

## Biomacromolecules as novel green flame retardant systems for textiles: an overview

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### SUPPLEMENTARY INFORMATION

#### *Materials*

Cotton (COT, 200 g/m<sup>2</sup>), polyester (PET, 175 g/m<sup>2</sup>) and a blend consisting of 65% PET and 35% COT (PET-COT, 245 g/m<sup>2</sup>) were purchased from Fratelli Ballesio S.r.l. (Torino, Italy).

DNA from herring sperm, caseins (12-15  $\alpha$ -s<sub>1</sub>, 3-4  $\alpha$ -s<sub>2</sub>, 9-11  $\beta$  and 2-4  $\kappa$ ) and chitosan powders (all reagent grade) were purchased from Sigma-Aldrich S.r.l. (Milano, Italy) and stored at 4°C before its application to the fabrics.

A commercial hydrophobin solution (H Star Protein B liquid<sup>®</sup>) was kindly supplied from BASF (Italy). The aqueous solution contains 5% hydrophobins (a mixture of class I and class II: the composition is unknown).

WPI powder (93.5 wt.% protein) was purchased from Anderson Research (Cervaro (FR), Italy); its overall composition also includes lipids (ca. 0.5 wt.%), carbohydrates (ca. 1 wt.%), ash (ca. 2.2 wt.%), and moisture (ca. 2.8 wt.%).

The structures of DNA,  $\alpha$ -caseins and hydrophobins (class II) are schematized in Figure S1.

All the suspensions/solutions of these biomacromolecules were prepared using 18.2 M $\Omega$  deionized water supplied by a Q20 Millipore system (Milano, Italy).

#### *Characterization techniques*

The surface morphology of the treated samples was studied using a LEO-1450VP Scanning Electron Microscope (beam voltages: 5 and 20 kV for fabrics and residues,

respectively); an X-ray probe (INCA Energy Oxford, Cu-K $\alpha$  X-ray source,  $k=1.540562 \text{ \AA}$ ) was used to perform elemental analysis. Fabric pieces ( $5 \times 5 \text{ mm}^2$ ) were cut and fixed to conductive adhesive tapes and gold-metallized.

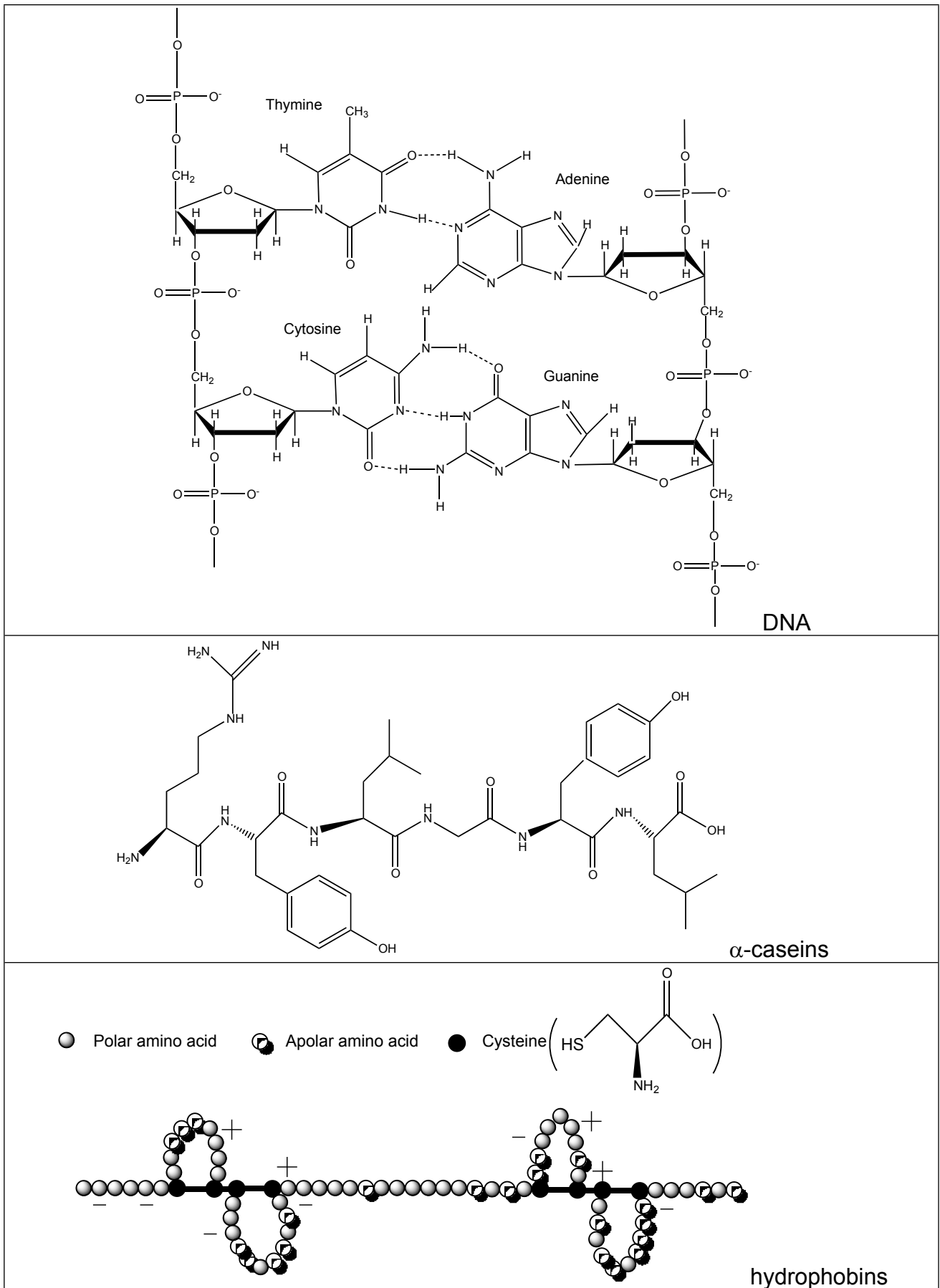
The thermal and thermo-oxidative stability of the fabrics was evaluated by thermogravimetric (TG) analyses in nitrogen and in air, respectively, from 50 to 800°C with a heating rate of 10°C/min. A TAQ500 analyzer was used, placing the samples (about 10 mg) in open alumina pans, in inert or oxidative atmosphere (gas flux: 60 ml/min). In the followings,  $T_{\text{onset}10\%}$  and  $T_{\text{max}}$  will be defined as the temperature corresponding to a weight loss of 10% and the maximum weight loss rate, respectively.

Flammability tests in horizontal configuration were carried out by applying a 25 mm methane flame for 3 s on the short unclamped side of the specimen ( $25 \times 100 \times 0.5 \text{ mm}^3$ ), which was clamped in its three quarters by using a U-shaped metallic frame. These tests were repeated 3 times for each formulation. Total burning time (s), char length (mm), total burning rate (calculated as the ratio between the char length and total burning rate, mm/s) after the flame application, as well as the final residue (%) were evaluated.

In addition, LOI (Limiting Oxygen Index) tests were performed with a FIRE oxygen index apparatus according to the ASTM D2863 standard.

The combustion behaviour of square fabric samples ( $50 \times 50 \times 0.5 \text{ mm}^3$ ) was investigated by cone calorimetry (Fire Testing Technology, FTT). The measurements were carried out under two irradiative heat fluxes (35 or 50 kW/m $^2$ ), in horizontal configuration, following the procedure described elsewhere (Tata J, Alongi J, Carosio F, Frache A. Optimization of the procedure to burn textile fabrics by cone calorimeter: part I. Combustion behavior of polyester. *Fire and Materials* 2011;35(6):397-409.). Such parameters as Time To Ignition (TTI, s), Flame Out (FO, s) and peak of Heat Release Rate (pkHRR, kW/m $^2$ ) were measured. The experiments were repeated four times for each material investigated to ensure reproducible and significant data; the experimental error was within 5%.

Prior to flammability and combustion tests, all the specimens were conditioned at  $23 \pm 1^\circ\text{C}$  for 48 h at 50% R.H. in a climatic chamber.



**Figure S1** Structures of DNA,  $\alpha$ -caseins and hydrophobins (class II; + and - signs indicate charged amino acids)