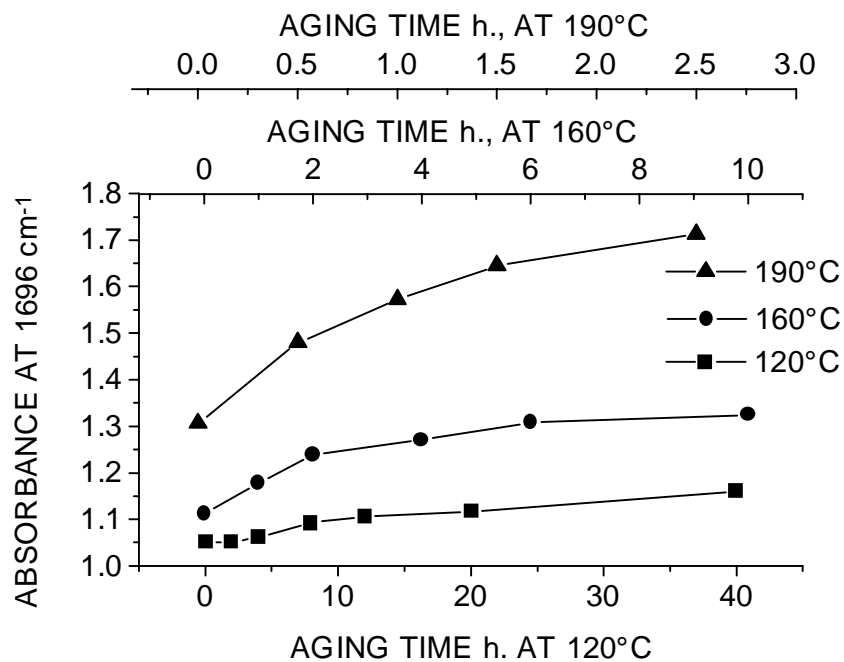


Figure 5.4 Change in carbonyl peak absorption of nylon 66 with aging time at 120, 160 and 190°C

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.

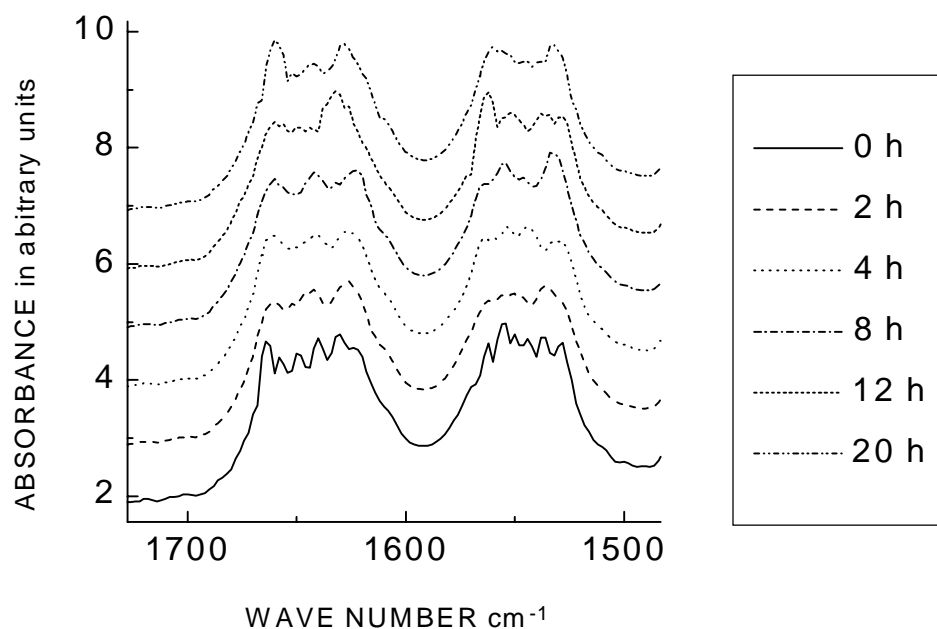


Figure 5.5.a Change in IR spectra of nylon 66 due to formation of conjugated species during thermal aging at 120°C

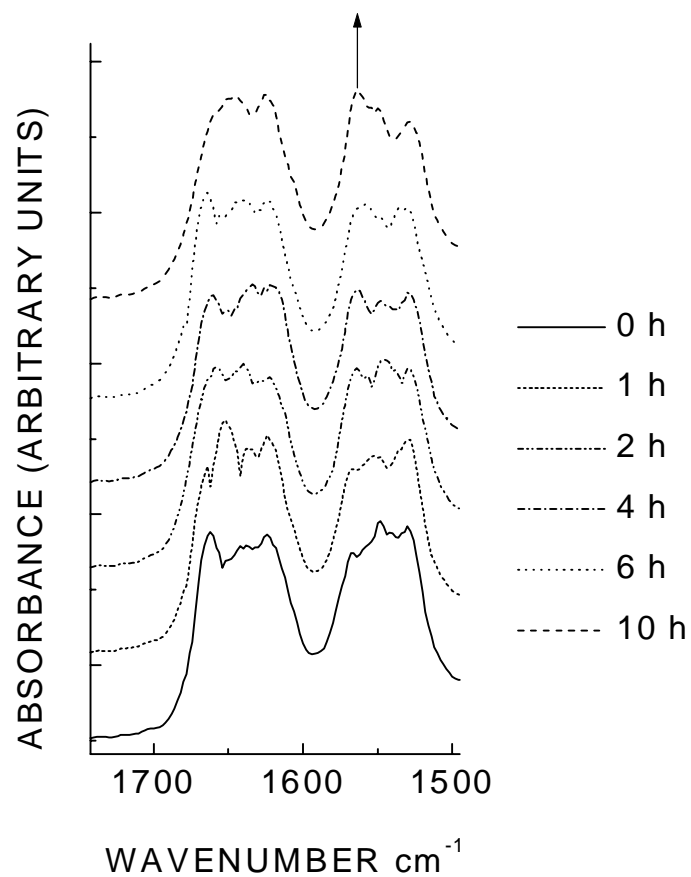


Figure 5.5.b Change in IR spectra of nylon 66 due to formation of conjugated species during thermal aging at 160°C

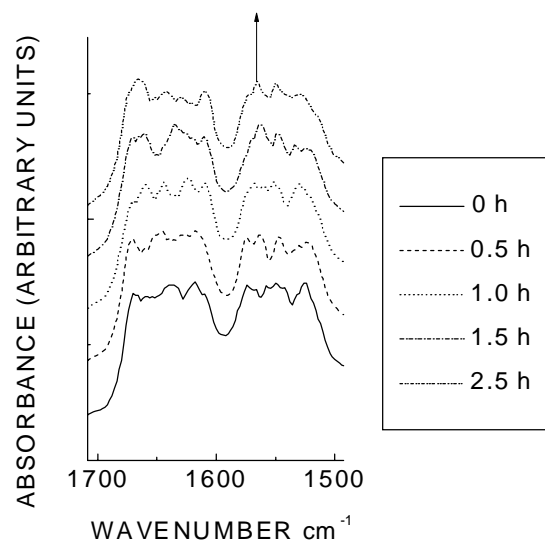


Figure 5.5.c Change in IR spectra of nylon 66 due to formation of conjugated species during thermal aging at 190°C

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.

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

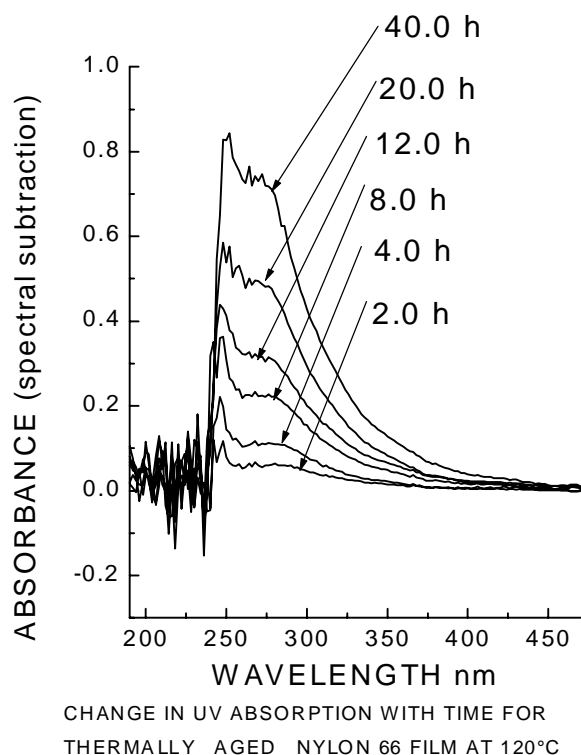


Figure 5.6.a Change in UV-visible absorption of nylon 66 during thermal aging at 120°C

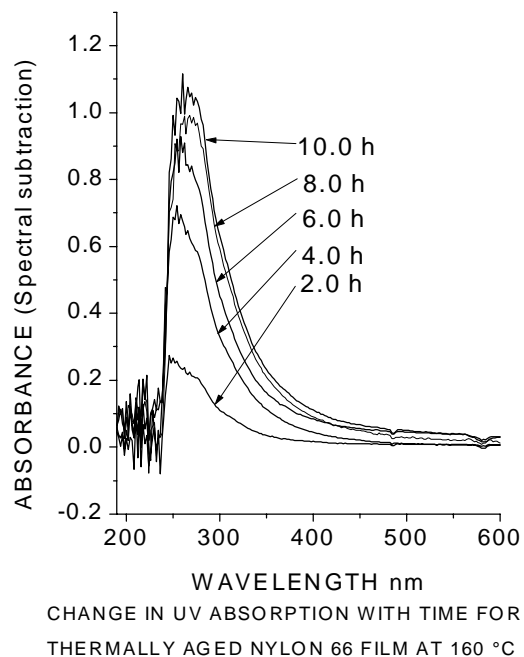


Figure 5.6.b Change in UV-visible absorption of nylon 66 during thermal aging at 160°C

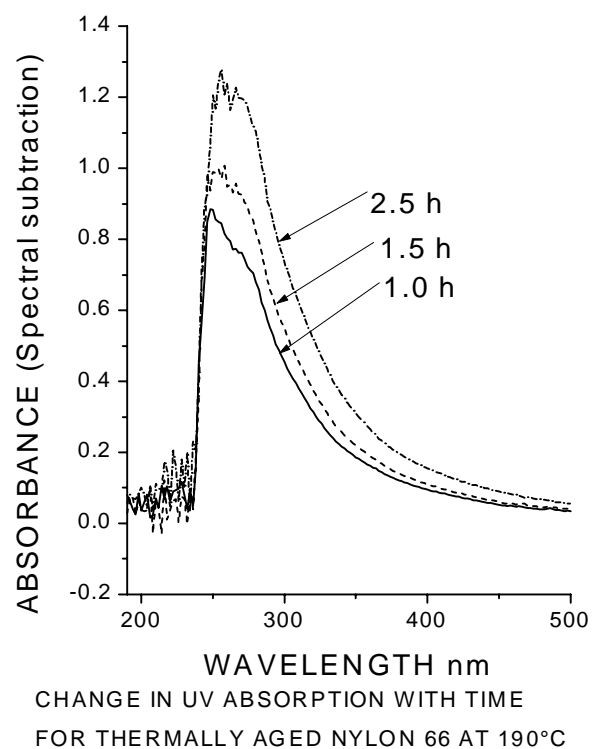
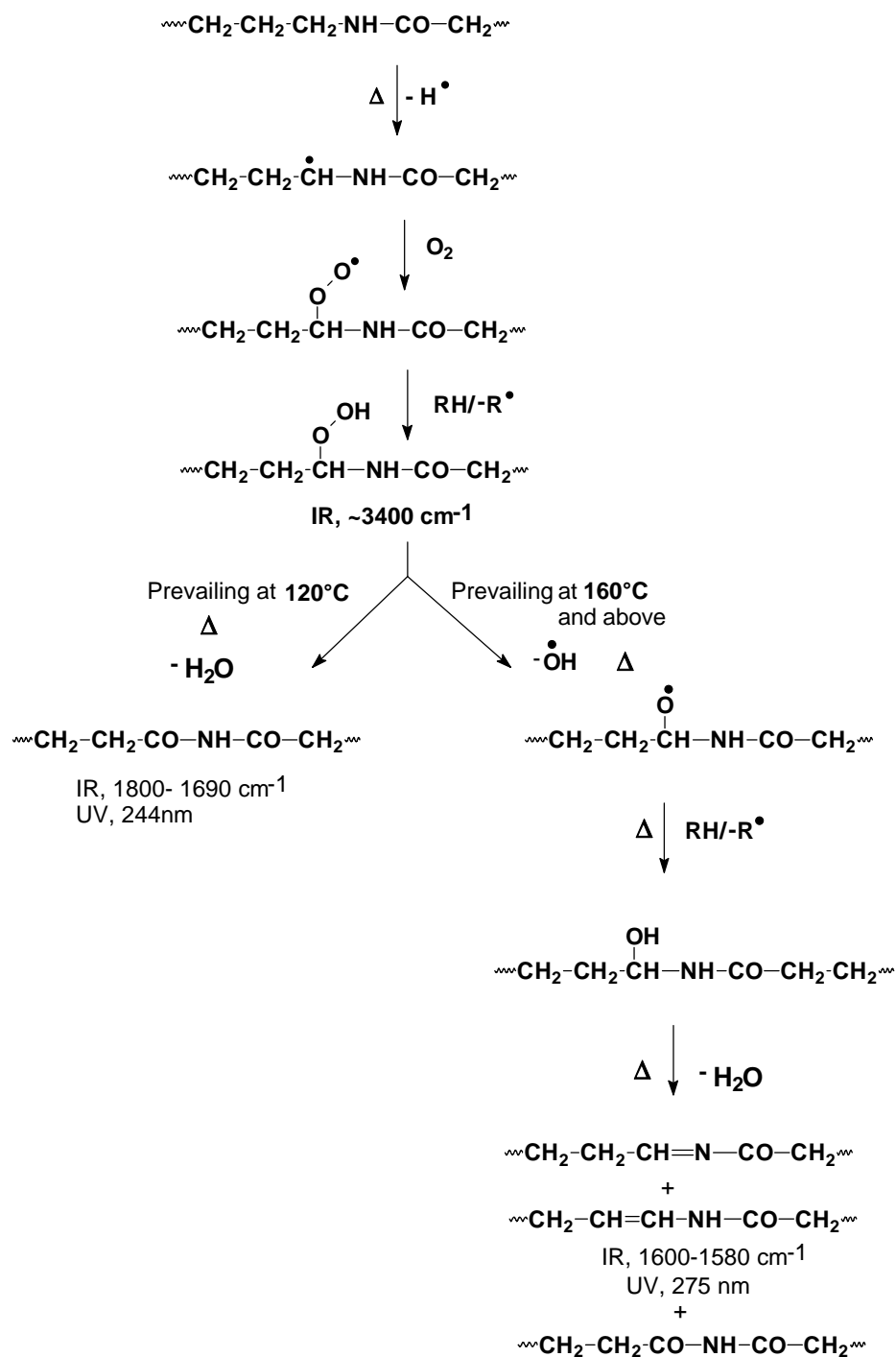


Figure 5.6.c Change in UV-visible absorption of nylon 66 during thermal aging at 190°C

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.

It is now very much clear that depending on aging temperature, two different oxidation mechanism 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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