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Thermal stability and fastness properties of wool fabric dyed with an eco-friendly natural dye "sambucus nigra" under the effect of different mordants

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ABSTRACT

Wool fabric samples were dyed with the natural dye sambucus nigra, then post-mordanted with three different mordants individually: alum, chrome and ferrous. Thermal analysis of the undyed (blank), dyed and dyed mordanted samples is applied to study the thermal stability of the samples under investigation using thermogravimetry (TG) and differential scanning calorimetry (DSC) techniques. TG tested results indicate that the thermal stability of dyed wool mordanted with ferrous is enhanced than the blank (undyed) and other dyed mordanted samples. The relative TG results show that char residue of the wool samples after 600 °C is higher than the blank one, meaning lesser volatile hazardous components. DSC measurements show remarkable variation in the thermal behavior according to the type of mordant. Also, there is a change in the char yield and the temperature of decomposition. Fastness properties of the examined dyed wool fabrics were also examined and reported.

Introduction

Wool, a natural biological polymer, consists of crystalline and amorphous phases. Thermal characterization of each phase is important to understand the fine structure and associated physical properties of wool. Wool has complex structure due to its different important chemical groups and the intermolecular forces of attraction that are formed [1], i.e. the polar peptide groups (i.e. –CO-NH-) and the oxygen of the carbonyl groups (-CO-) of slightly negative charge which will form hydrogen bond with the slightly positively charged hydrogen of the imins groups (-NH-) of other peptide groups. Cystine, containing the sulfur attached to the amide group is capable of forming disulfides cross linking tends towards greater chemical stability, resulting in less dye absorption. The cystine linkage is sensitive to chemical attack and is removed and/or modified by aqueous chlorination and high radiant energy. Also, the very absorbent nature of wool is caused by the polarity of the peptide groups, the salt linkage and the amorphous nature of its polymer system. It has high nitrogen content (16%), high moisture content (10-14%) [2], high ignition temperature (570- 600 ˚C) [3] low heat of combustion (20.5 KJ/g), low flame temperature (677 ˚C) and high limiting oxygen index (25-28%). Wool is not exclusively a keratin protein; it also has external lipid content and a small amount of specific internal wool lipids (1.5%). These internal lipids have ceramide content, with smaller amounts sulfates. They resemble human hair or stratum corneum from skin [4].

The wool fiber surface plays an important role in the dyeability [1] the light fastness characteristics, and color parameters,…etc. The oxidation of cystine content on the surface of the wool fabric is responsible for its hydrophobic nature and limited wettability and dyeability, forming cysteic acid and thus modifying or volatilizing the surface lipids.

Among the natural dyes sambucus nigra whose common name is elder which a tall tree –like shrub is. It contains about 190 species and 4 genera and mainly distributed across Europe, Asia and North Africa. A number of chemical constituents such as flavoniods, steroids, tannins, glycosides, cardiac glycosides, caffeic acid derivatives, ebulitins and volatile substances have been isolated from this plant [5].

Mordanting is the treatment of textile fabrics with metallic salts or other complex forming agents which bind the natural mordantable dyes onto the textile fibers. Different types and selective mordants or their combination can be applied on the textile fabrics to obtain varying color/shade, to increase the dye uptake and to improve the color fastness behavior of any natural dye [6].

The thermal analysis of wool is much more complicated than other polymeric materials. This is caused by a low melting enthalpy and a relatively low thermal degradation temperature for the other histological components as well as the moisture dependence of the melting behavior of the crystallites and the thermal degradation [7] .The instruments used for studying the thermal properties of polymers by colorimetric methods allow simple and rapid measurements with reasonably accurate results. They are nowadays in routine use in many areas and for many purposes.

Thermogravimetric analysis (TG) provides a measurement of the weight loss of a sample as a function of temperature, which enables us to reach the onset temperature of the thermal degradation of the fiber. DSC commonly used to determine crstallinity in polymers involves the measurement of the enthalpy of melting. DSC curves present three thermal events: glass transition, water evaporation and denaturation [8].

When textiles exposed to the fire, the outputs of volatile components caused by the fire, whether gas or solid (ash), have a large impact on the surrounding environment because of their hazardous effect to health. Accordingly, this research has been conducting to demonstrate the influence of natural dyeing with

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certain type of eco-friendly dyes, as well as different mordant types, on the improvement of the thermal stability of some natural fabrics such as wool when exposed to high temperatures aiming to decrease the pollutants resulting from the burned dyed fabrics.

Experimental Work:

Materials and methods :

Pure wool fabric (100%), weight is 176.61g/m2 and thickness is 0.528 mm was kindly supplied by Golden Tex. Co., Egypt. It was scoured with a solution containing 2 g/l of non-ionic detergent using liquor ratio 1:50 at temperature 60°C for 15 minutes. Finally, all the samples were thoroughly washed with tap water and dried at ambient conditions [9].

50 g of the crushed barks of sambucus nigra were soaked in 500 ml of distilled water and allowed to boil for one hour. Finally, the solution was filtered to obtain clear mother solution for dyeing process. Dyeing was carried out at 80˚C for 1 hour using liquor ratio 1:50

5g\l alum [K_2SO_4. Al_2 $(SO_4)_3$.24 H_2O], 2g\l chrome ($K_2Cr_2O_7$) and 5g/l ferrous ($FeSO_4.7H_2O$) were used separately as post mordants. The dyed samples were soaked in the mordant solution at 80˚C for one hour using liquor ration 1:50 [10].

Measurements, Testing and Analysis:

Thermal analysis:

Thermo-gravimetric analysis (TGA) was performed on a TGA-50 Shimadzu instrument at a flow rate of 30 ml/min. under nitrogen atmosphere with temperature range from room temperature to 650 °C, where the thermal behaviour of all the samples was investigated. A Shimadzu DSC-50 Japan Analyzer was used for differential scanning calorimetric. DSC experiments were carried out on all samples with heating rate 10 ºC/min., using dry nitrogen (N2) as a carrier gas and at a flow rate of 30 ml/min. Samples were repeated three times to ensure repeatability . Scans are started at temperature 30 °C to a final temperature of 750 °C. The next figure clarifies the DSC curve of the used natural dye sambucus nigra using the above mentioned conditions.

Fastness properties:

The improvement in both wettability and permeability of the mordanting fabrics led to an increase in their swellability during wetting process, which increase their dyeability and the aggregation of the dye molecules inside the fiber pores and produce an enhancement in light fastness.

Fastness to Light: Exposure of the dyed mordanted samples alongside with standard blue scale to artificial daylight was performed using Tera Light fastness Tester [11] for 160 hours at temperature of 25 ± 2ºC and relative humidity of 65 ± 5%. The light fastness was assessed after exposure using ASTM standard method vol. 14.04 G53-96

Fastness to Wash and Perspiration: The color fastness of the dyed and dyed mordanted silk samples to both washing and perspiration solutions (acidic and alkaline conditions) were determined according to ISO 105- C06 and ISO 105-E 04, respectively.

Main Results

Thermal Analysis:

Thermo-gravimetric Analysis (TGA):

TGA is widely used to investigate the thermal decomposition of polymers to determine the thermal decomposition kinetic parameters such as activation energy and reaction order. These parameters can be used to obtain a better understanding of thermal stability of polymers. Also, TGA enables to determine a value of the moisture loss of the fibers in addition to that obtained by conventional methods. Figure 2 represents the TG curves of the blank (undyed), dyed and dyed mordanted wool samples using alum, chrome or ferrous mordants respectively. The kinetic parameters obtained from these curves are listed in table 1

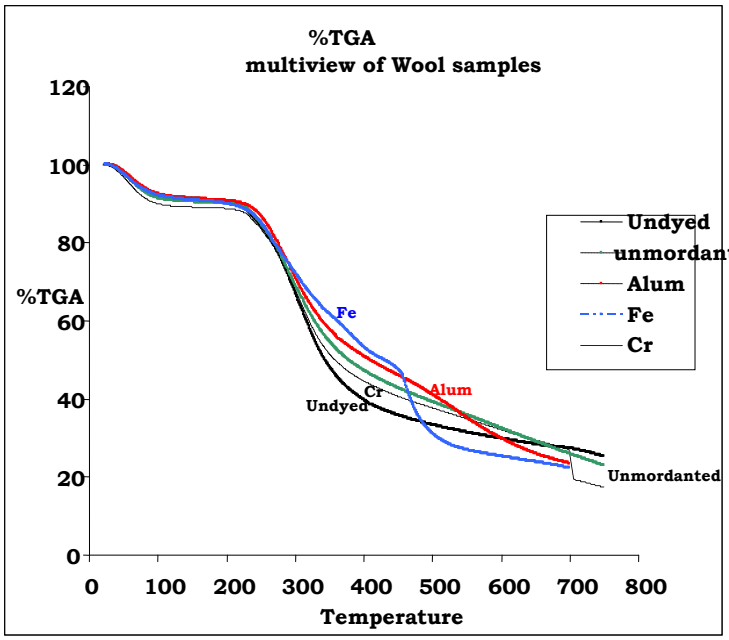


Figure 1: Thermo gravimetric analysis (%TGA) of wool samples under the effect of different mordants

Two evident weight loss steps are observed in the TGA curves. The weight loss in the first step corresponds to the evaporation of bound water (the desorption of water physically bound to fiber and the dehydration of wool). This process produces a broad /sharp endothermic peak and ends at around 90-100 ºC. So, an initial weight resulting from moisture departing appeared starting from room temperature up to around 100 ºC. It is well known that, the melting temperature of wool decreases with increasing moisture content [12].

The second loss peak , starting at above 200 ºC, is ascribed to crystal cleavage (most clear in the control sample figure 1) and may be attributed to melting and degradation of different morphological components forming the highly complex hierarchical structure of wool [7].

It was characterized by the presence of the typical bimodal melting endotherm with two peaks at 236 ºC and 239 ºC appeared clearly in figure 3.

This second step corresponds to the weight loss caused by the decomposition of the protein fiber structure [13], and coincides with the temperature range over which a number of defined pyrolysis reactions takes place in wool.

The hydrogen bond peptide helical structure ruptures and the ordered regions of wool undergo a solid to liquid phase change. The initial temperature of the thermal decomposition stage is usually used to compare the thermal stability of the samples [14].

Zhang et al [3] explained in their work that the weight loss between 250 ºC and 425 ºC is resulted from the decomposition of cystine and terminal amino groups and from decarboxylation.

The second weight loss between 427 ºC and 597 ºC was due to carbonization of the wool and the oxidation of the charred residue.

In thermal reaction, molecules in their ground state can be raised to higher vibrational levels of electronic ground state by collisions with other molecules or walls and the thermal energy is a factor controlling the frequency and probability of such

collisions. Chemical change occurs when a particular bond accumulate sufficient energy for bond dissociation. In general, the degradation of polymers is a heterogeneous reaction on which the increase of temperature causes the loss of mass [15].

By following figure 2 and table 1 representing the TGA of all the samples, it is noticed that the first step of weight loss increases for all wool samples above the loss of the blank sample except the dyed sample mordanted with alum, its loss is lesser by a very small value than that of the blank one. Mid-point temperature for all used samples- of this stage shifts towards higher degree except that of the dyed sample mordanted with chrome, which has the lowest weight loss% value.

The second step of weight loss (decomposition stage) is shown in the same figure (2) and its details in table 1. The highest loss occurs for the blank wool sample (52.76%) and the lowest value is that for the dyed unmordanted sample (38.91%). This value of decomposition weight loss increases for all the dyed mordanted samples following the order: ferrous (44.528) > chrome (44.150) > alum (41.237). This means that, the best post-mordant for wool is ferrous sulphate.

The third stage of decomposition showed that the lowest value of the weight loss in this stage is that for blank wool sample (12%).

The dyed unmordanted samples showed the highest weight loss of its components (28%), while for dyed samples mordanted with alum this loss is (25.34%) followed by the loss of dyed samples mordanted with chrome and ferrous respectively (≈ 17.5%).

It is clear that the differences between the weight loss values at this stage compared to the blank, is due to the presence of dye or mordant in these fabrics.

The temperature of the mid-point of this decomposition step is nearly the same for the dyed unmordanted samples and the dyed mordanted with alum and chrome (≈533 ºC). While for blank samples this temperature is the highest (549 ºC) and for dyed mordanted with ferrous is the lowest one (480 ºC).

The value of the total weight loss at the end of the thermal degradation of the samples under test, show that the total weight loss of the dyed sample mordanted with chrome has the lowest value, i.e. the char residue for this sample is the highest in weight.

Char residue = W1 –W2

Where w1 is the total weight of the sample at the beginning of the thermal process and W2 is the total weight loss of the sample [15].

If the weight of the char residue is increased, it behaves as a carbonized replica of the original fabric and functions as thermal barrier. The decomposition temperature of the fabrics is enhanced and the formation of flammable volatiles is decreased and hence the fabrics show good flame retardancy when exposed to fire.

Differential Thermo-gravimetric Analysis (DTGA):

Many DTGA studies [16] on wool show that, there was a broad endotherm around 230 ˚C and a small one around 245 ˚C. The lower was ascribed to crystal cleavage, and the melting of α- keratin. Above 250 ˚C, the degradation was observed and was very weak. This shows that degradation was almost occurred under 250 ˚C.

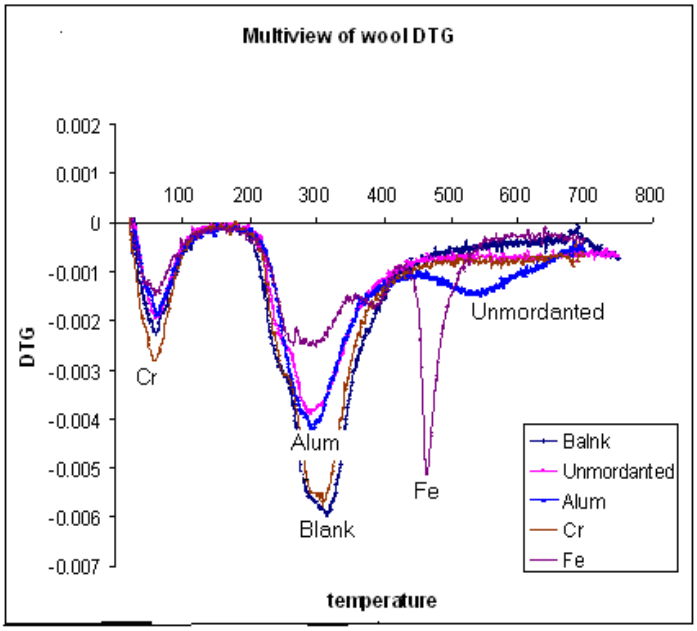


Figure 2: DTG of wool samples under the effect of different mordants

From the DTGA curves (figure 3), the peaks of the first step of the thermal process differs in shape and depth. The dyed unmordanted samples and the dyed mordanted with chrome or alum has the same depth, but the last one has broader peak with lower left shoulder than the right one. The dyed mordanted samples with ferrous has a shallow broad peak higher in place than the other three samples mentioned above. The thermo gram shows the improvement of thermal stability of the dyed wool sample mordanted with ferrous.

The peak representing the second step of thermal degradation of wool fabrics under investigation differ completely in shape and depth. The deepest peak is that for dyed sample mordanted with alum then little in depth that dyed samples mordanted with chrome, the peak of the dyed unmordanted sample is above peaks of both of those two samples by a noticeable distance. All these three peaks have nearly the same peak width and have shoulder either in left or right side or at both sides as in case of dyed unmordanted samples. The appearance of a shoulder in the peaks means the presence of impurities in the sample. This second peak when using ferrous as a mordant for wool fabric is shallow and wide in shape. A small sharp shoulder at its left side and its original right ending point is so lower than its left starting point.

Differential Scanning Calorimetry (DSC):

There are currently difficulties in measuring the melting transition of wool owing to its fibrous nature since level of cystine content may influence DSC analysis, and to the moisture sensibility of thermal transition[4].

The differences in DSC parameters can be related to the matrix material, i.e. the nonhelical parts of the intermediate filaments, the material between the filaments and all other amorphous, morphological components.

DSC has been used to measure temperature and heat of transitions, specific heat (which is a paramount thermal property), thermal emissivity and certain isothermal functions [17].

Within these general headings fall the measurement of glass transition Tg, crystallinity including the measurement of

enthalpy of melting, purity, rate of reactions, rate of crystallization and rate of decomposition.

DSC present three thermal events: glass transition, water evaporation and denaturation [4]. The first Tg observed , which normally ranges from ≈ 40 ˚C to ≈ 60 ˚C showing the glass transition, is difficult to be identified because the overlapping with the beginning of the big peak corresponding to water evaporation.

This peak appears at around 90-100 ˚C. The peak which is associated with the denaturation of the helicoidally material appears at around 230 ˚C.

Peaks are characterized by the peak temperature and the area of the peak. The glass transition is a second-order transition caused by relaxation of the chain segments in the amorphous portion of the polymer [15]

As literature reported [18], there are two different kinds of structure in the wool fiber, below 120 ˚C, wool mostly consists of normal keratin structure and above 130 ˚C the fiber will contract in the length and shows β-keratin structure.

The DSC curve exhibits a significant upward shift starting from around 210 ˚C, which is believed to correspond with the TGA (figure 1) However, superimposed on the abrupt upward shift is a small endotherm starting from 210 ˚C with its peak around 230 ˚C, which results from melting of the α- form crystallites in wool [16].

Table (II) shows the values of the heat of fusion (heat release) J/g, which is represented by the area under the endotherm peak of the decomposition step, and its rate, has been found to be very effective to evaluate fire hazards. It can be detected that for the first step, the dyed sample mordanted with chrome has the highest heat release value (-1.26 KJ/g), while that dyed and mordanted by ferrous has the lowest heat release (-64.03 KJ/g).

For the second step (decomposition step) the highest value is that for sample mordanted with alum followed by that mordanted with ferrous mordant (-863.34 J/g, -856.38 J/g respectively) and the lowest value is that for dyed unmordanted samples (49.45 J/g).

The decomposition temperature of any polymer depends on its molecular weight and its purity; also it is affected by its morphology. This decomposition temperature depends on the crystallinity of the polymer; the higher crystallinity has the higher decomposition peak [19].

The decomposition temperature represented in table (II) clarifies that, the lowest value occurs for sample mordanted with Fe (≈ 222 ˚C), while the highest decomposition temperature value (370 ˚C) is for the dyed unmordanted sample.

By highlighting figure (3), it can be noticed that there is a difference in the shape and area of the decomposition endotherms. As in the case of silk, the difference in shape can be attributed to the different degree of crystallinity.

However, wool is completely different from silk, as far as structure and morphology is concerned. The presence of segregated cellular compartments might have hindered diffusion of the additives with the bulkier aromatic side group. Peaks broadened as O-H content declined. Also, the extent of crystallinity or molecules order causes a reduction in the peak area [20].

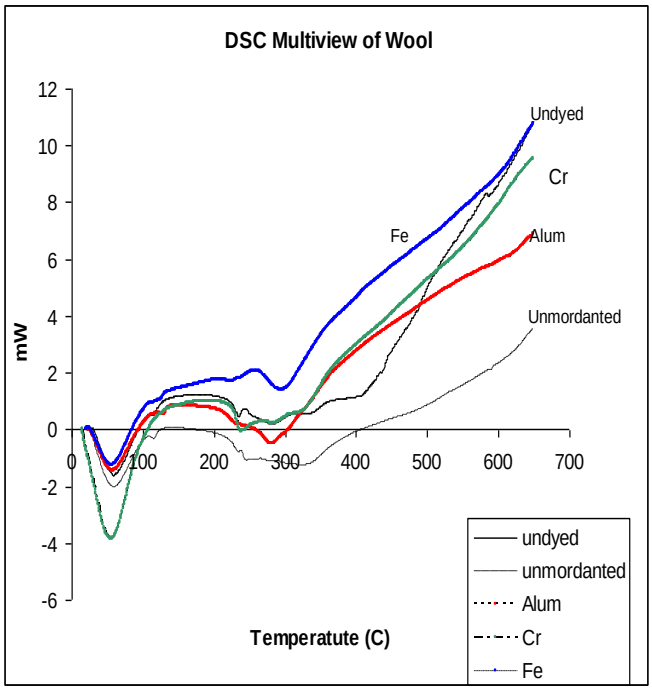


Figure 3: Differential scanning colorimetry (DSC) of wool samples under the effect of different mordants

An increase in the melting temperature is detected, meaning that the crystallinity and perfection of the crystal structure were enhanced, and it is reduced with increasing the degree of cross-linking of the hydroxyl groups of wool by hydrogen bonding with dye or mordant molecules in the amorphous phase.

Color Fastness to Light, Wash and perspiration:

The visual light fastness evaluated by the standard method of inspection for all the wool samples are given in table 3. It was noticed that the blank (unmordanted sample) was darkened after the exposure to artificial daylight and takes the lowest grade (3) while the largest value is for samples that dyed and mordanted with ferrous (5), i.e. good light fastness. The light fastness ranking order was as follows:

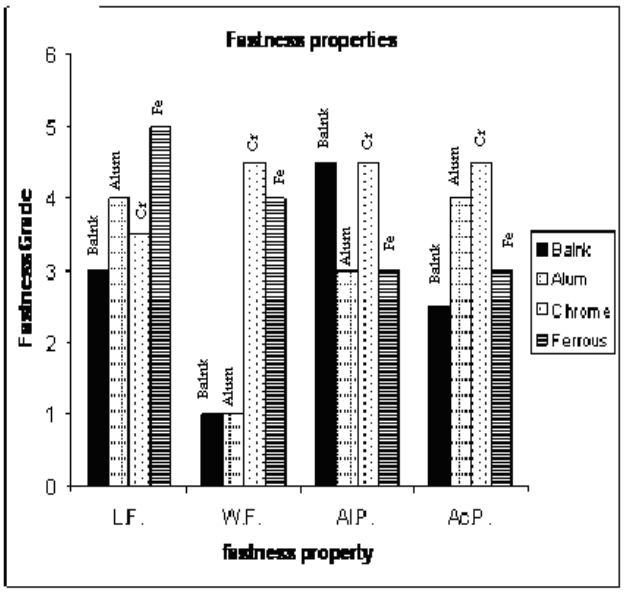
Fe> Alum > Cr > Blank

Regarding to the washing fastness listed in table 3 for all of the dyed and dyed mordanted wool samples, it is shown that both the dyed unmordanted sample and that mordanted with alum have the lowest alteration value (1), followed by the samples mordanted with ferrous and finally that mordanted with chrome. It is noticed that the unmordanted dyed samples darkened (turned from yellow to reddish brown) after washing taking the same alteration grade of their corresponding samples mordanted with alum (poor wash fastness).

In concerning the fastness to acidic perspiration, it is clarified that the dyed samples mordanted with chrome has the highest fastness to perspiration (4-5), while the dyed unmordanted (blank0 samples have the lowest (2-3).

Besides, the alkaline perspiration reveals that, both dyed unmordanted samples and that mordanted with chrome showed the highest alteration grade (4-5) followed by that mordanted with ferrous and alum. The alteration on wool samples takes the order:

For the acidic perspiration: Chrome > Alum> Ferrous > >blank



For alkaline perspiration: Chrome =Blank> Alum= Ferrous

Figure 4: Different fastness properties of the dyed samples under the effect of different mordants

Finally, we can say that, chrome post mordant shows almost the highest fastness properties when applying on naturally dyed wool samples on using sambucus nigra dye.

Conclusion

Sambucus nigra was used to dye wool fabric samples. The procedures of dyeing and mordanting were applied easily in the limits of the legal environmental conditions, with low costs and the dye uptake including the fastness to washing, perspiration and light for the dyed and dyed mordanted wool fabric samples is noticeable where fair to good fastness levels were obtained

Thermal analysis technique is a very accurate tool to differentiate between the thermal stability of wool fabric samples after dyeing and\or mordanting and to understand the mechanism of mordanting. TGA and DSC analysis showed that the mechanism of mordanting by chrome converts the wool fabric to a carbonaceous residue or char when exposed to high temperature and hence reduce the volatile formation. The initial decomposition temperature (breaking of water linkage) for all the samples is nearly comparable, while the heat release (J\g) differ from one sample to another and the highest value is for dyed sample mordanted with chrome .

Studying the fastness properties of the samples under test should that, chrome had almost the highest fastness grade compared to the other corresponding samples, which agree well with the results obtained from the thermal analysis. This means that, dyed wool samples with sambucus nigra and post mordanted with chrome may act as eco-friendly and flame resistant textile apparel.

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Table 1: The weight loss of the blank (undyed), dyed and dyed and mordanted wool samples using different Mordants

Sample	First step		Second step		Third step		Total	
	Weight loss %	Mid Point (˚C)	Weight loss %	Mid Point (˚C)	Weight loss %	Mid Point (˚C)	Weight loss %	Mid Point (˚C)
Blank (undyed)	-9.497	66.46	-52.76	307.79	-12.091	532.81	-74.75	311.25
Dyed unmordanted	-9.689	68.00	-38.913	297.81	-28.011	535.24	-76.988	323.76
Mordanted with Alum	-9.403	69.35	-41.237	303.29	-25.377	534.54	-76.920	332.720
Mordanted with Chrome	-11.276	62.96	-44.150	304.49	-17.520	480.59	-73.041	312.09
Mordanted with Ferrous	-10.958	71.42	-44.528	322.41	-17.810	549.12	-77.844	354.81