



**ICCOM-COLORTEX-
ENEA - ICCOMCNR-
SERICHIM-INESCOP**

**Study on the different
fatliquoring agents
currently used in the
EU tanneries**

DELIVERABLE D2

ACTION 1-2

January 2012–May 2013

**LIFE ECOFATTING PROJECT
LIFE10 ENV/IT/000364**

**ENVIRONMENTALLY
FRIENDLY NATURAL
PRODUCTS INSTEAD OF
CLOROPARAFFINES IN THE
FATTING PHASE OF THE
TANNING CYCLE**



TABLE OF CONTENTS

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4. ECOFATTING NOTICE BOARD IN ENEA PREMISES.....

**1) THERMOGRAVIMETRIC ANALYSIS ON THE DIFFERENT FATLIQUORING
AGENTS CURRENTLY USED IN THE EU TANNERIES.....P. 3**

2) THERMOGRAVIMETRIC ANALYSIS IN AIR.....P. 8

- THERMOGRAVIMETRIC ANALYSIS ON THE DIFFERENT FATLIQUORING AGENTS CURRENTLY USED IN THE EU TANNERIES

In order to investigate the thermal behaviour of different fatliquoring agents currently used in EU tanneries, thermogravimetric analysis has been performed on 12 samples of leather and fatliquoring components, as reported below:

- 1) Light chrome tanned leather (CL) named SKIN POWDER (SCP,CP30,CP44,BLANK)
- 2) GELATIN B (SCP,BLANK)
- 3) SKIN POWDER + H₂O (SCP,CP44, BLANK)
- 4) GELATIN B + H₂O (SCP,CP30,BLANK)

Heating program the analysis was performed by using NETSCH instrument in particular STA 401 C model (Figure 1). This instrument is equipped with four main components:

- a) Furnace
- b) Sample carrier and crucible
- c) Balance
- d) Electronic control



Figure 1: Balance and furnace in TG NETZSCH 409 C.

Dynamic flux in argon and air were used for different set of measurements respectively in a temperature ranging between 30 °C-1000 °C. The temperature of the

furnace is controlled by thermocouple type B whereas thermocouple type S on the sample carrier is used for measurements.

For analysis in argon flow, the chamber of the furnace was washed three times, making vacuum and subsequently introducing argon. Sample carrier and crucible used for these analysis are made completely in alumina.

The program heating is set up to 2°/min from 30°C up to 200°C and 10°C/min from 200°C up to 1000°C.

For all the measures 15-20 mg of sample were used.

Thermogravimetric analysis was performed on several samples samples by ENEA and it is still in progress in order to evaluate the effects of tanning and fatliquoring agents on the thermal stability of gelatin and chrometanned leather.

TGA analysis has been focused so far on gelatin and CL samples treated following d) procedure.

Figures 2 shows TG curves in argon flow (A) and air flow (B) of untreated CL. shows two main inflections, which proved by DTG.

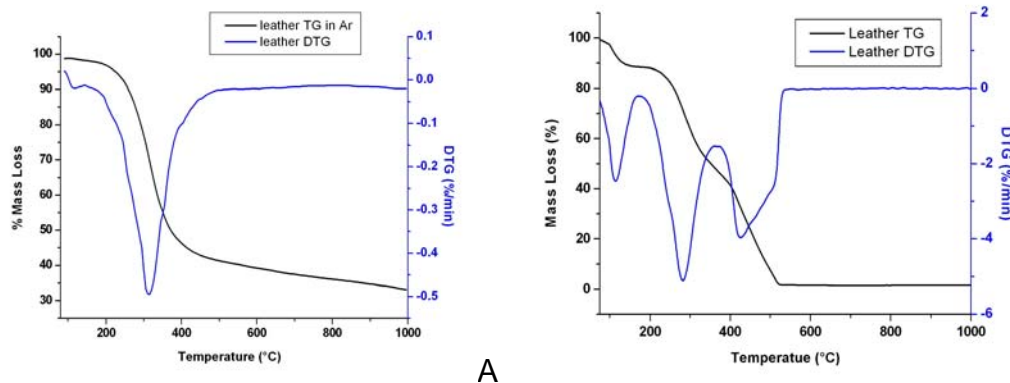


Figure 2. TG and DTG of CL in argon flow (A, pyrolysis) and air flow (B, combustion) of untreated CL.

The first inflection starts around 75 °C, which corresponds to 2% weight loss in the leather sample due to the release of humidity entrapped by leather fibers and reaches the highest losses around 122 °C. Then, the leather sample started to decompose at 268 °C up to maximum transition reaches at 310 °C, which corresponded to the decomposition temperature of chrome-tanned leather with weight loss of 57 % (figure 1.17A).

TG in air flow (Figure 1.17 B) shows an initial weight loss of 11% starting around 75°C; the main decomposition takes place in two steps starting from 220°C, where a gradual decomposition of the tanned leather began; the first inflection occurred at 282 °C with weight loss 41% and the last inflection appeared at 426°C with weight loss 46 %.

1) THERMOANALYSIS IN ARGON (pyrolysis)

- Skin Powder (CL)

Skin Powder + SCP	Line Green
Skin Powder + CP30	Line Red
Skin Powder + CP44	Line Blue
Skin Powder Blank	Line Violet

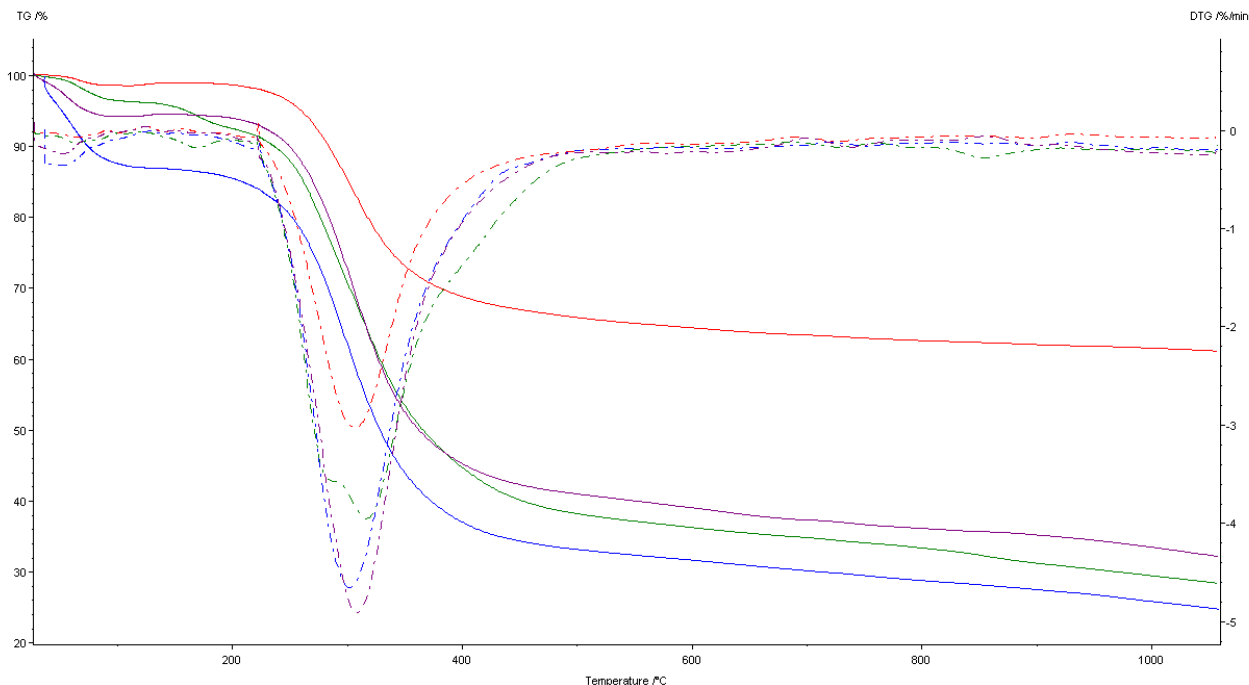


Figure 3: TG and DTG curves for Skin Powder samples

samples	I STEP	TEMP I STEP	II STEP	TEMP II
Skin Powder + SCP	8.53 %	63.6 °C	63.68 %	316 °C
Skin Powder + CP30	1.78 %	68.4 °C	40.57 %	306 °C
Skin Powder + CP44	16.03 %	51.1 °C	59.21 %	302 °C
Skin Powder Blank	6.64 %	51.8 °C	60.78 %	308 °C

The first inflection is around 52 °C, which corresponds to 7% weight loss in the untreated leather sample due to the release of humidity entrapped by leather fibers. The untreated leather sample started to decompose at 268 °C and the maximum transition was reached at 308 °C, which corresponded to the decomposition temperature of chrome-tanned leather with weight loss of 61 % (figure 3). The treatment with CPs did not significantly change the decomposition temperature, while the treatment with SCP increases of about 8°C this temperature, suggesting a stabilization of the material.

- **Gelatin B**

Gelatin B + SCP	Line Green
Gelatin B Blank	Line Red

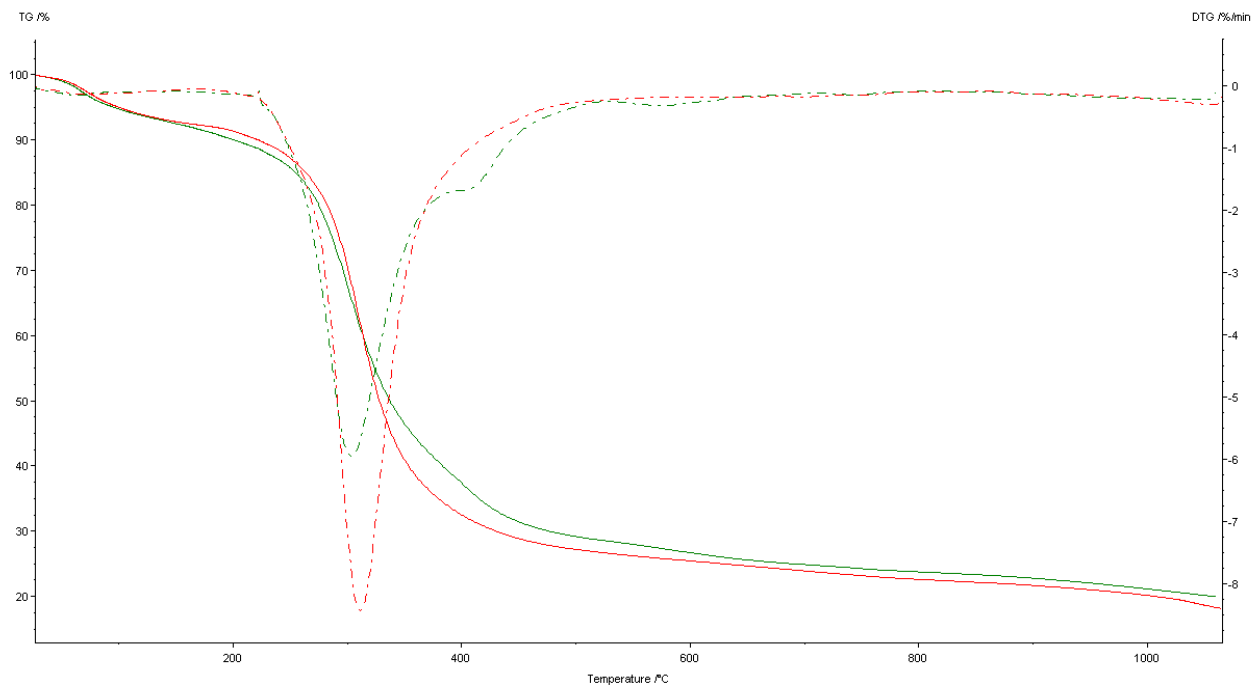


Figure 4: TG and DTG curves for Gelatin B samples

Sample	I STEP	TEMP I STEP	II STEP	TEMP II STEP
SCP	9.85 %	64 °C	68.73 %	303 °C
Blank	8.48 %	68 °C	71.94 %	311 °C

In GSB showed a decrease of the main peak related to the decomposition temperature. However, a shoulder around 410 °C was suggestive of a fraction of GSB molecules modified by SCP and strongly stabilized by the interaction with SCP.

- **Skin Powder + H2O**

SCP	Line Green
Powder CP44	Line Red
Blank	Line blue

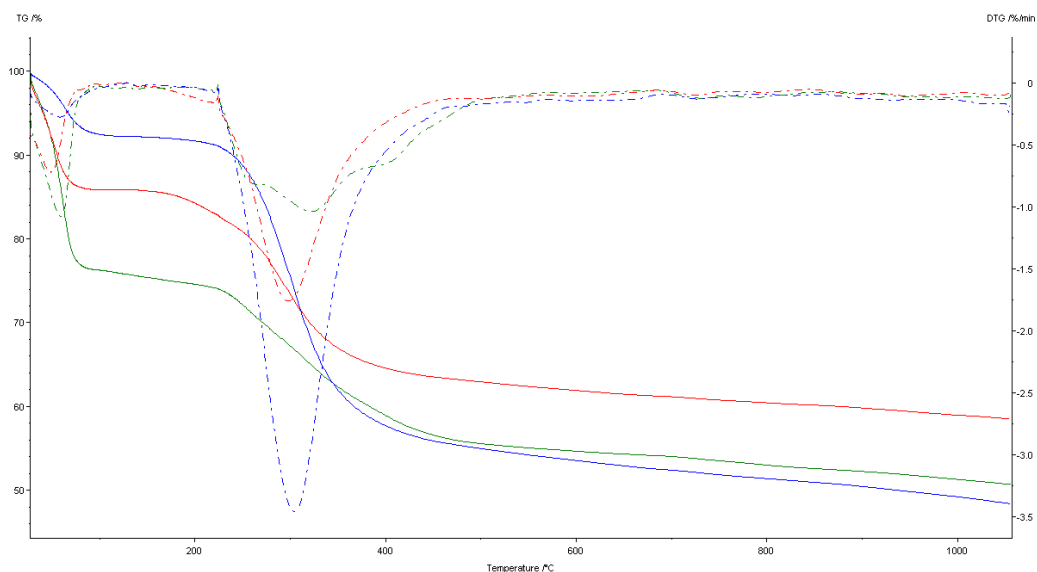


Figure 5: TG and DTG curves for Skin Powder + H₂O samples

Sample	I STEP	TEMP I STEP	II STEP	TEMP II STEP
Powder + H2O + SCP	25.27 %	59 °C	23.46 %	321 °C
Powder + H2O + CP44	15.57 %	57 °C	26.93 %	297 °C
Powder + H2O + Blank	8.17 %	48 °C	42.89 %	304 °C

TGA analysis was performed also on wet samples. Also in this case the significant results is the increase of the temperature of the main decomposition peak in SCP-treated sample from 304 to 321 °C.

In this case CP- and SCP-treated GSB samples showed a decrease of the main peak related to the decomposition temperature from 319°C to 299 nd 307°C. Also in this case the SCP-treated GSB presents a shoulder around 400-410 °C.

- **Sample Gelatin B + H2O**

SCP	Line Green
Powder CP30	Line Red
Blank	Line blue

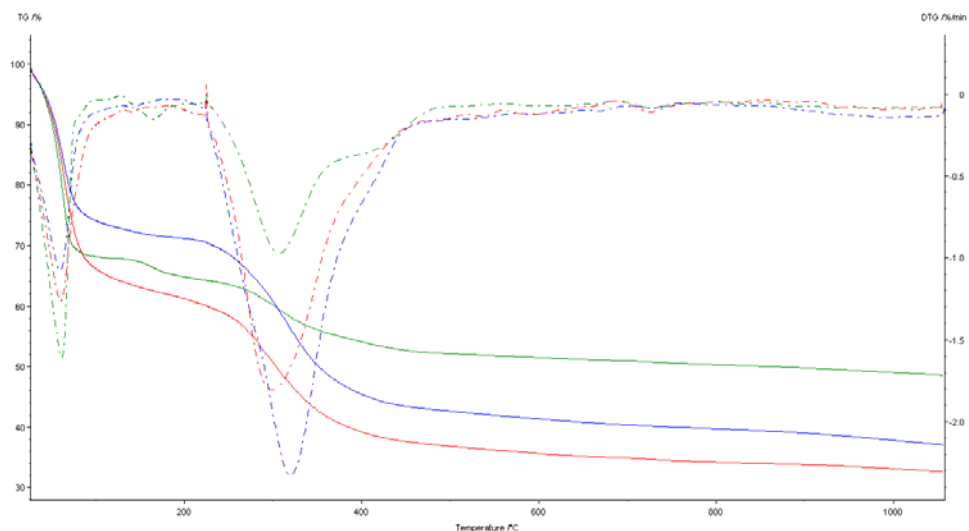


Figure 6: TG and DTG curves for Gelatin B + H₂O samples

Sample	I STEP	TEMP I STEP	II STEP	TEMP II STEP
SCP	35.07 %	61 °C	23.29 %	307 °C
CP44	38.53 %	60 °C	42.50 %	299 °C
BLANK	28.62 %	60 °C	25.28 %	319 °C

2) THERMOGRAVIMETRIC ANALYSIS IN AIR

- SKIN POWDER

Skin Powder + SCP	Line Green
Skin Powder + CP30	Line Red
Skin Powder + CP44	Line Blue
Skin Powder Blank	Line Violet

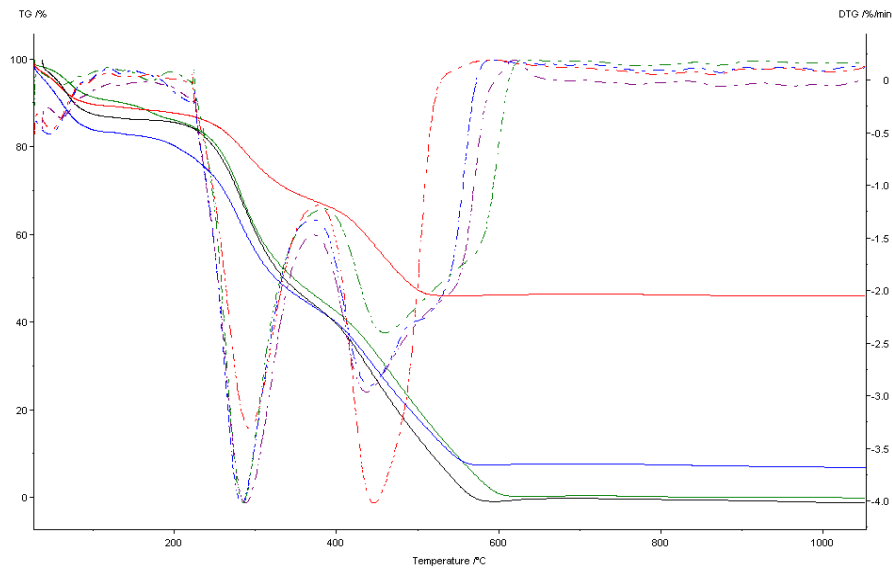


Figure 7: TG and DTG curves for Skin Powder samples

Sample	Step I	Temp I	Step II	Temp II	Step III	Temp III
SCP	13.77 %	61 °C	41.66 %	285 °C	44.01 %	461 °C
CP30	12.16 %	48 °C	20.74 %	284 °C	21.16 %	445 °C
CP44	19.68%	45 °C	37.58 %	282 °C	36.11 %	440 °C
Blank	14.29 %	61 °C	41.44 %	287 °C	45.11 %	437 °C

- **GELATIN B**

Gelatin B + SCP	Line Green
Gelatin B Blank	Line Red

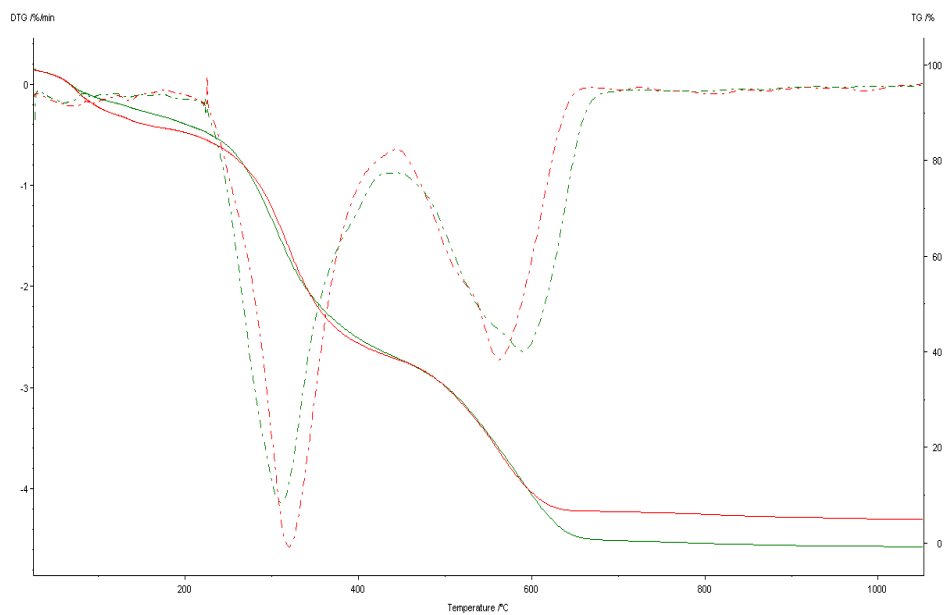


Figure 8: TG and DTG curves for Gelatin B in air.

Sample	Step I	Temp I	Step II	Temp II	Step III	Temp III
B SCP	12.15 %	66 °C	49.19 %	310 °C	37.98%	589 °C
B Blank	13.88 %	61 °C	47.75 %	319 °C	31.63 %	562 °C

- SKIN POWDER + H2O

Skin Powder + SCP	Line Green
Skin Powder + CP44	Line Blue
Skin Powder Blank	Line Violet

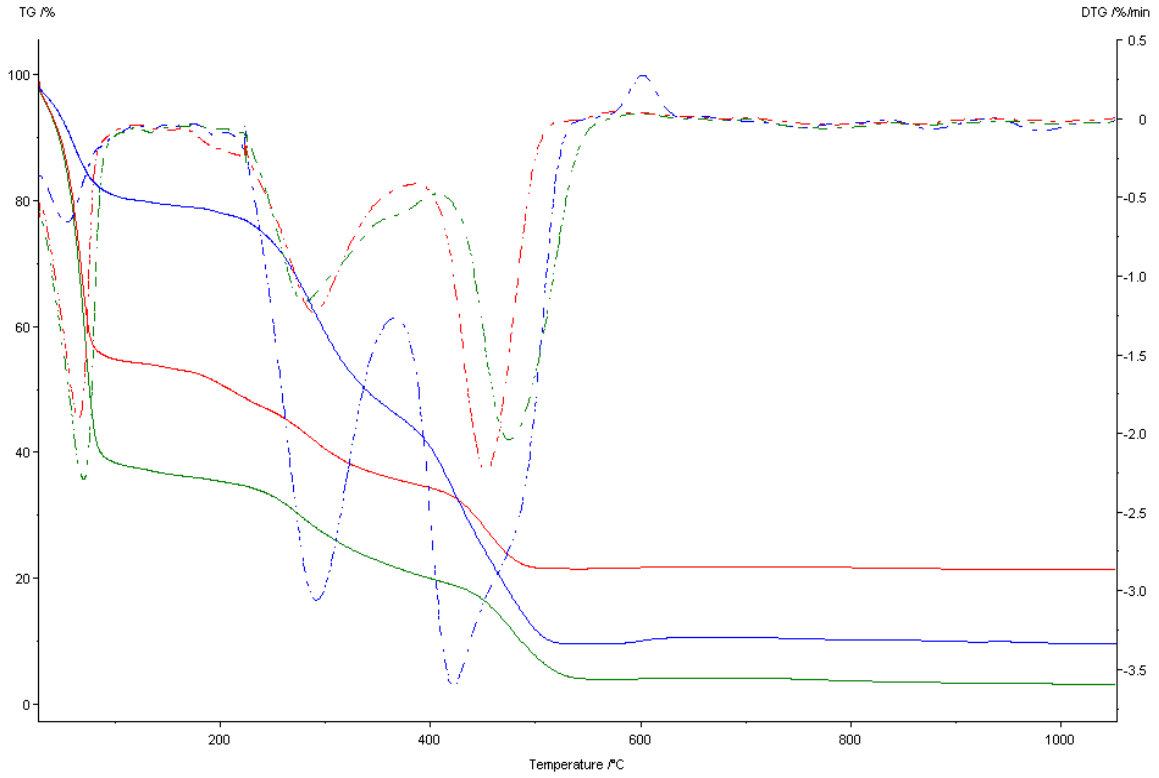


Figure 9: TG and DTG curves for Skin Powder + H₂O samples

Sample	Step I	Temp I	Step II	Temp II	Step III	Temp III
Powder+SCP	62.29 %	53 °C	31.90 %	279 °C	17.51 %	474 °C
Powder+CP44	47.07 %	65 °C	15.27 %	288 °C	14.25 %	452 °C
Powder+Blank	21.79 %	69 °C	13.72 %	291 °C	36.61 %	421 °C

- **Sample GELATIN Sigma B + H₂O**

GB + SCP	Line Green
GB + CP30	Line Red
Skin Powder Blank	Line Blue

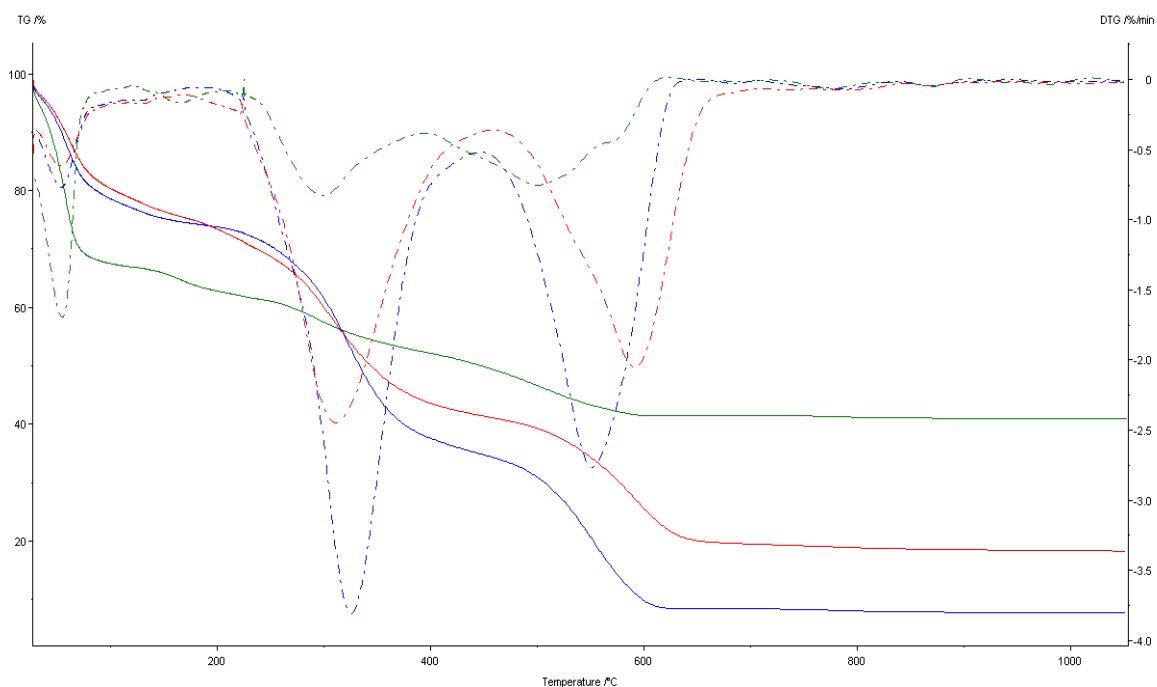


Figure 10: TG and DTG curves for Gelatin B + H₂O samples

Sample	Step I	Temp I	Step II	Temp II	Step III	Temp III
SCP	36.98 %	54 °C	10.39 %	300 °C	11.50 %	500 °C
CP30	26.45 %	53 °C	31.50 %	311 °C	22.21 %	591 °C
Blank	26.02 %	53 °C	38.28 %	325 °C	27.01 %	552 °C

Conclusions.

TG results obtained in argon flow generally show that SCP-treated samples present a shift of the main decomposition peak at higher temperature, suggestive of a stabilization of protein structure, or the appearance of a shoulder around 400-410°C. In air the combustion peak at 437 and 421 °C found in dry or wet untreated CL showed a strong increase both for CP as well as for SCP treated samples. This could correlate with the strong interaction of CP and SCP with CL fibers. GSB data showed analogous results. However wet GSA samples showed a decrease of the temperature of the two main combustion peaks, likely due to a competition of water molecules with CPs and SCP products.