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TG CHARACTERISTICS OF WOOL AND COTTON FIBERS IMPREGNATED WITH AZO-DYES

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The impregnation of AV17, AB90, AR1 and DR80 dyes on wool and on cotton AV17 and DR80 was carried out at optimized conditions of shaking time and pH for the maximum uptake of the dyes by the fibers. The effects of the dyes impregnation on thermal oxidation of wool and cotton fibers were studied by employing thermogravimetric analysis. The results show that the weight loss of wool fiber was in a single step and the impregnation of AR1 on wool fiber results in a significant decrease in the decomposition temperature. The impregnation of AV17 and DR80 on wool fiber changes the nature of the thermogravimetric pattern and two steps weight losses were observed as compared to the single step weight loss observed in virgin wool fiber. The impregnation of AV17 and DR80 dyes on cotton fiber does not change the nature of the thermogravimetric behavior of the fiber and two stage weight loss were observed for both virgin and impregnated cotton fiber. It has been found out that impregnation only affects the weight loss in both the steps. These results are important in relation to the dyeing of wool and cotton fibers.

Keywords: Azo-dyes, Wool, Cotton, Impregnation, TG characteristics

1. Introduction

Azo dyes are the compounds containing azo group (-N=N-) which are linked to sp-hybridized carbon atom, and described as mono-, dis-, and tetrakis- according to the number of such groups attached to carbon atom. The azo groups are mainly bound to benzene or naphthalene rings, but in some cases they are also attached to aromatic heterocycle (e.g., pyrazole) or enolizable aliphatic groups (e.g., acetoacetic acid derivatives) [1]. Most of the azo dyes are synthetic and are mostly produced by azo coupling i.e., the reaction of an aromatic or hetroaromatic diazo compound with a coupling component [2]. Generally, the acute toxicity of azo dyes is low and may cause skin and eye irritation, weakness and dizziness [3]. Few dyes showed LD_{50} values below 250 mg/kg body weight, whereas majority showed LD_{50} values between 0.25 – 14 g/kg body weight [4-5].

Azo dyes are often used to dye the textiles made of cotton and wool fibers. Dyeing capability of these fibers depends upon the nature of the fiber, dyes and dyeing medium, and may results in the modification of the structure and the chemical properties of the fibers [6]. This paper aims at elaborating the thermal properties of locally available wool and cotton fibers impregnated with some azo dyes. The effects of the impregnation of some azo dyes [Acid Violet 17 (AV17), Acid Blue 90 (AB90), Acid Red 1 (AR1) and Direct Red 80 (DR80) on wool and Acid Violet 17 (AV17) and Direct Red 80 (DR80) on cotton fiber] on the stability of the fibers have been studied by employing the thermogravimetric (TG) analysis.

2. Experimental

2.1. Material, chemical and reagent

Wool and cotton fibers were collected in loose form from Soon Sakesar, Pind Dadan Khan, District Khushab of Punjab Province. The other chemicals and reagents used were; acid red 1 (Fluka, Catalog No. 08720), acid violet 17 (Fluka, Catalog No. 27817), acid blue 90 (Fluka, Catalog No. 27815), direct red 80 (Fluka, Catalog No. 43665), petroleum ether (BDH, Catalog No. 26153), methanol (Merck, Catalog No. 106008). Double distilled water was used for making solutions.

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Table 1. Experimental conditions of impregnation of wool and cotton fibers [13-14].

Dye	Solution Concentration	Sorbent	pH	Shaking Time (min)	Dye Impregnation (%)
AV17	5×10^{-6} M	Wool	2.0	50	65.40
		Cotton	8.0	30	52.00
AB90	5×10^{-6} M	Wool	2.0	60	69.80
		Cotton	-	-	-
AR1	1×10^{-5} M	Wool	1.5	50	90.00
		Cotton	-	-	-
DR80	5×10^{-6} M	Wool	2.5	50	68.36
		Cotton	8.5	50	24.85

2.2. Washing of wool

Wool was first cleaned by hand to remove animal and plant debris. Its tips and roots were cut to get even surface thickness. It was then thoroughly washed with doubly distilled water to remove the water soluble impurities and dried for 02 hours at 60 ^{o}C. The dry wool was treated with petroleum ether and dried again [7-8]. This washed wool was used for further studies.

2.3. Washing of cotton

Cotton was first cleaned by hand to remove vegetable, animal and plant debris etc. It was then washed thoroughly with doubly distilled water to remove the pectic acid, brown coloring matter and other water soluble impurities and dried for 02 hours at 70^{o}C. The dry cotton was then washed with methanol to remove the cotton wax and dried again [9] and used as such in the subsequent studies.

2.4. Impregnation of dyes on wool and cotton fibers

Wool and cotton samples impregnated with some azo-dyes [acid violet 17 (AV17), acid blue 90 (AB90), acid red 1(AR1) and direct red 80 (DR80)] were prepared by batch technique at room temperature 23 ± 1 ^{o}C by shaking 0.15 g of washed wool and cotton fibers in 25 ml of dye solution of known concentration in 250 ml reagent glass bottle at a speed of 120 strokes /min for a pre-optimized time and pH for maximum uptake of the dyes by wool and cotton fibers mentioned in Table 1. After the pre-determined time, solutions were then filtered through filter paper. The first 3-4 ml portion of the filtrate was rejected because of the sorption of dyes on filter paper. Concentration of the dye in solutions was determined by means of UV-Visible spectrophotometer (Shimadzu UV-120-02) and was corrected for losses due to sorption of dyes on the wall of glass bottles by running blank experiments (i.e., without wool or cotton added). The percentage of the dye impregnated on wool and cotton fibers were computed in usual way.

2.5. Thermal studies

TG analyses were carried out for the virgin and impregnated wool and cotton fibers samples from ambient to 750^{o}C (where otherwise specified) on a Perkin Elmer Thermal Analyzer model TGA-7. Known amount of each sample were heated in air at a heating rate of 20^{o}C/min. TGA data obtained for wool and cotton fibers are given in Table 2. All the reported results are the average of triplicate independent measurements. The determined relative standard deviation was found within ± 5.0%.

3. Results and Discussion

TGA data for the virgin and dyes impregnated wool and cotton fibers are shown in Table 2. This

Table 2. TGA data for the virgin and impregnated wool and cotton fibers.

Sample	Weight Loss (%)				Total Weight Loss (%)
	Stage I		Stage II		
	Temperature Range (^oC)	Weight Loss (%)	Temperature Range (^oC)	Weight Loss (%)	
Wool (virgin)	184 - 581	73.7	-	-	73.7
Wool-AV17	25 - 122	12.5	170 - 606	62	74.5
Wool–AB90	32 - 122	10.5	178 - 608	51	61.5
Wool-AR1	120 - 295	96	-	-	96
Wool-DR80	24 - 145	14	165 - 590	58	72
Cotton (virgin)	22 - 110	6	184 - 600	80	86
Cotton-AV17	32 - 120	6	217 - 632	68	74
Cotton-DR80	26 - 98	7.5	170 - 590	70	77.5

table indicates that no weight loss was observed for the virgin wool fibers upto 184^{o}C and the weight loss starts above 184^{o}C and continues upto 581^{o}C. This may be due to the loss of bound water molecules which were sorbed in the bulk of polymeric matrix of the wool fiber. This water act as plasticizing agent and give elasticity to the wool fiber [10], after the loss of bound water molecule, the wool fiber become brittle and thermal decomposition of the fiber starts, which depends upon the strength of different chemical bonds in the fiber. The total weight loss of the wool fiber was observed as 73.7% in a single step in the temperature range of 184 ^{o}C to 581 ^{o}C.

TGA data for the wool fiber impregnated with AR1 reveals that weight loss starts at 120 ^{o}C and fiber decomposes completely upto 295 ^{o}C. About 96% of weight loss was observed in the temperature range of 120 – 295 ^{o}C. This shows that the fiber was severely damaged by the impregnation of AR1. The strong acidic medium (pH 1.5) used for impregnation of AR1 damages the wool fiber and rupture the polymeric chain of the fiber, as a result the weight loss occurred drastically at lower and narrow temperature range as compared to the virgin wool fiber.

Impregnation of AV17 and AB90 on wool fiber shows different TG behavior as compared to the virgin wool fiber. The weight losses occurred in two steps. For AV17-wool system, the weight loss of 12.5 % was observed in the temperature range of 25 - 122^{o}C and of 62 % in the second stage i.e., in the temperature range of 170 – 606 ^{o}C. There is a region of thermal stability in between the temperature range of 122 – 170 ^{o}C. The initial loss of 12.5% may be due to de-sorption of water molecules, dye ions/molecules, etc., which are weekly adsorbed on the surface of the wool fiber. The second weight loss of 62 % may be due the decomposition of the wool itself [11]. AB90 impregnation on wool fiber shows the same type of behavior i.e., weight loss occurs in two steps. But the weight losses in both the steps are lesser than that of AV17. It may be due to the fact that the lesser number of water molecules to sorb in the fiber so the weight loss is lesser in case of AB90 impregnation. TG behavior of wool fiber treated with DR80 also shows two steps of weight loss i.e., 14 % from 24 – 145^{o}C and 58 % from 165 – 590^{o}C. The first step of weight loss terminates at slightly higher temperature (145^{o}C) as compared to that of AV17 and AB90. This could probably be due to the bulky molecule of the dye (DR80) containing maximum $–SO_3^-$ group per molecule,

which is more tightly bound and cover the wool surface by adsorption thus hindering the easy escape of water molecules from the sample.

TGA data for virgin cotton fiber shows two steps of weight loss; the first step weight loss of 6 % is due to loss of water molecule present on the surface of the cotton fiber. In the second step, a weight loss of 80 % was observed in the temperature range of 184^{o}C to 600^{o}C, which may be due to the decomposition of the fiber. It was also observed that the net weight loss in case of cotton fiber (mainly composed of cellulose or polysaccharide) is more as compared to wool fiber (mainly polyamide). This may be due to the facts that (i) thermal stability of polyamide is comparatively more than that of cellulose; (ii) larger number of –OH group are present in cotton (cellulose) which makes hydrogen bonding with the water molecules; hence larger amount of water is sorbed by the cotton fiber than the wool fiber and appears as more weight loss in TGA. TGA data of cotton fiber impregnated with DR80 also shows two steps weight loss; 7.5 % weight loss upto 98^{o}C at the completion of first step whereas 70 % weight loss is observed in the second step from 170^{o}C to 590 ^{o}C. It is also interesting to note that second step of weight loss starts at rather higher temperature (170^{o}C) and the weight loss is smaller than that of virgin cotton fiber. This may be due to the possibility that the dye molecules are preferentially attracted by the fiber than the water molecule and cover the fiber surface and thus restrict the water molecules to sorb on the fiber. The lesser weight loss in the second step is not only due to the presence of lesser number of water molecule present in the bulk of the fiber [12] but also due to the gain in stability of the fiber due to sorbed dye molecules. A similar trend was also observed for cotton impregnation with AV17.

4. Conclusion

It is concluded from the above discussion that the total weight loss of wool fiber occurred in single step and the impregnation of AR1 damages the wool fiber and rupture the polymeric chain of the fiber, as a result of which the weight loss occurred drastically in shorter temperature range (120 - 295^{o}C) as compared to the virgin wool fiber (184 - 581^{o}C). This is very important as it clearly indicates that dyeing with AR1 dye decrease the strength of wool fiber and the use of AR1 thus should be avoided. The impregnation of AV17 and AB90 changes the thermo-gravimetric behavior of the wool fiber i.e., the weight loss occurred in two steps against single step in virgin wool fiber. The impregnation of AV17 and DR80 dyes on cotton fiber does not change the thermo-gravimetric behavir and the total weight loss occurred in two steps. The order of the weight loss observed is: cotton virgin (86%) > cotton-DR80 (77.5%) > cotton-AV17 (74%).

References

[1] H. Zollinger, in: Color Chemistry, VCH Press, Germany (1983) p.85.

[2] H. Zollinger, in: Color Chemistry, VCH Press, Germany (1983) p.110.

[3] Ullmann, Encyclopedia of Industrial Chemistry, 5th Edition, VCH Verlagsgesell-schaft, Weinheim, Deutschland.

[4] E.A. Clark and R. Anliker, in: Organic Dyes and Pigments, Handbook of Environmental Chemistry, Springer Verlag (1980).

[5] K. Hunger and R. Jung, Chimia, **45** (1991) 297.

[6] I.A. Siddiqui, The Art of Dyeing with Vegetable Colors, National Book Foundation, Pakistan (1976) p.9-15.

[7] H.T. Lookhande, J. Appl. Polym. Sci.; **22** (1978) 1243.

[8] H. Zollinger, in: Color Chemistry, VCH Press, Germany (1983) p.218.

[9] T. Pirzada, M.Phil Thesis, Department of Chemistry, Quaid-i-Azam Univ., Islamabad, Pakistan (1997).

[10] T. Barr, F.M. Rowe and J.B. Speakman, J. Soc. Dyers Colors**, 58** (1942) 52.

[11] J.W. Dodd and K.H. Tonge, in Thermal Methods of Analytical Chemistry by Open Learning, John Willey & Sons, Chichester (1987) pp. 33

[12] D. Balkase and H. Baltacioglu, J. Chem. Tech. Biotechnol; **54** (1992) 393.

[13] M.Saleem, T. Pirzada and R. Qadeer, Colloid and Surfaces A: Physiochemical & Eng. Aspects, **260** (2005) 183.

[14] M. Saleem, T. Pirzada and R. Qadeer, Colloid and Surfaces A: Physiochemical & Eng. Aspects, 292 (2007) 246.