

## CHANGE IN THERMAL PROPERTIES OF WOOL AFTER TREATMENT WITH LIQUID AMMONIA

*A. Włochowicz and E. Stelmasiak*

TEXTILE INSTITUTE, TECHNICAL UNIVERSITY OF ŁÓDŹ BRANCH IN BIELSKO-BIAŁA,  
43-300 BIELSKO-BIAŁA, FINDERA 32, POLAND

(Received June 1, 1982; in revised form September 29, 1982)

The changes caused in wool fibres by treatment with liquid ammonia were investigated with DTA, TG and DTG. It was established that the thermal stability of wool undergoes a significant increase, depending on the duration of treatment with liquid  $\text{NH}_3$ .

The assessment of the changes in wool keratin during its heating in dry air, water of vacuum and on treatment with various chemical agents has already been the subject of some experiments [1–5]. The complex molecular and anatomical structure of wool, together with the use of a wide range of experimental conditions of thermal analysis, do not allow a clear-cut interpretation of the changes that take place in the treated fibres.

Wool displays different thermal properties, depending on the humidity [5]. Elements of wool anatomical structure, such as the cuticle and the cortex, tested by means of thermal analysis, undergo hydrolytic cleavage and thermal destruction through different mechanism [5].

From recent investigations [1] it can be assumed that the following changes take place in non-dried wool keratin during heating:

- at temperatures up to 118°: desorption of water bound physically to the fibre;
- at nearly 160°: desorption of water bound physically and chemically to the fibre;
- within the range 160–210°: supercontraction, disordering of the  $\alpha$ -helical regions of keratin, chemical reactions between  $-\text{NH}_2$  and  $-\text{COOH}$  groups, which cause cross-linking of the keratin amorphous region through imide bonds, liberation of gases (mainly  $\text{NH}_3$  and  $\text{H}_2\text{O}$ ) as a result of decomposition of asparagine and glutamine;
- within the range 220–240°: cystin bridges are decomposed (the temperature of this reaction is a function of the initial fibre humidity);
- at temperatures above 240°: endotherms appear that are characteristic of the degradation process, their intensity and maximum depending upon the chemical pretreatment of the fibre.

At present, investigations are being carried out on the chemical treatment of wool fibres with liquid ammonia [9, 10]. Thus it appeared useful to carry out experiments to determine the influence of liquid ammonia on the parameters of the molecular and fine structure of wool [6–8]. In this work thermoanalytical observations are reported on the changes in wool following treatment with liquid ammonia.

## Experimental

Experiments were carried out on Australian Merino Super Fine greasy wool staple (80 mm and 19–21  $\mu\text{m}$  average diameter). The wool washed in soap solution and rinsed in water three times at 30–35°. In order to remove the suint from the washed wool, the fibres were extracted with diethyl ether for 15 hours in a Soxhlet. The washed and extracted wool was conditioned for 96 hours under standard conditions: 20°, 65% R.H.

Treatment of 500 mg loose fibre with liquid ammonia was carried out in a 0.5 dm<sup>3</sup> vacuum flask for 1, 5, 10, 30, 60 or 120 minutes.

Excess NH<sub>3</sub> was removed from the fibre by evaporation. The fibres treated with NH<sub>3</sub> were dried at 35° for 30 hours, and then conditioned for 72 hours.

The following parameters were determined on the treated fibres:

- moisture content [11];
- cystine content, using Folin's colorimetric method [12];
- changes taking place in wool treated with ammonia during heating between 20 and 500°.

The experiments were carried out on a Q-1500D derivatograph (Hungary) at a heating rate 10 degree/min, a recording range of 5 mm/min, a sensitivity of 2 mg per cm and a sample weight of 50 mg. Changes in mass (TG, DTG) were recorded simultaneously as functions of time and temperature (Fig. 1). Changes in mass were referred to the initial weight of the sample.

Readings were made at characteristic points in the DTG, TG curves, i.e. at the following temperatures:

- 78–80° – i.e. when the maximum rate of H<sub>2</sub>O desorption appears in the DTG curves;
- 115° – temperature of water desorption from the fibre [1];
- 200° – point of DTG and TG curves indicating that the initial temperature of keratin decomposition has been exceeded;
- 220–240° – first maximum in keratin decomposition;
- 304–370° – second maximum in keratin degradation;
- 350–430° – temperature range of half mass loss of the fibre, i.e. range in which half dry fibre mass is destroyed.

## Analysis of results

The observed data are presented in Table 1.

The maximum in the water desorption lies in the range 78–80°. The amount of H<sub>2</sub>O desorbed from the fibre does not depend on the treatment time and is 4.4–4.8% in relation to the fibre weight. At 200° distinct points can be noticed in the DTG and TG curves (Fig. 1). The observed fractional mass loss from 20° to 200° suggests that other gaseous products besides water result from keratin [2]. This can be

Table 1 Cystine content and thermal mass loss of wool after treatment with liquid ammonia

Duration of treatment with liquid ammonia min	Equilibrium regain at 20°, 65% R. H. %	Cystine content, %	Mass change, %				Temperature °C	Temperature of half mass loss, °C
			78-80	115	200	220-240		
reference wool	12.35	9.24	-4.4	-7.9	-13.2	-16.7	304° -40.43	352
1	10.75	12.64	-4.8	-8.0	-13.6	-16.8	303° -40.0	356
5	10.61	13.01	-4.8	-7.7	-10.2	-11.0	316° -36.7	420
10	10.61	12.83	-4.6	-9.2	-12.4	-16.8	316° -38.1	384
30	10.61	11.11	-4.2	-8.6	-8.6	-17.2	320° -36.8	388
60	11.11	9.64	-4.4	-7.5	-11.6	-14.1	310° -38.3	381
120	10.98	9.33	-4.6	-9.2	-13.6	-13.8	370° -40.0	430

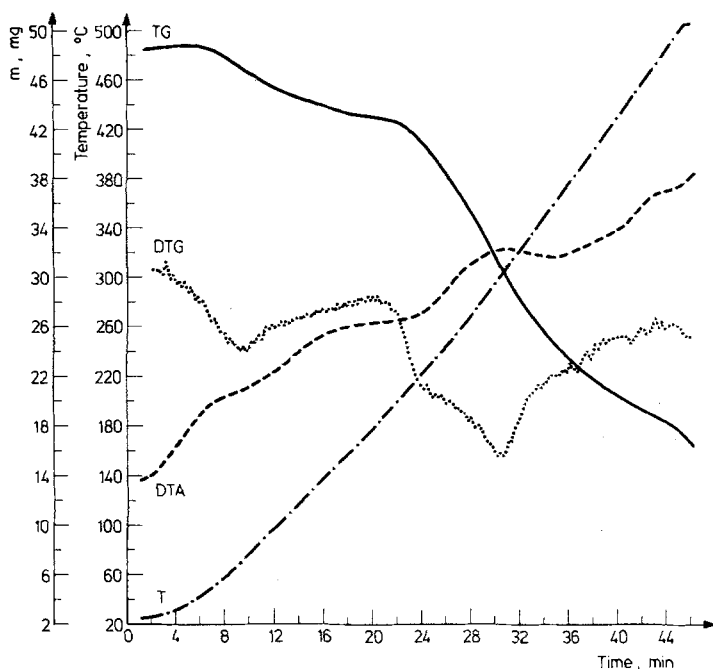
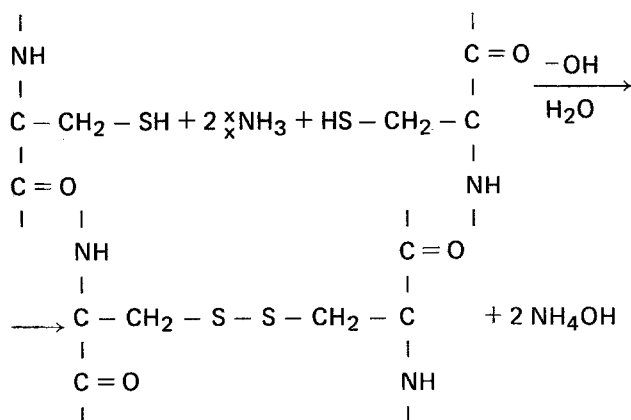


Fig. 1 Thermoanalytical curves of wool treated with liquid ammonia

ammonia [6]. At 220°, when the maximum keratin decomposition begins, proportional changes of weight as a function of treatment time are insignificant.

The maximum rate of mass loss was observed at 270–320°. With increasing duration of liquid ammonia treatment, the temperature of decomposition becomes displaced towards higher values whereas the maximum in the mass loss remains at the same level. The measured temperature of half mass loss ( $T_{0.5}$ ) suggests that the thermal stability of wool increases with the duration of treatment. In the case of treatment for 1–60 minutes this increase is significant; above 60 minutes it is lower, but even then it is higher than for untreated wool. In wool samples treated with liquid ammonia (independently of the treatment time) there is a higher cystine content. Liquid ammonia can cause an increase in the cross-linking degree of wool fibre because of the presence of a catalytic quantity of  $H_2O$ , linking two cysteine residues in side-chains, according to the reaction:



Cross-linking of wool fibre with additional cysteine bridges can be one of the reasons for the increase in its thermal stability. Liquid ammonia can also cause an increase in the asparagine and glutamine contents, because of reactions between ammonia and radicals of glutamic and aspartic acids in the side-chains [6].

## Conclusion

Treatment of wool with liquid ammonia results in an increase in its thermal stability. This is most probably caused by increases in the cross-linking degree and in the cystine and imide bonds in the fibre keratin.

## References

- 1 J. S. Crighton and W. M. Findin, *J. Thermal Anal.*, 11 (1977) 305.
- 2 J. S. Crighton, W. M. Findon and F. Happey, *Appl. Polym. Symp.*, 18 (1971) 847.
- 3 J. S. Crighton and P. N. Hole, *Proc. of International Wool Textile Research Conference Aachen, 1975*, vol. II, p. 499.
- 4 A. Włochowicz and M. Eder, *J. Thermal Anal.* (in press).
- 5 H. Marfels and P. Kassenbeck, *Melliand Textilbericht*, 59 (1978) 756; J. Rusznak, L. Trezel, A. Bereck and G. Bildo, *Appl. Polym. Symp.*, 18 (1971) 175; R. S. Schwenker and J. H. Dusenburg, *Textile Res. J.*, 30 (1960) 800.
- 6 E. Stelmasiak, Thesis, Textile Institute, Technical University of Łódź, Łódź 1980; E. Stelmasiak and A. Włochowicz, *Textile Res. J.*, 52 (1982) 485; A. Włochowicz and E. Stelmasiak, *Acta Polymerica* (in press).
- 7 E. Troppe, *Textile Res. J.*, 50 (1980) 162.
- 8 Z. B. Chasina, *Text. Promysl.*, No 11 (1979) 4, 57.
- 9 P. A. Barkhuysen, *Sawtri Tech. Rep.*, No 447 (1979).
- 10 J. S. M. Pitts, *Jour. Text. Inst.*, 67 (1976) 12.
- 11 PN/P - 04601 (Poland).
- 12 IWTO - 15-66 (E).

**Zusammenfassung** – Die in Wollfasern durch Behandlung mit flüssigen Ammoniak verursachten Veränderungen wurden mittels DTA, TG und DTG untersucht. Es wurde festgestellt, dass sich die thermische Stabilität der Wolle in Abhängigkeit von der Dauer der Behandlung mit flüssigen Ammoniak signifikant erhöht.

**Резюме** – С помощью ДТА, ТГ и ДТГ были исследованы изменения, происходящие в шерстяных волокнах при обработке их аммиаком. Установлено, что термостойкость шерсти значительно увеличивается в зависимости от продолжительности обработки ее аммиаком.