Defence Academy of the United Kingdom

Cranfield UNIVERSITY

Study on crystallinity and ageing behaviour of post-precipitated nitrocellulose

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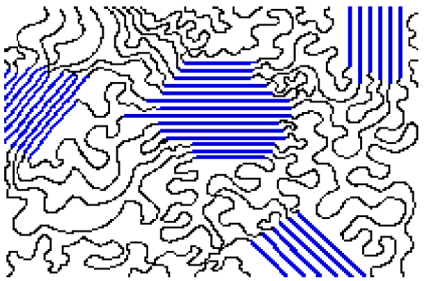
Introduction

- Nitrocellulose is a polymer.
- It can be either in the amorphous form or semicrystalline form.
- NC crystal structure is formed either by intermolecular or intramolecular stacking/folding of polymer chains.
- Crystallinity contributes to the stability of NC.
- Stability of NC is seriously jeopardised at higher temperature by the presence of certain solvent such as MEK.

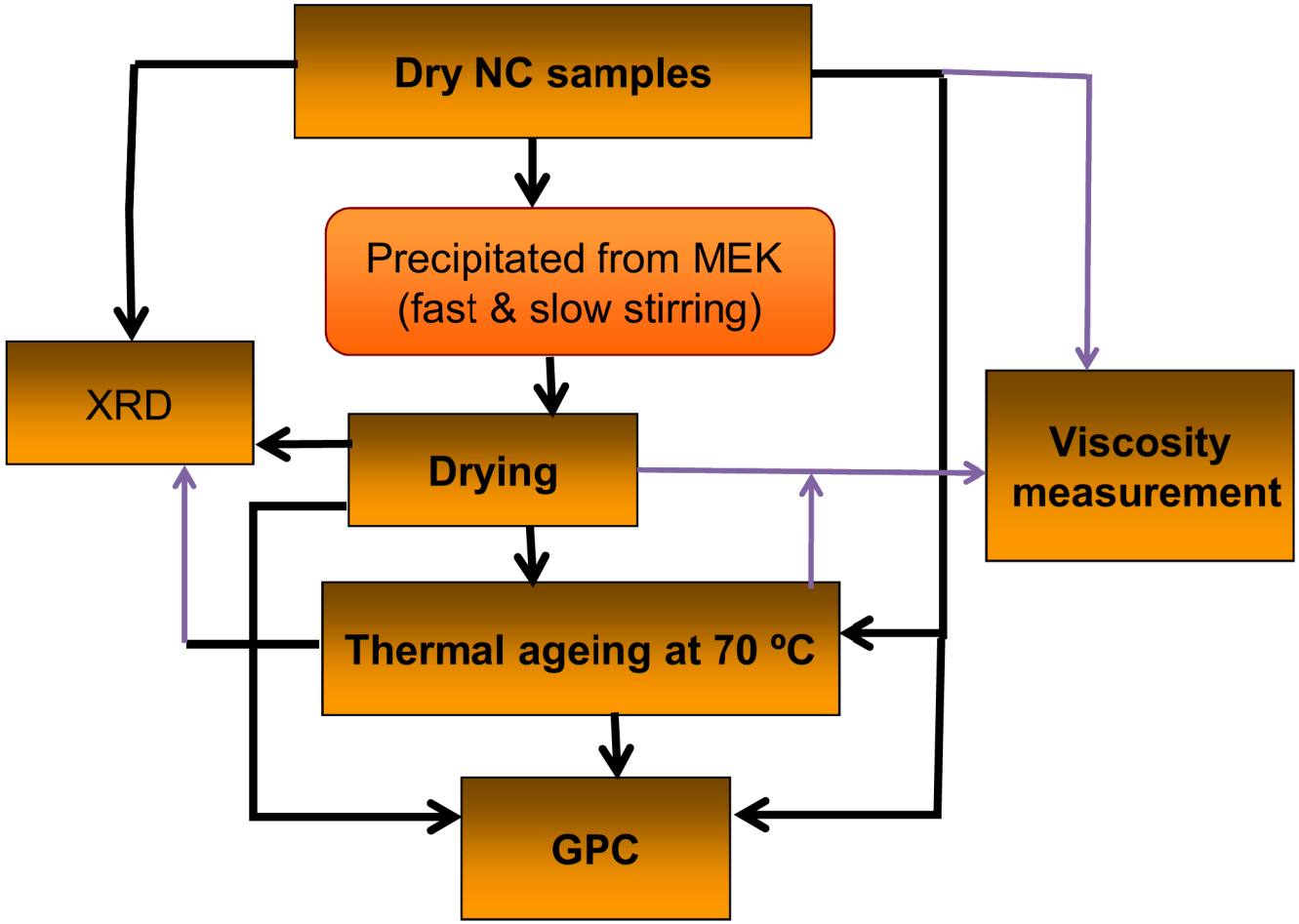


Chem wiki

Aims

- Measure the crystallinity of four NC samples containing 11.69%, 12.15%, 12.71% and 13.55% N.
- Crash precipitate the NC from methyl ethyl ketone (MEK) with and without a stabiliser to destroy crystallinity.
- Carry out ageing of the pre- and post-precipitated NC and reassess their crystallinity .
- Determine the molecular mass by SEC.
- Determine the viscosity of pre- and post precipitated NC samples using a rotational rheometer.

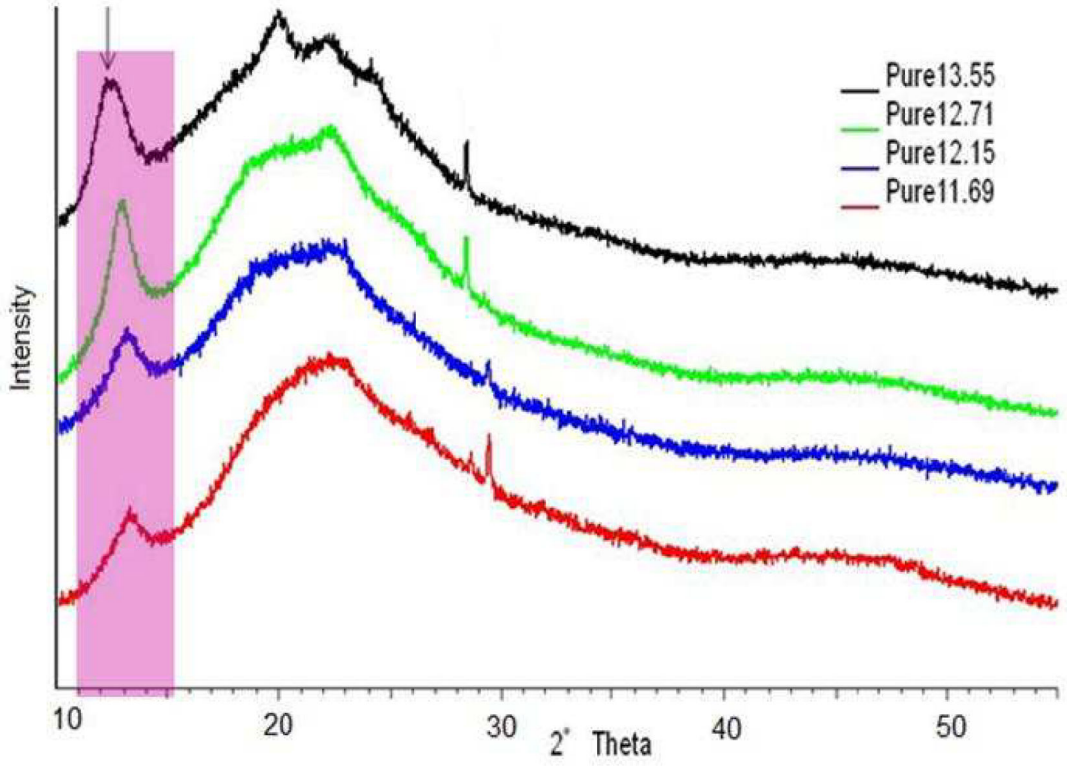
Experimental



Results

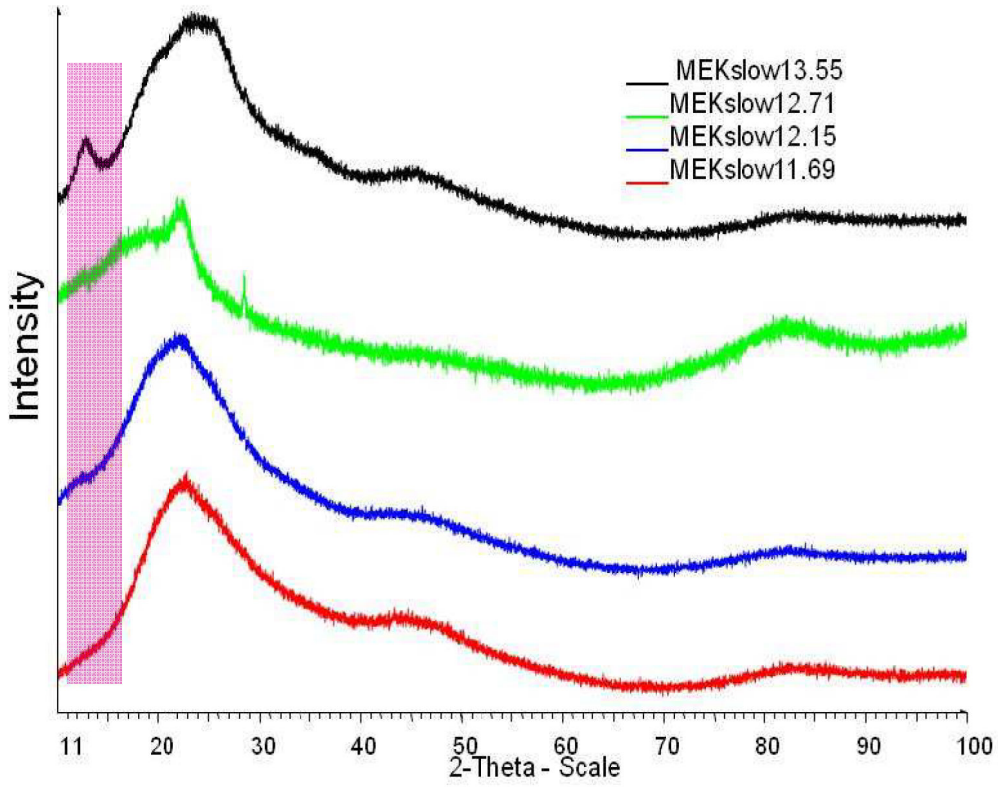
Crystallinity of pristine samples

- Crystalline peaks (sharp peaks) increases with increasing N content.
- Peaks within the angle of 15-30º are broad and assigned to be due to the amorphous NC.



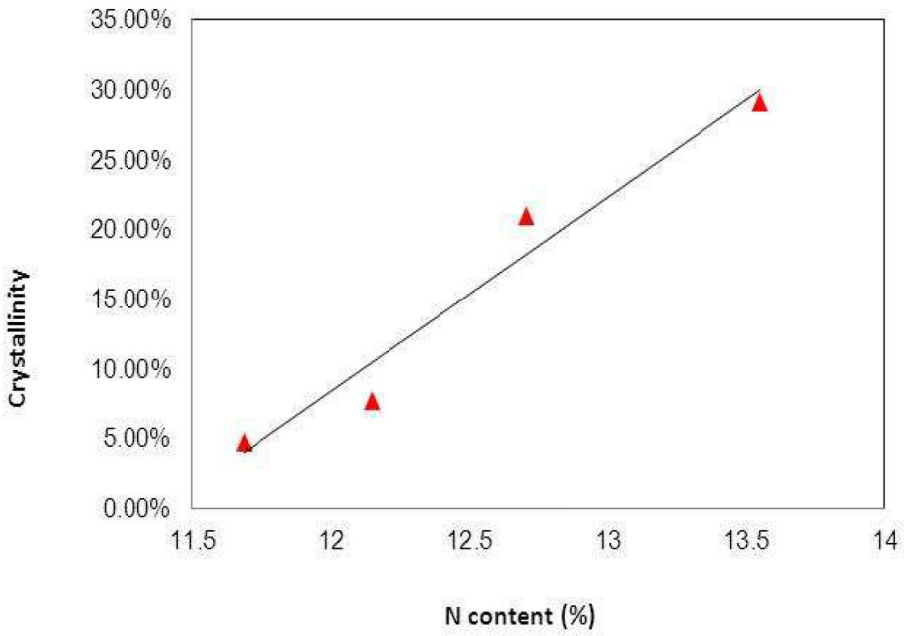
Crystallinity of precipitated samples

- Crystalline peaks intensity decrease in precipitated NC.
- The decreases are related to nitrogen content.
- NC containing 11.69% N become completely amorphous.



Degree of nitration
Crystallinity

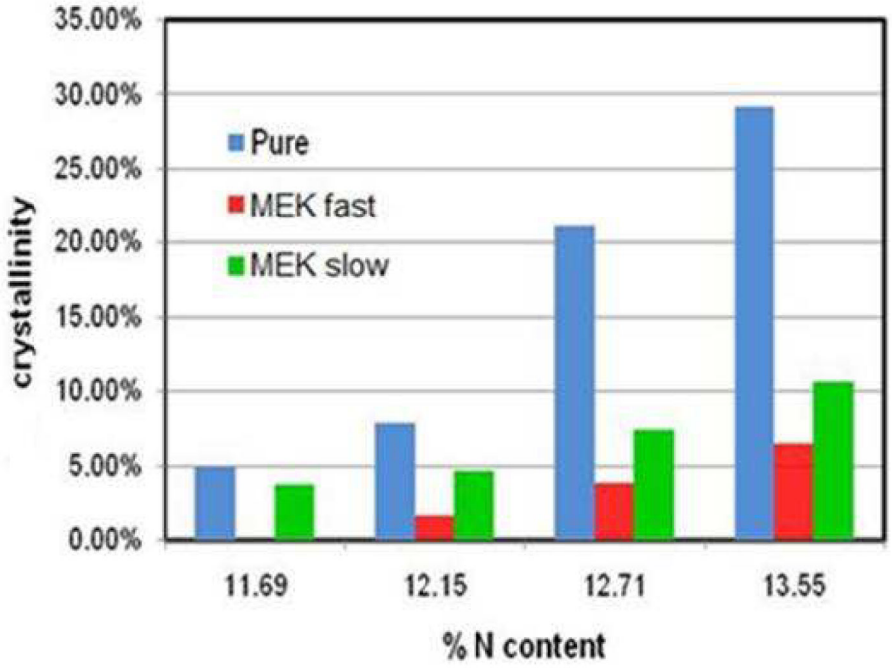
- Crystallinity increases with increasing the degree of nitration.
- The crystallinity is attributed to chain folding/stacking by attractive forces between nitro groups.



Precipitation condition

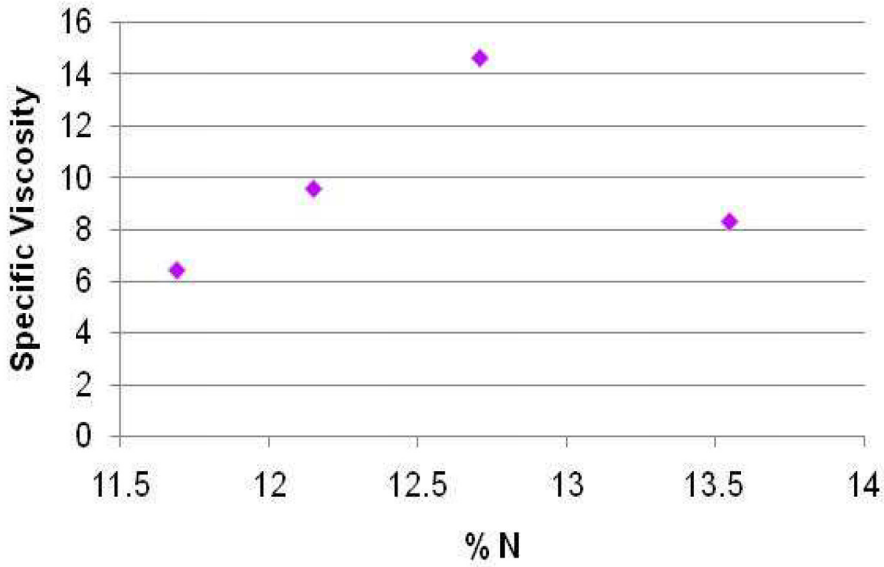
Crystallinity

- Crystallinity decreases with stirring during precipitation.
- Faster the stirring higher the loss of crystallinity.
- Complete loss of crystallinity is in NC with the lowest N content (11.69%).



Specific viscosity of NC solution

- Viscosity was measured in γ-butyrolactone (10 ml/g).
- Viscosity increases linearly up to 12.71 % N.
- Above 12.71% N Mw decreases rapidly due to the use of stronger reagents for nitration.



Comparison of properties of NC

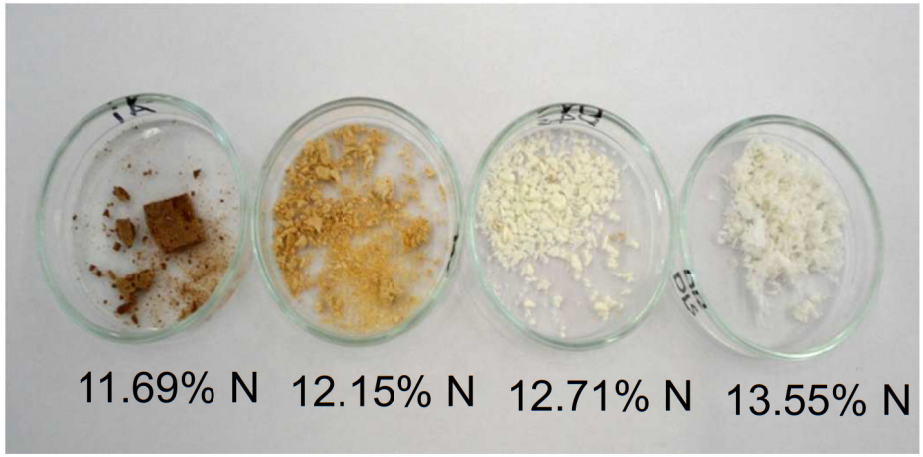
13.55% NC

Sample	Viscosity	Mw	Crystallinity
Pure NC	8.5	401,000	29
Aged pure NC	3.6	328,000	24.7
Ppt from MEK	5.75	362,000	10.5
Aged ppt from MEK	2.75	285,000	10
MEK ppt with DPA	7.8	426,000	12
Aged MEK ppt with DPA	9.5	445,000	12

- NC precipitated with DPA shows increase in Mw and viscosity with little changes in crystallinity.
- This can be explained in terms of the reaction of NC radicals with DPA.

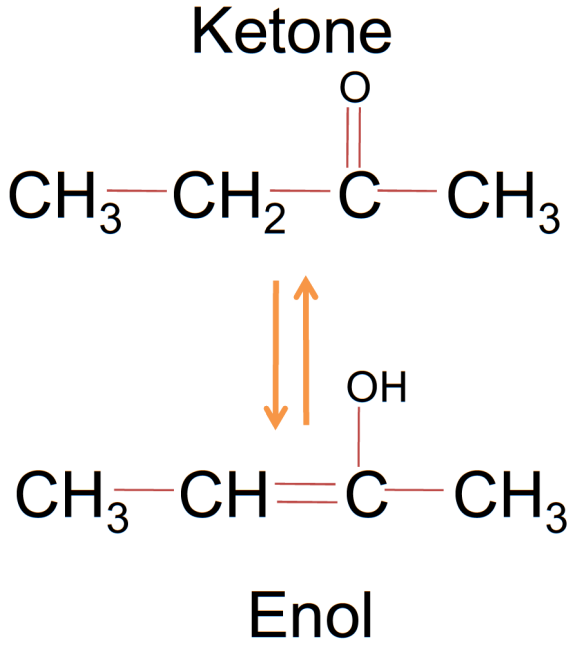
Ageing effects
NC Colour and Solubility

- Samples were aged at 70 ºC for 14 days.
- Colour changes upon ageing is a function of nitrogen content.
- Lowest N containing NC is the darkest in colour.
- Solubility decrease was observed, indicating the formation of cross-linked NC.



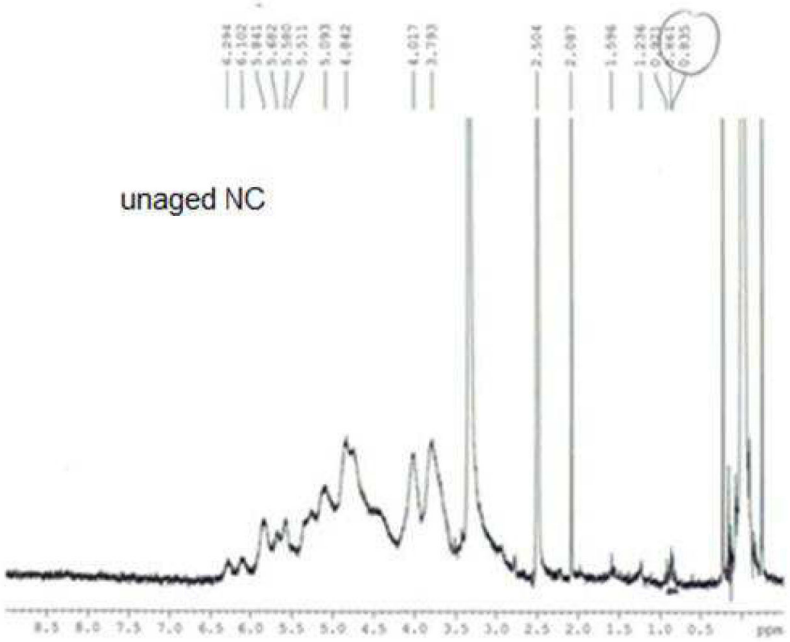
Enolketo-Tautomer in MEK

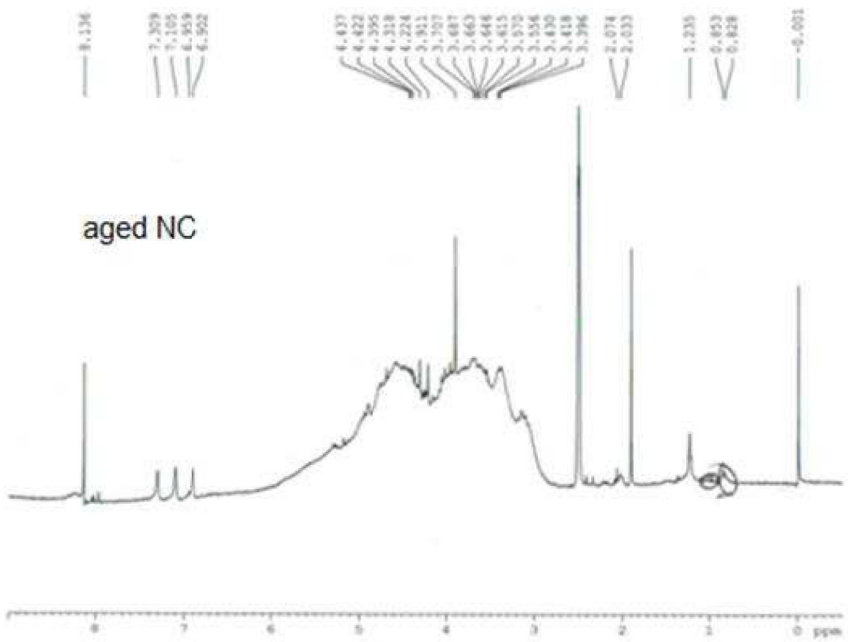
- Precipitated NC from MEK showed colour formation.
- This colour formation was thought to have caused by the reaction between keto-enol and OH groups of NC.
- NC was thought to have cross-linked with the keto-enol.
- Higher the number of OH groups (in 11.69%N) larger the degree of cross-linking.



NMR spectra

Unaged and Aged NC (11.69%N)





Conclusions

- Degree of crystallinity increases with degree of nitration.
- There is little relationship between molecular weight and degree of crystallinity indicating that crystals are formed by intermolecular NC polymer chains stacking.
- Precipitation of NC from MEK reduces the crystallinity.
- Lower nitrogen containing NC (11.69%N) showed complete loss of crystallinity.
- Specific viscosity of NC increases up to a critical nitrogen value and above that the relationship is not valid.

Conclusions

- Precipitation of NC with DPA gave NC with higher specific viscosity and higher Mw but no remarkable changes in the degree of crystallinity.
- NC precipitated from MEK showed colour changes and coloration is influenced by the degree of nitration.
- The colour is formed by the reaction between the keto-enol and OH groups in NC.
- There is an evidence of cross-linking of NC in presence of MEK at higher temperature making them insoluble in common solvents for the pure NC.

Acknowledgement

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Synthesis & Formulation	Characterisation & Ageing	Test & Evaluation	Chemical Safety, Fuels & Environmental