

COMBUSTION BEHAVIOUR OF NITROCELLULOSE AND ITS COMPLEXES WITH COPPER OXIDE Hot stage microscopic studies

*R. R. Mahajan, P. S. Makashir and J. P. Agrawal**

High Energy Materials Research Laboratory, Sutarwadi, Pune – 411 021, India

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Abstract

Complexes of nitrocellulose (NC – low and high nitrogen content) with copper oxide (CuO) have been synthesized and studied for morphological behaviour on heating from room temperature to 500°C with the help of hot stage microscopy (HSM).

During decomposition, NC: CuO complexes show contraction of fibrous boundaries followed by mass movement of matrix, with the evolution of brown yellow colour gas at higher temperatures as compared to NC alone.

Keywords: combustion behaviour, copper oxide, high-temperature behaviour, nitrocellulose, nitrocellulose complexes

Introduction

Nitrocellulose is widely used as a chief ingredient in the production of smokeless powders, blasting gelatin, dynamites, single-base and double-base gun and rocket propellants. Nitrocelluloses of varying nitrogen content were examined microscopically [1] under polarized light with crossed Nicol. Tissot [2] also studied this aspect extensively and concluded that highly nitrated nitrocellulose had a pale blue colour in polarized light and as nitrogen content decreases, colour changes from dark blue to indigo, violet, red, orange and yellow. Thus the nitrogen content may be predicted from the colour. Further, the colour does not depend solely on chemical constitution but is also linked with the refractive index of the liquid in which the fibres of NC are immersed, physical modification in the structure of fibre and composition of mixed acids used for nitration. Mosenthal [3] reported that cellulose derived from cotton, wood and flax when nitrated to the same nitrogen content produces entirely different colours under polarized light. It has been reported that oxide or hydroxide of calcium cause very fast gelation of nitrocellulose [4] in acetone, amyl acetate and ethylalcohol

* Author to whom all correspondence should be addressed.

solutions and it is due to the complex formation between nitrocellulose (NC) and oxide/hydroxide of calcium. Neal [5] also suggested that copper oxide/hydroxide [5] and cellulose molecules form a complex. In Gloor's and Spurlin's [6] opinion the same compounds are formed between NC and powdered metal by means of secondary valences. On the contrary, Waele [7] suggested that NC combines with metal oxides through the carboxylic groups and forms complexes.

Various thermoanalytical methods such as differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetry (TG), derivative thermogravimetry (DTG) etc. are commonly used for studying the reactions of high-energy materials [8–12]. The hot stage microscopy (HSM) under polarized light is a very useful technique for the interpretation of thermal analysis [12, 13] and may be used to identify the process like foaming of liquid melt, sintering etc., which could complicate the interpretation of DTA curve. It appears from literature that no work seems to have been reported on the morphology of nitrocellulose at elevated temperature using hot stage microscopic (HSM) technique under polarized light.

This paper discusses the morphology of nitrocellulose of high and low nitrogen content and their complexes with CuO under dynamic heating conditions up to 500°C using HSM under polarized light. The observations on heating NC and its complexes in question are supplemented by 35 mm microphotographs.

Experimental

Materials

Nitrocellulose having 12.2 and 13.1% nitrogen content was used. Solvents, metal oxide and nitrocellulose utilized for synthesis of complexes were of chemically pure grade.

Synthesis

Finely powdered copper oxide (4%) was slowly added while stirring 5% of NC in acetone–water (1:1) mixed solvent. After the completion of addition, it was refluxed at 50–80°C for 4–5 h. The complex was precipitated using hot water and filtered. The complex was dried in water-jacketed oven at 40°C till constant mass is achieved.

Hot stage microscopy

Hot stage microscopic studies under polarized light were performed using Leitz orthoplan polarizing microscope (German make). About 1 to 1.5 mg of NC and NC:CuO complexes were used for studies. The heating rate was 10–20°C min⁻¹ and microphotographs were taken using 35 mm Leitz orthoplan camera at the magnification of 300. The sample was dynamically heated in static air atmosphere.

Thermal analysis

Thermal analysis study was carried out using STA 409 Netzsch thermoanalyzer (German made) having facilities for simultaneous measurement of mass change, differential thermal analysis as a function of time or temperature. Pt–Pt 10% Rh thermocouples forming an integral junction with thermocups were used. Calcined alumina was used as a reference material. The sample used for thermal analysis was 5–7 mg and heating rate was $10^{\circ}\text{C min}^{-1}$.

Results and discussion

When dried nitrocellulose of low nitrogen content (12.2% N) is observed under polarizing microscope at room temperature, it appears as a fibre having non uniform meshy transparent matrix as indicated by arrows in Fig. 1a. Boundaries of fibrous structure are transparent showing greenish and pale bluish colour. The matrix also indicates brownish yellow colour.

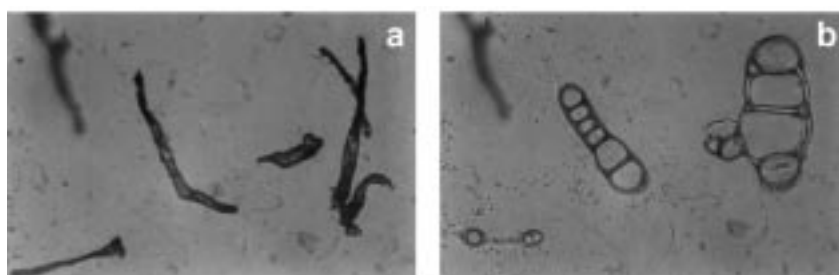


Fig. 1 Photomicrographs of nitrocellulose (12.2% N); a – at room temperature; b – at 210°C

When NC is heated to 60°C , more transparent matrix and breadth-wise expansion of structure is noticed. At 160°C , the evolution of brownish coloured gas and slight disturbance in structure of the matrix is observed. On further heating, there is a rapid movement of crystal structure and cell boundaries start disappearing at 180 – 185°C temperature range. Around 185 – 190°C , fast movement inside matrix structure followed by melting and bubbling in molten mass of the matrix is viewed. DTA registers an exotherm at around 187°C (Fig. 2) which supports the above morphological phase changes. It is interesting to note that large size blow holes formation takes place inside the matrix at 210°C as indicated by arrows in Fig. 1b and boundaries of the blowholes start becoming thicker with pale brown colouration. At 230 – 240°C , profuse evolution of reddish brown gases is observed from the molten matrix as well as centers of blowholes while the size and shape of the blowholes remain intact. This is the combustion phase of NC and charring of matrix structure takes place at around 280 – 300°C . The colour of the matrix remains reddish yellowish brown. Finally, a charred skeleton is observed. This is perhaps attributed to the last stage of complete combustion of nitrocellulose.

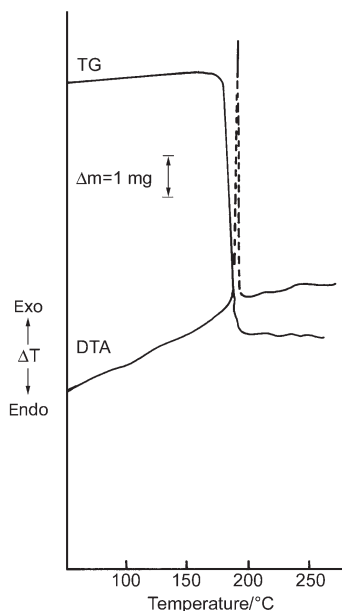


Fig. 2 TG/DTA curve of nitrocellulose (12.2% N), mass: 7.3 mg, heating rate: $10^{\circ}\text{C min}^{-1}$, references: alumina, atmosphere: static air

At room temperature, the complex of copper oxide (CuO 4%) with low nitrogen nitrocellulose (12.2% N) shows a hard, pale bluish tinged white compound. When observed under polarized light, it shows irregular shaped mass having dark brown coloured non-transparent matrix. On heating, boundaries of the mass indicate small globular mass with no change in transparency of matrix at 60°C . In the $110\text{--}120^{\circ}\text{C}$ temperature range, contraction of entire structure is observed without any change in matrix structure. This continues up to 200°C . At $200\text{--}205^{\circ}\text{C}$, a fast movement of mass of complex starts with sudden melting of matrix following vigorous bubbling of molten matrix. DTA of NC (12.2% N) shows an exotherm at 187°C , which is lower as compared to complex. This is due to the formation of stable complex of CuO with low nitrogen NC. Yellowish brown coloured gas is observed evolving at a faster rate through the matrix as well as bubbles. This is mainly due to the evolution of NO, NO_2 gas during combustion process. However, change in size and shape of the charred mass is noticed except dark reddish brown coloured matrix at $240\text{--}250^{\circ}\text{C}$.

Dry nitrocellulose of 13.1% N shows white coloured fibrous structure having a long thread like shape at room temperature. A tubular shape with transparent pinkish green coloured matrix is observed inside the fibrous mass. The boundaries of the cell are thin and transparent. On slow heating, expansion of the thread shape with slight disturbance inside the matrix structure at $60\text{--}80^{\circ}\text{C}$. There is no appreciable change except slight evolution of gas around 150°C and a change in matrix colour from pale pinkish green to yellowish brown colour at 160°C . At $190\text{--}192^{\circ}\text{C}$, melting and bubbling of molten matrix started simultaneously with the formation of small sized blow-

holes. The yellow brown coloured gas starts coming out from small blowholes at 190–200°C followed by profuse evolution of gas at 205–210°C. At 240°C, there is no change in size and shape of blowholes in the matrix but show the presence of small dark brown coloured tiny lumps. Charring process starts at 260°C keeping the boundaries transparent with pale yellow brown colour. No change is observed at temperatures beyond 300°C.

The complex of NC (13.1% N) with CuO is of white colour with pale bluish tinge and fibrous, light weight irregular shaped lump at room temperature. There is no meshy structure inside the matrix but small lumpy brownish matter is observed as indicated by arrows in Fig. 3a. A 50°C, matrix shows increase in transparency with yellowish colouration. A coagulated structure is noticed inside the matrix at about 110–120°C, along with expansion of the shape. At 200–210°C, matrix mass registers contraction followed by sudden melting with bubbling of gas through the molten matrix vigorously. The evolution of brown red coloured gas becomes more vigorous at 240°C. It is interesting to note very few small size blowholes inside the matrix as indicated by arrows in Fig. 3b. These blowholes further turn into small cellular structure with dark brown coloured boundaries. This phenomenon is attributed to the combustion of NC in air, resulting in gaseous products like NO, NO₂, CO. The metal oxide (CuO) present in NC–CuO complex delays the combustion of the complex to 220–240°C. The formation of dark brown coloured boundaries of blowholes indicates initial stage of charring of complex. Charring of mass starts at 260°C retaining the same dark brown coloured cellular structure intact. No further change is observed at temperatures beyond 300°C.

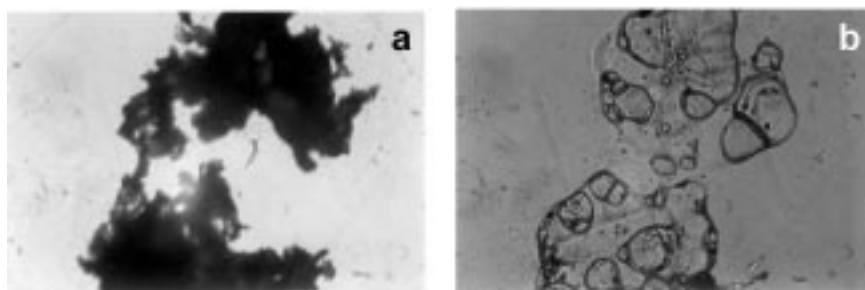


Fig. 3 Photomicrographs of nitrocellulose (13.1% N)–CuO (4%) complex; a – at room temperature; b – at 240°C

Thermal decomposition of NC (12.2% N) (Fig. 2) indicates no change in the mass (TG) up to 167°C. However, in the temperature range of 168–188.5°C, there is a very steep mass loss amounting to about 99% of the original mass. DTA registers a sharp exothermic change with peak maximum at 187.2°C, while NC–CuO complex shows exothermic peak at 197–200°C (Fig. 4). It is evident from the data on combustion of NC and NC–CuO complex under polarized light using HSM technique that decomposition of NC (12.2% N) alone starts profuse evolution of gas at localised points, while NC (12.2% N)–CuO complex shows a movement of fibrous structure as

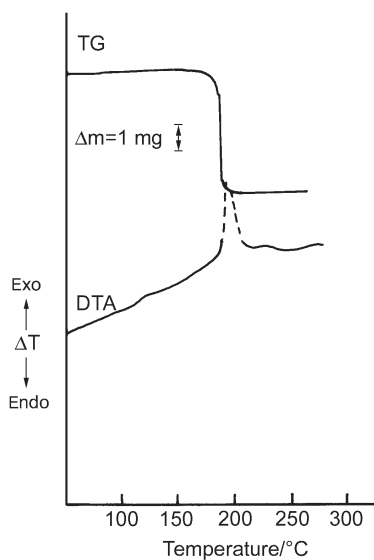


Fig. 4 TG/DTA curve of nitrocellulose (12.2% N)-CuO (4%) complex, mass: 5 mg, heating rate: $10^\circ\text{C min}^{-1}$, reference: alumina, atmosphere: static air

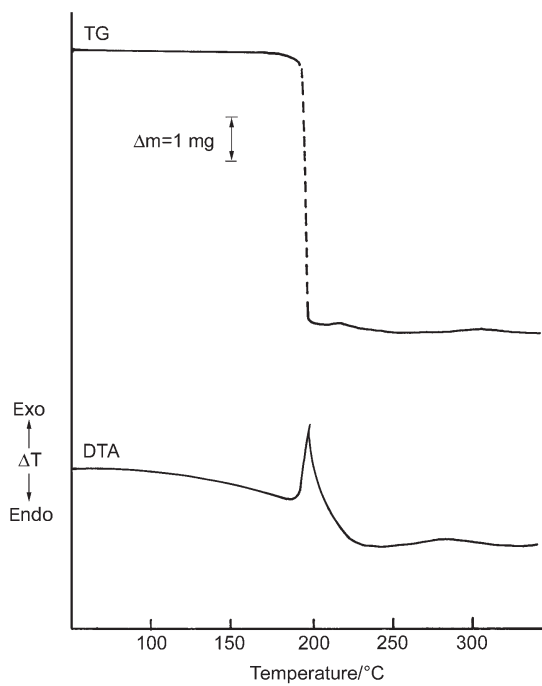


Fig. 5 TG/DTA curve of nitrocellulose (13.1% N), mass: 6.9 mg, heating rate: $10^\circ\text{C min}^{-1}$, reference: alumina, atmosphere: static air

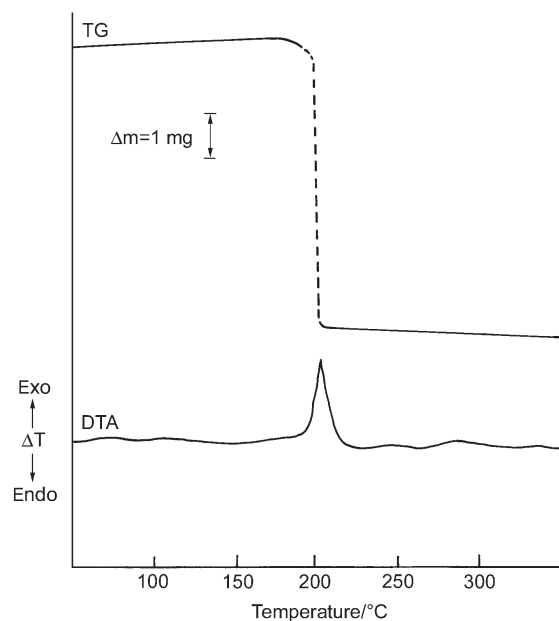


Fig. 6 TG/DTA curve of nitrocellulose (13.1% N)-copper oxide (4%) complex, mass: 7.3 mg, heating rate: $10^{\circ}\text{C min}^{-1}$, reference: alumina, atmosphere: static air

contraction in mass from 120 to 200°C . On further heating, it shows fast movement of mass, melting and profuse evolution of gases.

The simultaneous TG/DTA curve of NC (13.1% N) (Fig. 5) shows that NC decomposes in one stage and registers a sharp exothermic change with a peak maximum at 198°C , while the simultaneous TG/DTA curve of NC (13.1% N)-CuO complex (Fig. 6) shows a peak maximum of exothermic change at 204°C :

Nitrocellulose (12.2% N)-copper oxide complex is a hard, pale bluish coloured mass and shows dark brown coloured non-transparent matrix under polarised light at room temperature whereas NC (13.1% N)-CuO complex is pale bluish tinged fibrous floppy and soft natured, irregular shaped mass. Contraction in structure is noticed from about 120°C in case of NC (12.2% N)-CuO complex, while NC (13.1% N)-CuO complex, first shows expansion of shape at $110\text{--}120^{\circ}\text{C}$ followed by contraction at about 200°C .

The preferential gas evolved during combustion/decomposition of NC is mainly a nitrogen dioxide [14]. The presence of copper oxide in the complex influences the combustion/thermal decomposition of NC in a way so as to retard the breaking of O-NO₂ bonds in solid phase. This is supported by the shift of DTA exothermic peak temperature (T_{max}) as compared to NC alone. Furthermore, at higher temperature, degassing reaction and formation of charred carbonaceous matter is also observed.

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