Journal of Thermal Analysis, Vol. 26 (1983) 225–232

EFFECTS OF TRICHLOROETHYLENE AND TETRACHLOROETHYLENE ON FINE STRUCTURE OF WOOL

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(Received April 29, 1982; in revised form September 29, 1982)

Studies have been made on the structure of wool fibres treated with trichloroethylene (TRI) and tetrachloroethylene (PER) by means of differential thermal analysis (DTA), differential scanning calorimetry (DSC) and X-ray diffractometry.

The samples were treated with TRI at temperatures ranging from 40° to 87°, and with PER at temperatures from 40° to 121°. TRI and PER treatment caused changes in the wool samples which were detected on the DTA curves. Changes in the degree of order brought about by TRI and PER, calculated from the DSC scans, were in accord with those determined from the X-ray data. The wool samples treated with TRI showed an increase, and those treated with PER a decrease, in the content of the ordered phase as the treatment time was increased.

In addition to other techniques, differential thermal analysis has recently been gaining ground in textile research and technology. The first DTA study concerning protein fibres was that of Schwenker and Dusenbury [1].

These and subsequent investigations [1–9] have resulted assignments of observed characteristics to structural features of the examined wool fibres. The specific thermally-induced transitions in the observed features have been discussed in relation to the thermal or chemical modification of the wool. The present study is concerned with DTA, DSC and X-ray diffraction examinations of wool samples treated with trichloroethylene (TRI) and tetrachloroethylene (PER). Our aim has been to extend the scope of conclusions on structural changes within wool fibre due to organic solvent application. The knowledge of these changes is of assistance in establishing the optimum process-engineering conditions for anhydrous treatment of wool, ensuring that the wool fibres preserve their high utility values.

Experimental

Investigations were carried out on Australian Merino greasy wool staple. The average fibre length and diameter were 65 mm and 18–20 μm, respectively. Fibres, when cleaned from trash and mechanical impurities by Soxhlet extraction with diethyl ether for 12 hours, were treated with TRI and PER. The wool fibre treatment conditions were as listed in Table 1.

Table 1 Heat of fusion, crystallinity index and relative degree of order of wool following treatment with trichloroethylene and tetrachloroethylene

Wool treatment conditions	DSC		X-ray	
	Heat of fusion, J/g	Relative degree of order	Crystallinity index[x] W_k, %	Relative degree of order
Trichloroethylene, 40°				
0.5 min	12.1 ± 0.4	0.69	20	0.72
1 min	14.6 ± 0.8	0.83	25	0.88
30 min	20.9 ± 1.2	1.2	29	1.03
Trichloroethylene, 65°				
0.5 min	9.6 ± 0.4	0.56	22	0.79
1 min	11.3 ± 0.4	0.64	24	0.83
30 min	12.1 ± 0.4	0.69	25	0.87
Trichloroethylene, 87°				
0.5 min	12.1 ± 0.4	0.69	23	0.80
1 min	16.3 ± 0.8	0.92	24	0.84
30 min	17.1 ± 0.8	0.99	26	0.93
60 min	17.1 ± 0.8	0.98	26	0.91
180 min	17.5 ± 0.8	0.99	27	0.95
Tetrachloroethylene, 40°				
0.5 min	18.8 ± 0.8	1.1	25	0.88
1 min	18.4 ± 0.8	1.04	24	0.85
30 min	17.5 ± 0.8	1.0	24	0.83
Tetrachloroethylene, 80°				
0.5 min	14.2 ± 0.4	0.8	24	0.84
1 min	10.4 ± 0.4	0.59	23	0.81
30 min	9.6 ± 0.4	0.54	23	0.81
Tetrachloroethylene, 121°				
0.5 min	17.5 ± 0.8	1.0	27	0.94
1 min	11.3 ± 0.4	0.63	22	0.77
30 min	8.8 ± 0.4	0.51	21	0.75
60 min	8.8 ± 0.4	0.50	21	0.73
180 min	9.2 ± 0.4	0.51	21	0.75
Reference wool sample	17.5 ± 0.8	1.0	28	1.0

[x] The error of the method was equal to 3%

To attain isotropic samples the wool samples were cut into 30 μm sections on a Hardy microtome. The wool samples were then conditioned at 20° and 65% R.H. for 48 hours. The DTA curves were obtained with the use of a Du Pont 990 thermal analyzer with a standard DTA cell. 8 mg of the powder substance was packed to a depth of 3 mm in a 4 mm diameter glass tube. Chromel-alumel thermocouples were inserted into the wool sample and reference balanced glass beads in a glass tube with the use of ceramic centering sleeves. The preparation was placed in a silver heating block and heated in an air atmosphere at a rate of 20 deg/min, from 20° up to 350°.

The amplified analogue voltage reflecting the temperature difference (ΔT) between sample and reference was plotted as a function of sample temperature. The ΔT signals were recorded at a scaling of 0.5 deg/inch up to 170°, and at 0.2 deg/inch from 170° up to 350° sample temperature.

To obtain the DSC scans, 8 mg of cut wool in an open aluminium pan was placed in the Du Pont DSC cell and heated at a rate of 20 deg/min from 20° to 350°. An empty aluminium pan was used as a reference.

The analogue voltage, which reflects the differential heat input (dq/dt) into the sample compared with the reference, was recorded as a function of time (1 min/inch) at a scaling of 0.1 mcal $\sec^{-1}$ inch^{-1}.

The heats of fusion were calculated from the areas measured between DSC curves and the baseline, which was the continuation of the straight lines observed before and after completion of the transition. The DSC cell calibration coefficient at the temperature of interest was found from separate measurements made on tin with heat of fusion 14.14 cal/g (256.1 J/g) and melting point 231.9°. In view of the lack of a 100% crystalline standard, no absolute values for the degree of order could be determined. Only relative degrees of order were found, from the formula:

$$\alpha = \frac{\Delta H_i}{\Delta H_{\text{ext}}} \tag{1}$$

where: α is the relative degree of order of the given sample,
ΔH_i is the heat of fusion of the given wool sample, and
ΔH_{ext} is the heat of fusion of a reference wool sample extracted with ethyl ether only.

The apparatus used for X-ray analyses was a Rigaku-Denki diffractometer. The wool samples were presented in the diffractometer on a glass carrier 0.5 mm deep and 15 x 20 mm in area. The X-ray diffractograms were made by the focusing technique under the following conditions: radiation: CuK_α, accelerating voltage: 35 kV, anode current: 25 mA, angular velocity of scintillation counter: 2 deg/min.

The crystallinity index W_k was found according to the method proposed by Wakelin *et al.* [10]. The X-ray curve obtained for the 100% amorphous sodium caseinate standard was subtracted from the experimental curves $I = f(2\theta)$ for the given samples. The degrees of order were calculated from the areas of the (100) and (001) lattice plane series.

Results and discussion

In the case of wool samples extracted with diethyl ether only, the DTA curves (Fig. 1A) correspond in character to those obtained by other authors [1–6]. The DTA curve shows a major endotherm spanning a wide range of temperature, with its peak at 123°, which is attributed to the loss of sorbed water [1,3,5]. No separate endothermic peak for loss of the tightly-bound water was found at 160°. A second endothermic shoulder was observed by Schwenker and Dusenbury [1] and ascribed to loss of the strongly-bonded water ascertained to be present in wool by Watt *et al.* [11].

There was also no indiçation of a thermal effect at 180°, assigned to the formation of isopeptide crosslinks of the involvement of asparagine [5,6].

The observed endothermic doublet with maxima at 230.5° and 240° has been assigned to the disordering of the α-keratin [5]. From his sudies of the torsional properties of Lincoln wool fibres, Menefee [12] concluded that a helix-to-amorphous transition occurs in this temperature region. The two stages of the transition can be associated with the two different thermal stability zones proposed by Feughelman and Haly [2]. Menefee [13] and Crighton *et al.* [6] explained the endothermic doublet by the disordering of α-keratin present in two distinct environments (i.e. fibrillar and matrix).

Since the major loss of cystine accompanied by elimination of hydrogen sulphide has been reported [5,6] to occur in this region, the process taking place in the first part of the melting endotherm is attributed partly to this process.

The thermal effects observed at higher temperatures (279°, 290° and 326°) appear to be the result of overlapping degradation processes. The wool destruction is the resultant effect of the destructive processes; hydrolytic, oxidation and thermal [15]. The share and importance of each of these processes depend on the initial condition of the given fibre.

TRI and PER treatments result in a reproducible shift of the water desorption endotherm towards lower temperature (Figs 1 B,C,D and 2 A,B,C). The maximum shift was found for wool treated with TRI at the boiling temperature (Fig. 1 D). No TRI or PER residues were traced in the examined samples by either DTA or gas chromatography [14]. The DTA traces for TRI and PER-treated wool samples indicate distinct shifts of the endothermic peaks of melting and degradation relative to the reference wool sample (Figs 1 and 2). Moreover, new bands appear, with the previous ones decaying. Wool samples treated with TRI at 40° yield split melting endotherms. Hence, one could infer a greater number of regions in the wool material. TRI treatment at 65° causes a considerable drop in cystine bonds. This process is proved by the decay of the first part of the melting endotherms (Fig. 1 C) and by the infrared spectroscopy data [14]. Since the first maximum of the melting endotherm shifts by

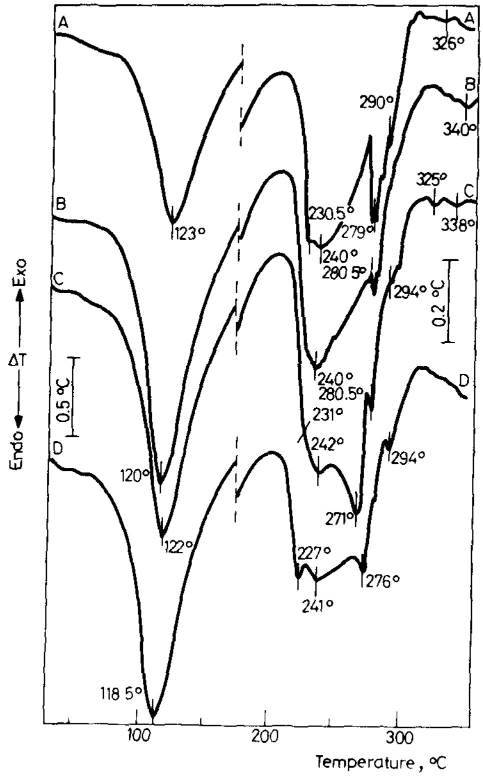

Fig. 1 DTA curves of wool extracted with diethyl ether (A); treated with trichloroethylene for 30 min at 40° (B); for 0.5 min at 65° (C); for 30 min at boiling point (D)

4.5° towards lower temperature (Fig. 1 D), TRI causes changes within the keratin matrix at the boiling temperature on prolonged treatment. The DTA curves of PER-treated wool at 40° (Fig. 2 A) demonstrate a split of the melting endotherm. Three bands are visible, at 230°, 236° and 243°. In the case of samples treated with PER at its boiling point it was found that the second maximum of the melting endotherm tends to shift towards higher temperature (Fig. 2 C). Table 1 lists the heats of fusion obtained from DSC measurements on the investigated wool samples. Depending on the treatment conditions, the heat of fusion varies between 2.14 and 5.02 cal/g. Since the degradation of wool occurs in the analysed temperature region, the estimated heat of fusion values are approximate. The changes in heat of fusion and degree of order are in accord with the results of X-ray analyses (Table 1). The changes in the degree of order determined from both kinds of measurement follow a similar course. After TRI treatment the fraction of order in the product fibre was larger than that in the untreated wool. The maximum rise in crystallinity was observed on 30 min treatment at 40°.

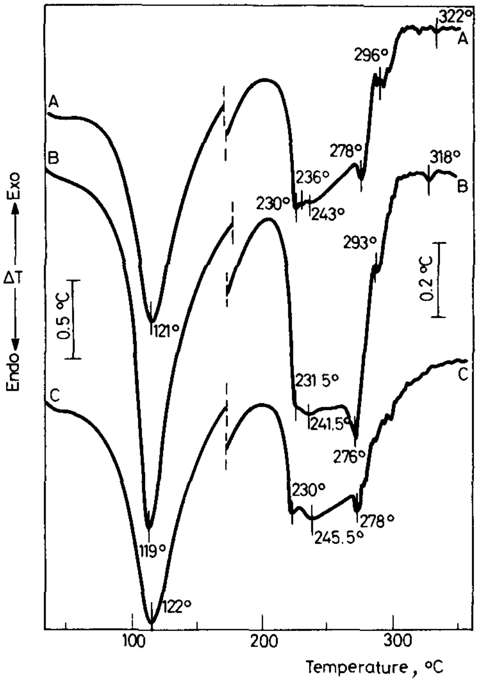

Fig. 2 DTA curves of wool treated with tetrachloroethylene for 30 min at 40° (A); for 1 min at 80° (B); for 30 min at boiling point (C)

The case is different with the PER-treated samples: with increasing treatment time the degree of order decreases. According to the obtained results, thermal processing of wool fibres involves essential persistent changes in their supramolecular structure. The effect of these changes depends primarily on the duration of thermal treatment and the solvent type. The changes observed appear to be connected with the shifting and regrouping of macromolecular fragments, due to disruption of the weakest intermolecular bonds as well as recrystallization and reorientation of the wool material in the heating process.

References

1 R.F. Schwenker and J.H. Dusenbury, Textile Res. J., 30 (1960) 800.

2 M. Feughelman and A.R. Haly, Kolloid-Z., 168 (1960) 107.

3 W.D. Felix, M.A. McDowell and H. Eyring, Textile Res. J., 33 (1963) 465.

4 J.S. Crighton, F. Happey and J. T. Ball, Conformation of Biopolymers, Pt.II, Ed. G. N. Ramachandran, Academic Press, New York, 1967 p.623.

5 J.S. Crighton and F. Happey, Symposium on Fibrous Proteins, Butterworths, Melbourn, 1967, p.409.

6 J.S. Crighton, W.M. Findon and F. Happey, J. Appl.Polymer Sci. Symp., 18 (1971) 847.

7 A.R. Haly and W. Snaith, Textile Res.J., 37 (1967) 898.

8 I. Rusznák and L. Trenzel, J. Appl.Polymer Sci.Symp., 18 (1971) 175.

9 G. Ebert and W. Stein, Angew. Macromol. Chem., 7 (1969) 57.

10 J.H. Wakelin, H.S. Virgin and E. Crystal, J. Appl.Phys., 30 (1959) 1654.

11 I.C. Watt, R.H. Kennett and J.F. James, Textile Res.J., 29 (1969) 975.

12 E. Menefee and G. Yee, Textile Res.J., 35 (1965) 801.

13 E. Menefee, J.Appl. Polymer Sci. Symp., 18 (1971) 809.

14 A. Włochowicz and B. Jurczak – (unpublisched study)

15 G. Urbańczyk, Fizyka Włókna, WNT, Warszawa, 1974, p.127.

Zusammenfassung – Die Struktur von mit Trichloräthylen (TRI) und Tetrachloräthylen (PER) behandelten Wollfasern wurde differentialthermoanalytisch (DTA), differentialscanningkalorimetrisch (DSC) und röntgendiffraktometrisch untersucht. Die Proben wurden mit TRI im Temperaturbereich von 40–87° und mit PER bei Temperaturen von 40–121° behandelt. Die Behandlung mit TRI und PER führte zu Veränderungen der Wollproben, die sich in den DTA-Kurven zu erkennen geben. TRI- und PER-Behandlung haben Veränderungen des aus Röntgendaten berechneten Ordungsgrades zur Folge. Die mit TRI behandelten Wollproben zeigten eine Vergrösserung, die mit PER behandelten dagegen eine Verminderung des Gehalts an geordneter Phase mit steigender Behandlungszeit.

Ресюме – С помощью ДТА, ДСК и рентгеновской диффрактометрии было проведено изучение структуры шерстяных волокон, обработанных трихлорэтиленом и тетрахлорэтиленом. Обработка трихлор этиленом проводилась в области температур 40–87°, а тетрахлорэтиленом – в области 40–121°. Проведенная обработка образцов вызывает изменения, обнаруженные на ДТА-кривых. На основе рентгенографических данных были вычислены изменения степени упорядочения, вызванные обработкой три- и тетрахлорэтиленом. Волокна, обработанные трихлорэтиленом, показали увеличение содержания упорядоченной фазы, а обработка тетрахлорэтиленом – уменьшение по мере увеличения времени обработки.