Photodegradation of Nitrocellulose Stabilised with Diphenyl amine

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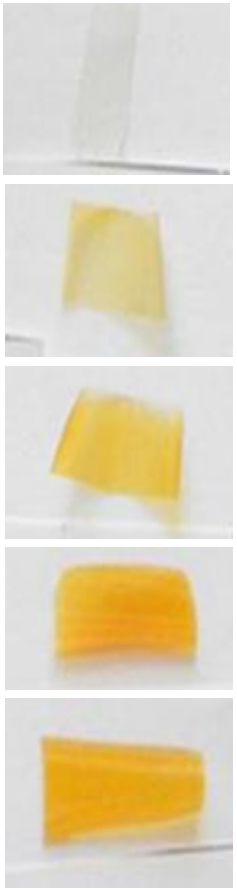
Photodegradation of NC

Research Background

- Exposure of NC to sunlight results in loss of colour and change of physical properties[1]
- More recent work on UV induced photodegradation of NC showed its effect on crystallinity[2]
  - Longer wavelength UV suggests no chain scission
  - Shorter wavelength shows chain scission



1. F. D. Miles, Cellulose Nitrate: The physical chemistry of nitrocellulose, its formation and use, Interscience Publishers, New York, 1955, 253.
2. Moniruzzaman et, Polym. Degrad. Stab. 96, 2011, 929.

Scope of Research

- Photodegradation of nitrocellulose (NC)
  - Effect of UV irradiation
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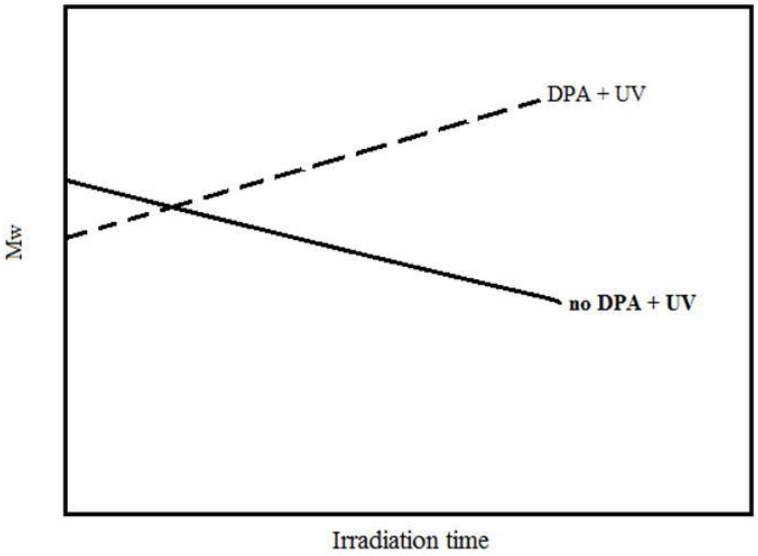
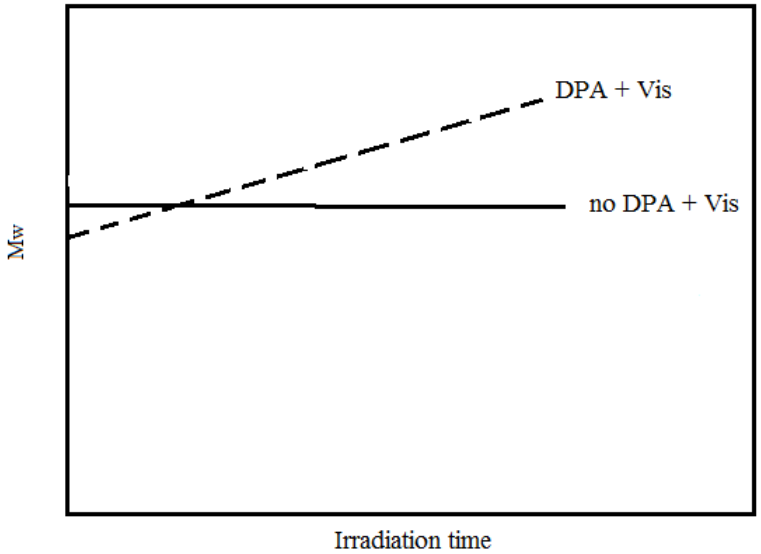




- Mechanical properties change by light
- Rate of stabiliser depletion by UV and visible light

Experimental

Preparation of NC Films

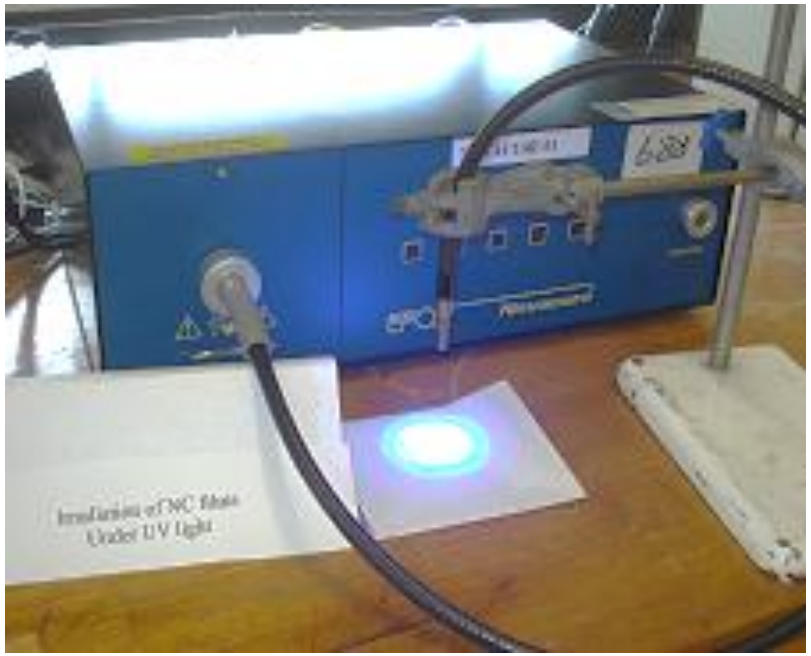
- NC (12.6% N)
  - unstabilised
  - stabilised with 5% DPA
- MEK (5% w/v) solution cast (2 ml) on microscope slides
- Dried at ambient temperature for 3 days and subsequently under vacuum at 40ºC for 3 days
- Covered with petri dish to slow down the evaporation of solvent in order to achieve good quality films

Experimental

UV/Vis Irradiation of Films

Novacure® 2100 light source

- UV filter (320-390 nm)
  - Intensity : 500 mW/cm^2
- Visible filter (400-500 nm)
  - Intensity : 3000 mW/cm^2
- Irradiation time:
  - 15, 30, 45, 60 min

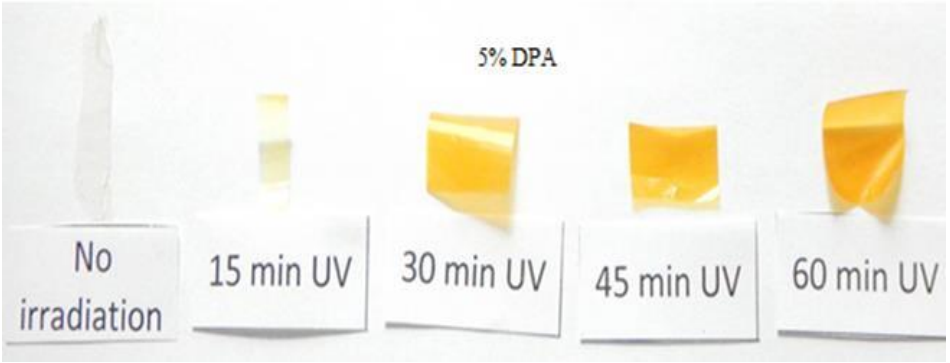


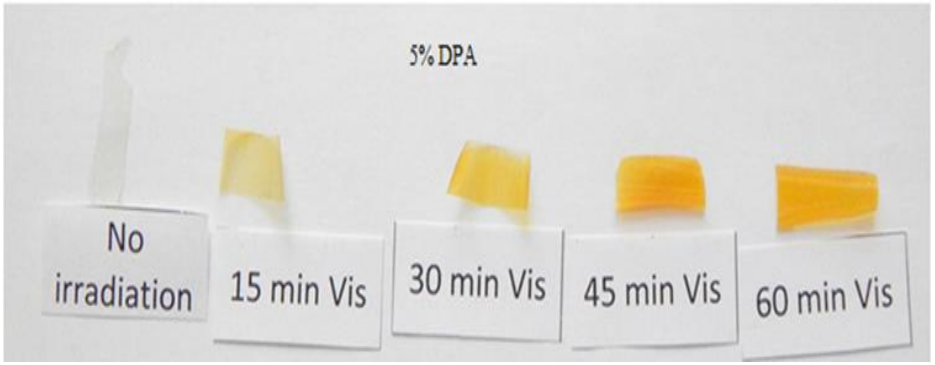
Results

Effect of UV /Vis Irradiation - Colour

- No colour change observed for unstabilised NC when exposed to UV or Vis irradiation

- Colour change observed for DPA stabilised NC when exposed to UV or Vis irradiation





Results

Effect of UV /Vis Irradiation -Solubility

- DPA stabilised NC films were partially soluble after Irradiation

UV irradiation	Vis irradiation
16% residue left after filtration	6% residue left after filtration

- Insoluble residue was highly coloured and tougher for Vis samples suggesting possible cross-linking of NC

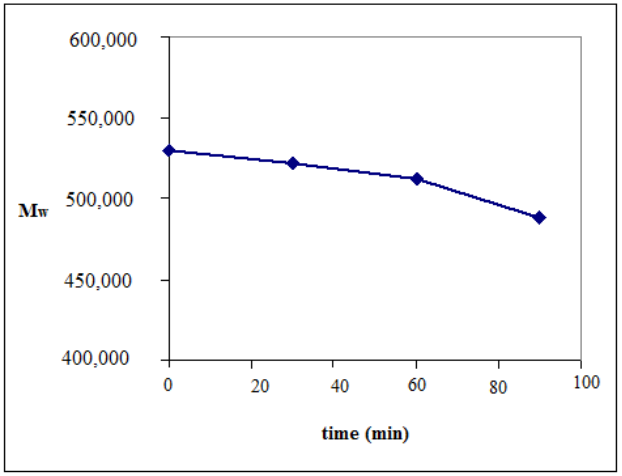
30 mins UV irradiated films after 24h in THF

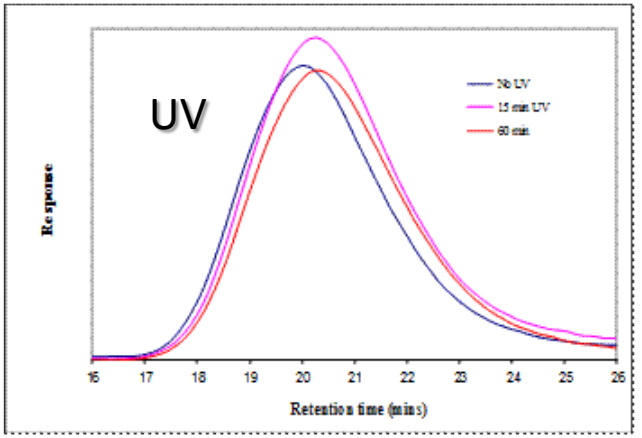
30 mins irradiated residue from MEK

Results

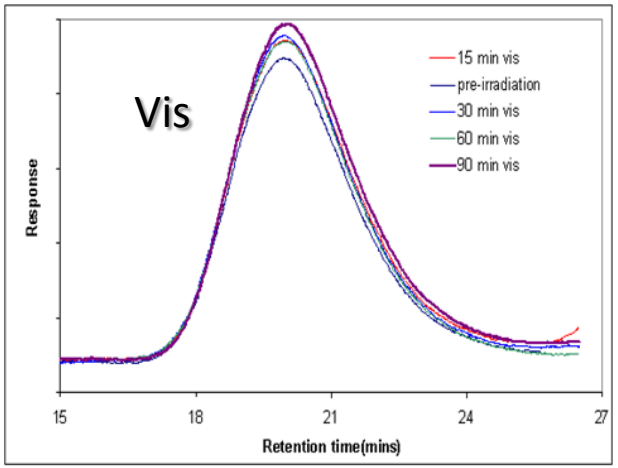
Effect of UV /Vis Irradiation-MMD-Unstabilised

- Upon UV irradiation of NC, M_w decreased 12% confirming polymer chain scission





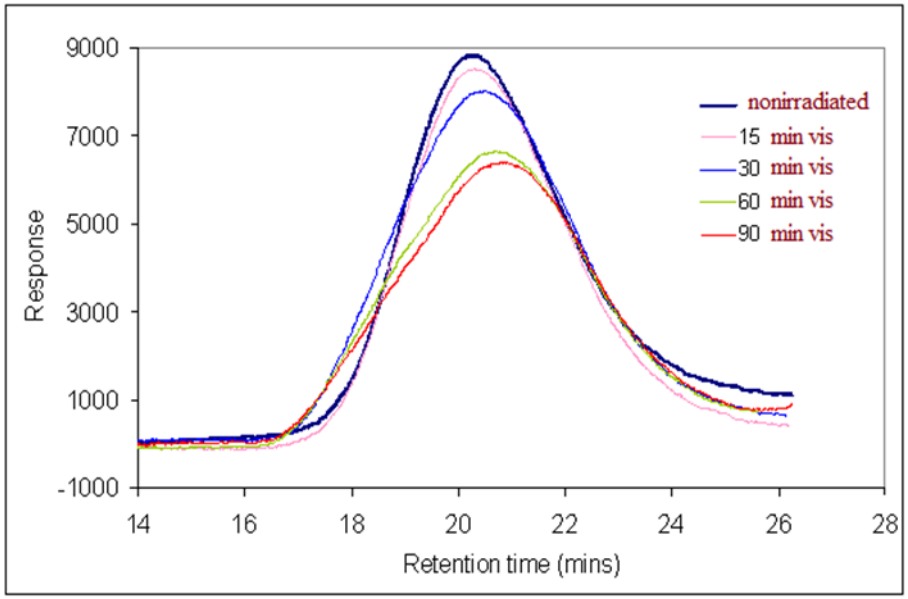
- Upon visible irradiation, MMD showed no remarkable change indicating that visible irradiation neither decomposes nitrate ester nor causes chain scission



Results

Effect of UV/Vis Irradiation –MMD-Stabilised

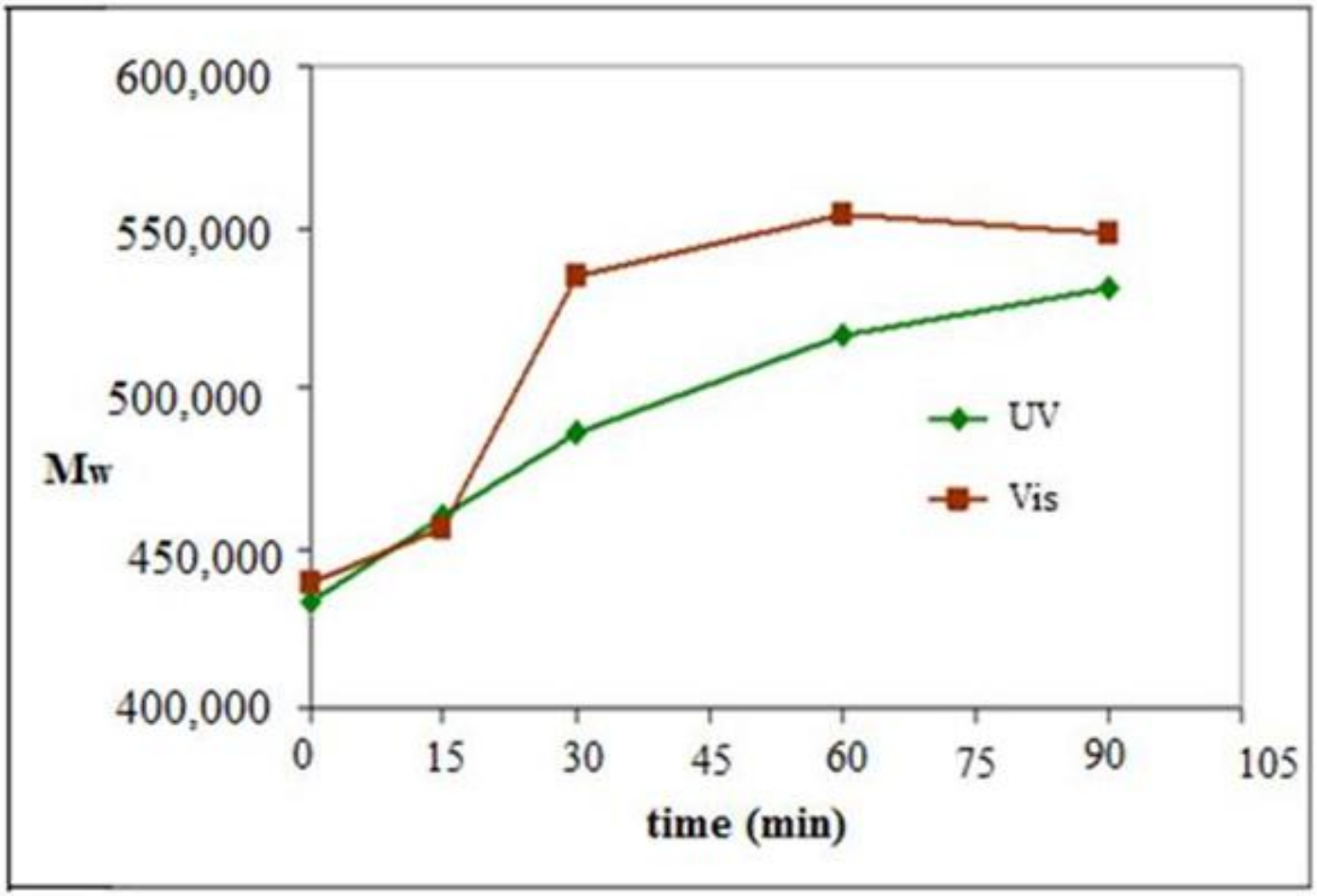
- M_w of DPA stabilised NC increased as a function of irradiation time
- Visible irradiation - polydispersity from 2.26 to 3.7 suggesting crosslinking
- Samples not fully soluble
  - Need to repeat with triple detection
  - small shoulder observed in the higher mass region ➔ higher Mw chain



UV irradiation (1h)	Vis irradiation (1h)
+ 19% Mw	+28% Mw

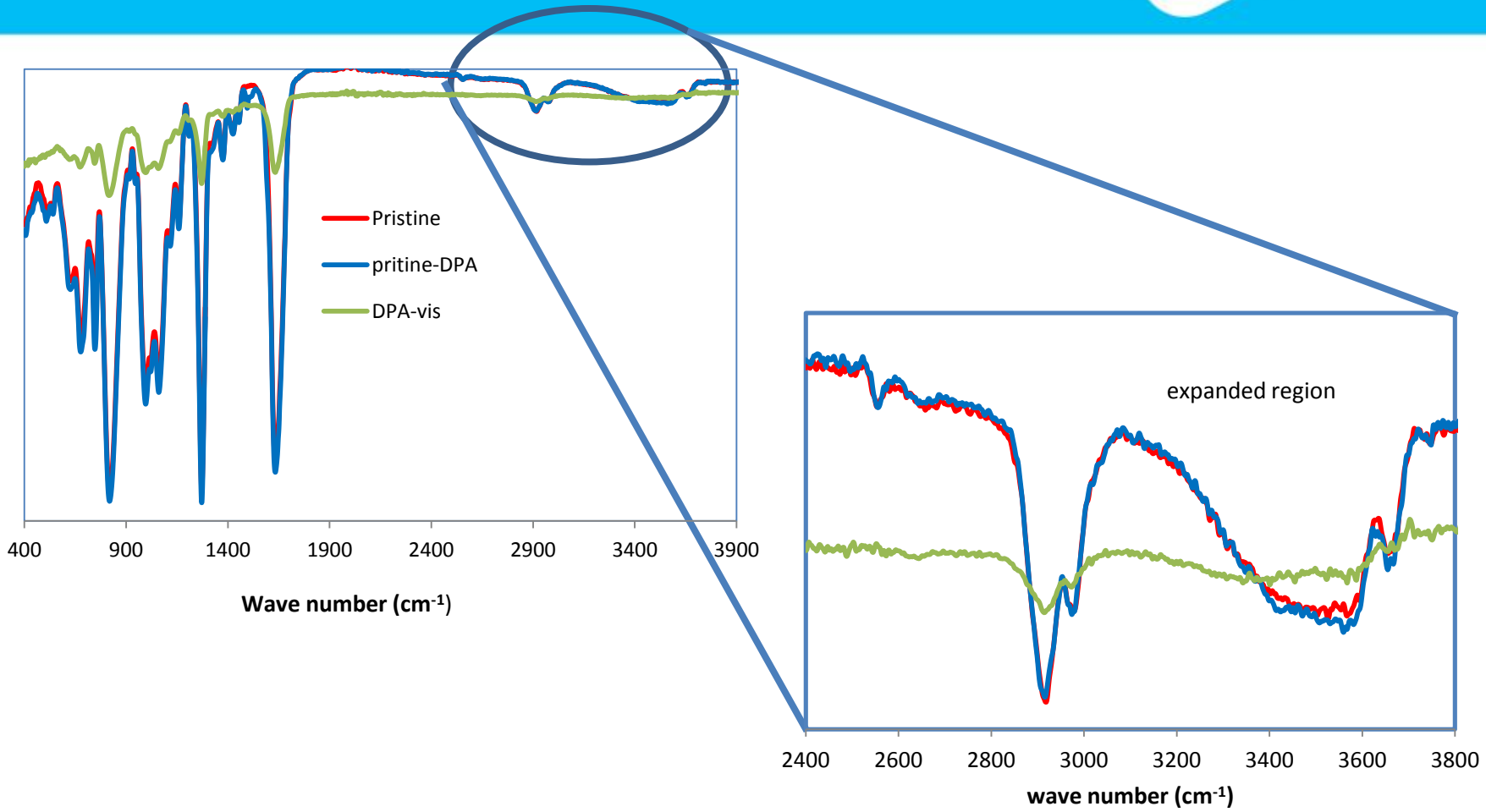
Results

Effect of UV/Vis Irradiation –MMD-Stabilised



Results

FTTR Analysis of Photo-crosslinked Unstabilised and DPA Stabilised NC



Results

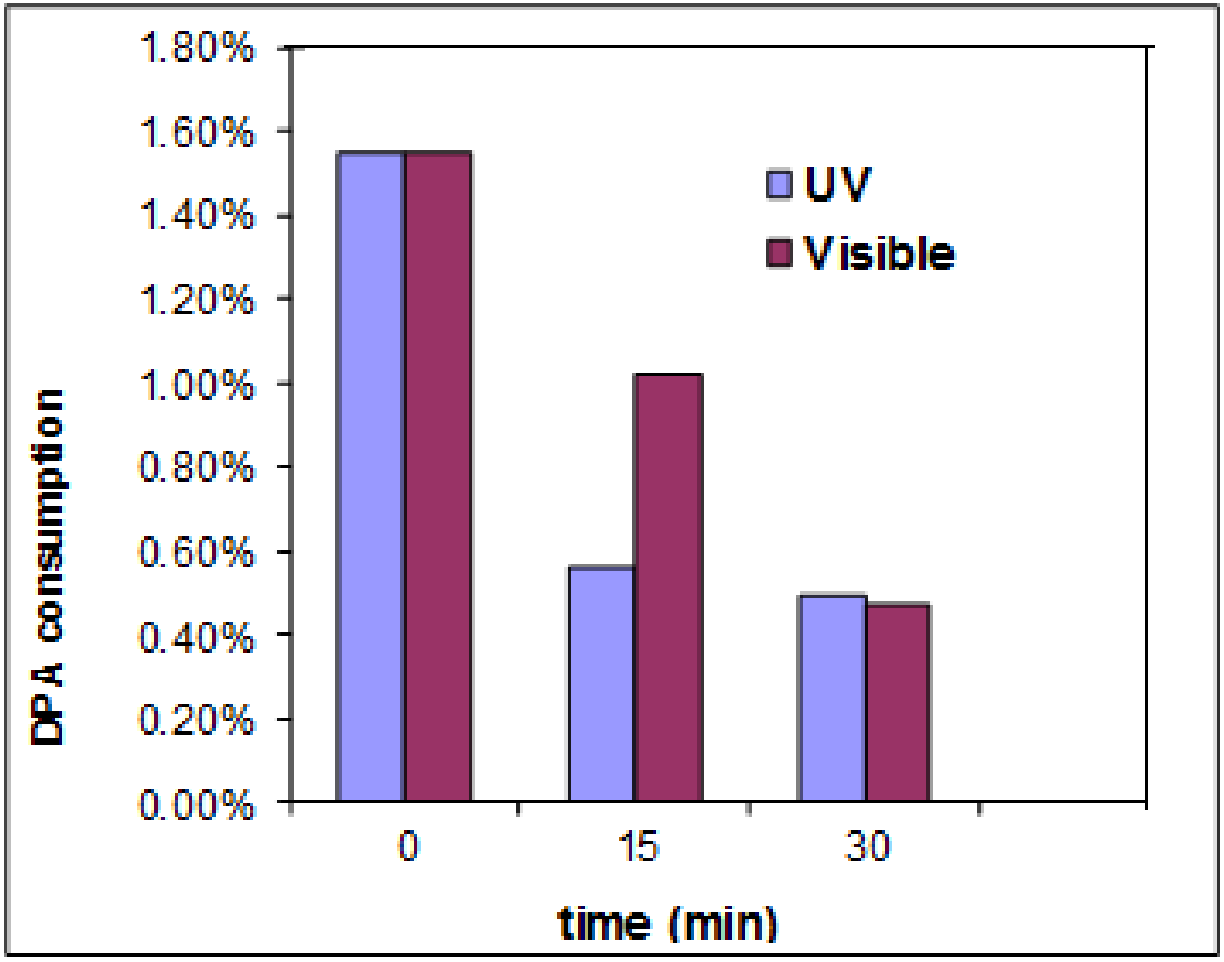
Effect of Vis Irradiation on Mechanical Properties

- Stiffness increase upon (45 min) Vis irradiation confirms toughening of NC
- Hardness remains unaffected by Vis irradiation
- Increase of creep at load confirms more plastic behaviour of NC after irradiation

Sample History	Pristine	Visible
Stiffness (GPa)	4.2	4.6
Stiffness change (%)	0	8
Hardness (Vicker)	20.4	20.5
Hardness change (%)	0	0
Creep at load held constant (%)	7.04	7.76
Creep at load held constant (%)	0	10

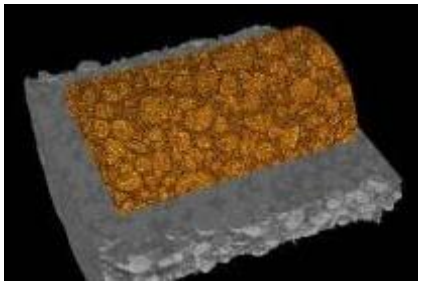
Results

Stabiliser loss (DPA) due to UV and Vis Irradiation



Conclusions

- **Unstabilsed NC**
  - UV irradiated – 12% decrease of M_w (chain scission)
  - Visible irradiated - does not affect the M_w
- **DPA stabilised NC**
  - UV irradiated – 19% increase of M_w (chain scission in parallel to nitrate ester decomposition with UV indicating an increase of M_w)
  - Visible irradiated - 28% increase in M_w high crosslinking through OH groups confirmed by M_w rise as well as absence of -OH str in IR spectra

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