# New Closed- and Open-Cell, Aldehyde-Free Protein Foams

María Cecilia Basso[1]* and Antonio Pizzi[1,2]

[1]*LERMAB, University of Lorraine, 27 Rue Philippe Seguin, 88000 Epinal, France*
[2]*Department of Physics, King Abdulaziz University, Jeddah, 21589, Saudi Arabia*

Received May 06, 2016; Accepted July 14, 2016

**ABSTRACT:** New aldehyde-free and isocyanate-free biofoams have been obtained by reacting albumin chicken egg white and dimethyl carbonate (DMC). The optimized formulations yielded lightweight foams whose densities were evaluated as 0.016–0.16 g/cm$^3$. Mechanical resistance was 0.023–0.34 MPa and residual pH nearly neutral. The new foams presented up to 57% of closed cells as measured by helium pycnometry and good thermal insulation. These new natural foams are environmentally friendly materials and show very promising properties.

**KEYWORDS:** Aldehyde-free and isocyanate-free, biobased foams, closed- and open-cell, dimethyl carbonate, protein

## 1 INTRODUCTION

Polymer foams are employed in a wide range of applications such as thermal insulation, sound absorption, packaging, structural use, buoyancy and more recently in the biomedical field, etc. [1–3]. Polyurethane, phenolic, polystyrene and polyoleofin foams are the main types of cellular materials which are composed of raw materials derived from petrochemical resources.

Nowadays, environmental and even economic considerations have encouraged the development of alternative materials from renewable resources [2, 4, 5]. In this way, thanks to their ubiquity of supply, abundance and high functionality, proteins constitute an attractive raw material for polymeric foam production [5]. Some old technologies exist to crosslink proteins effectively. Protein skeletal amido-groups, and also some amino-acid amino groups, i.e., in casein, react readily with aldehydes to form cross-linked, stable networks once heated [6, 7]. Based on this technology, some works concerning the preparation and properties of rigid/elastic foams derived from albumin egg white and formaldehyde have already been described [8, 9]. Further, tannin-albumin foams have been produced under either acid or alkaline conditions [10]. These materials showed densities higher than 0.15 g/cm$^3$ and open-cell structure, like classical tannin foams [11, 12].

Recently, Basso *et al.* [13] studied a novel and non-conventional crosslinking reaction of proteins, such as albumin, and dimethyl carbonate (DMC). This last compound reacts mainly with amino group of the side chains of the lysine and the –OH group of the side chain of glutamic acid, and not with the peptide skeletal group of the protein. New bioplastics and biofoams were so formulated which showed densities of 0.1 g/cm$^3$ and open-cell structure.

In this context, the present work focuses on the development of more lightweight and open- or closed-cell foams from albumin chicken egg white and DMC, without addition of either aldehydes or isocyanates. Several formulations of the new albumin-based foams are presented for the first time in this article and the main properties of these biomaterials are characterized.

## 2 EXPERIMENTAL

### 2.1 Materials

Albumin powder (chicken egg white) and pentane were supplied by ACROS (Geel, Belgium). Dimethyl carbonate and polyethylene glycol sorbitan monooleate (Tween 80) were purchased at Sigma-Aldrich (Steinheim, Germany). TEA-lauryl sulfate (Sulfetal LT) was provided by Zschimmer & Schwarz (Vercelli, Italy).

### 2.2 Foam Preparation

Several mixtures were prepared in order to obtain the new biobased foams according to the compositions shown in Table 1.

*Corresponding author: cecilia-c-c@hotmail.com

**DOI: 10.7569/JRM.2016.634124**

**Table 1** Formulations P1–P6 for the preparation of new natural foams based on albumin egg white–DMC reaction.

| Sample name | P1 | P2 | P3 | P4 | P5 | P6 |
|---|---|---|---|---|---|---|
| Water (%) | 48.5 | 70.2 | 54.3 | 56.9 | 59.5 | 53.2 |
| Albumin (%) | 24.2 | 14 | 17.4 | 18.2 | 19 | 27.7 |
| DMC (%) | 12.1 | 7 | 17.4 | 9.1 | 9.5 | 8.5 |
| Pentane (%) | 4.6 | 2.6 | 3.3 | 7.9 | 3.7 | 3.2 |
| Tween 80 (%) | 1.5 | 0.9 | 1.1 | 1.1 | 1.2 | 1.1 |
| Sulfetal LT (%) | 9.1 | 5.3 | 6.5 | 6.8 | 7.1 | 6.4 |

For each case, the protein was added to the blend previously prepared by mixing water and surfactants (Tween 80 and Sulfetal LT). The mixture was strongly beaten with an electrically driven mechanical whisk to obtain a white foam similar to what is known in cooking as whipped egg white. Subsequently, a mixture composed of DMC and pentane were incorporated and mechanically stirred for 20 s (pentane had to be used as blowing agent because the addition of DMC broke the aerated foam). Immediately, an endothermic reaction took place and the emulsion got dark and became instantly very thick and sticky. This reaction between albumin and DMC has already been properly described [13]. Afterwards, it was quickly put into a ceramic closed mold which was placed in a water bath at constant temperature of 60 ± 2 °C for 45 min to allow foam formation thanks to the evaporation of pentane. Finally, the specimen was deposited overnight in an oven preheated at 78 ± 2 °C where total hardening was carried out. The samples were stored for further analysis in a climatic chamber for one week using standard climate conditions (23 ± 2 °C and 65 ± 5% RH).

## 2.3 Foam Characterization

Blocks of foam with dimensions of 2.5 × 2.5 × 1.5 cm were weighed to obtain their bulk density. The cellular morphology of the foams prepared was observed by scanning electron microscopy (SEM) (TM3000, Hitachi, Japan) at x50 magnification (samples P4 and P5) and x100 magnification (sample P6). Different magnifications have been applied due to the differences between cell sizes of the samples being evaluated. A gas pycnometer (Model Accupyc 1330, Micromeritics, Georgia, USA) was employed in order to evaluate the proportion of closed/open-cells according to the ratio between skeletal density of foam and skeletal density of pulverized foam. The porosity Φ (dimensionless) is defined by: Φ = 1 – (bulk density/skeletal density) [14]. The mechanical resistance to compression was investigated with an Instron 4206 universal testing machine (Instron Corporation, Norwood, MA, USA) at a load rate of 2.0 mm/min. The thermal conductivity of the foam samples was measured by the transient plane source method (Hot Disk Model TPS 2500S, Hot Disk AB, Gothenberg, Sweden) at room temperature. The pH measurements were recorded by means of a Hanna pH meter (Hanna Instruments, Lingolsheim, France) at room temperature. Residual pH of the foams was measured after soaking and wringing a piece of 2 cm edge cubic sample in deionized water. To analyze the foams' water uptake kinetics, specimens of 2.5 × 2.5 × 1.5 cm were weighed (M1) and then placed on a beaker with water where water uptake by capillarity was evaluated for 2, 30, 120, 720 and 1560 min. After each time period the samples were drained for 10 min on a metal grid and then weighed again (M2). The percentage of water uptake (WU, in vol%) was calculated as:

$$WU = (M2 - M1) \times 100/BV \quad (1)$$

where BV is the block volume.

No significant differences in results were noticed within the specimens coming from the 4 foam repetitions prepared for each case.

# 3 RESULTS

Mixture P2 (Table 1) did not yield a solid sample due to its too high proportion of water. Crosslinking did not occur even when the curing time in the oven was extended to 36 h. Conversely, a non-foamed plastic was obtained from mixture P3, which included a very high proportion of crosslinking agent, i.e., DMC, because in this case complete crosslinking occurred before expansion took place. This plastic had a density of 0.71 g/cm$^3$ and was similar to the ones previously presented by Basso *et al.* [13].

The aspect of sample P1 was very heterogeneous because as the water content in the initial blend was too low (Table 1), it became too viscous and it could not be properly homogenized. Moreover, the average density of the P1 foam was higher than 0.25 g/cm$^3$ because the low water content did not lead to an appropriate equilibrium between rates of foam expansion and hardening. Thus, polymerization was too fast in relation to expansion.

The optimized proportions in compositions P4, P5 and P6 (Table 1) provided better control of the expansion/hardening ratio and yielded lightweight foams which were white-colored. Their main properties are shown in Table 2 and the macroscopic aspect of sample P4 is shown in Figure 1a.

These new materials are derived from albumin egg white and are completely aldehyde- and

  

isocyanate-free. Therefore they are much more environmentally acceptable than the albumin-derived foams previously reported [8, 9]. Furthermore, they are lighter than the biobased foams previously described by Li *et al.* [8, 9] and Lacoste *et al.* [10] because their foaming is based on the utilization of pentane as blowing agent, while the previous protein foams were expanded by aeration when the protein was mechanically beaten. Moreover, heat curing of these new foams was more gradual than for the biofoams prepared by Lacoste *et al.* [10]. Surfactants (see Table 1) were also used in order to improve the compatibility of the reactants and to prevent the cell wall from becoming unstable during foaming [15, 16].

**Table 2** Properties of natural foams P4–P6 obtained from albumin egg white–DMC reaction.

| Sample name | P4 | P5 | P6 |
|---|---|---|---|
| Bulk density (g/cm$^3$) | 0.016 | 0.025 | 0.16 |
| Residual pH | 7.6 | 7.7 | 7.7 |
| $WA_{26h}$ (vol%) | 29 | 35 | 87 |
| Compression strength at 20% strain (MPa) | 0.023 | 0.055 | 0.340 |
| Average cell size (mm) | 0.9 | 0.9 | 0.5 |
| Porosity | 0.979 | 0.978 | 0.881 |
| Closed-cell content (%) | 47 | 57 | 13 |
| Thermal conductivity (W/mK) | 0.034 | 0.031 | 0.044 |

The densities of these new biofoams (Table 2) were directly proportional to their albumin content (Table 2). Thus, the densities of samples P4 and P5 were lower than 0.03 g/cm$^3$. The density of sample P6 was higher because of its higher proportion of albumin. The albumin-DMC- pentane foams previously prepared by Basso *et al.* [13] have a density more than three times higher than that of new foams P4 and P5.

The thermal conductivities of the new albumin foams (Table 2) indicate good insulation properties as they are comparable or better, especially for P4 and P5 samples, than those evaluated for other foams derived from albumin and other natural renewable resources [9–11, 17, 18]. Such values are comparable with those of

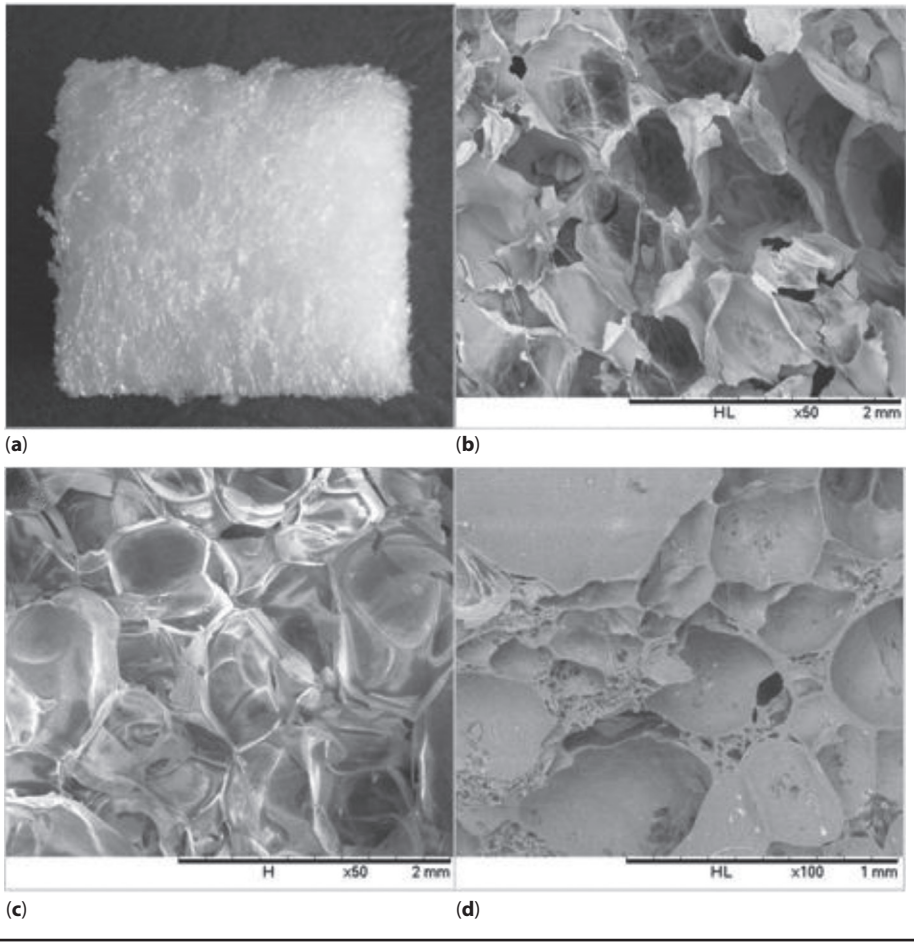


**Figure 1** New natural foams from albumin: (**a**) macroscopic examination of sample P4; (**b–d**) SEM images of samples P4, P5 and P6, respectively.

phenolic foams [2], e.g., 0.04–0.08 W/mK for densities 0.04–0.2 g/cm$^3$ [19], polyethylene foams and extruded polystyrene foams [2]. According to Table 2, thermal conductivity seems to decrease with the increasing closed-cell content of samples (see below).

The residual pH of samples P4, P5 and P6 was 7.7 ± 0.1. Thus, contrary to acid-catalyzed foams, they can be used as insulation in prolonged contact (i) with wood structures, like panels, without risk of hydrolysis of cellulose and hemicelluloses [20] and (ii) with metallic structures, without risk of acid corrosion [2].

The SEM images of samples P4, P5 and P6 are presented in Figures 1b, c and d, respectively. Samples P4 and P5 showed mainly closed-cells which were separated from their neighbors by thin membranes. In some places, the membranes were cracked. This occurred mainly in the structure of the P4 foam in which the proportion of pentane was highest. The average cell size of samples P4 and P5 was similar, but higher than for sample P6 (Table 2).The microscopic structure of sample P6 was rather different: the cell size distribution seemed very uneven, heterogeneous and irregular and most of the cells presented several microbreaks in their walls.

According to Table 2, the closed-cell proportion was higher when the content of DMC increased (Table 1), i.e., P5 > P4 > P6: the rise in the proportion of the hardener (DMC) favored crosslinking rather than expansion. This has been reported already for sample P3 (see above) which was such an extreme case that foaming did not take place at all. In sample P5, the polymeric network began to be generated before blowing. Therefore, the structure in formation was already resistant to supporting pentane evaporation without full cell breaking. Conversely, sample P6 exhibited mainly open-pore structure due to its low DMC content. Contrary to most tannin-derived foams [10, 11, 21], two factors seemed to contribute to closed-cell structure generation in the new biofoams: (i) the fast start of polymerization when DMC was added to albumin (see Section 2.2) and (ii) the lack of an abrupt exothermic reaction which would have led to the fast evaporation of volatiles and water and so to cell walls breaking.

Water uptake by capillarity (WA) of samples P4, P5 and P6 was evaluated at different times. From Figure 2 it was found that the great extent of WA was reached during the first hours and it depended directly on the albumin proportion in each formulation (Table 1). Proteins include polar amino acids able to bind water by hydrogen bonds. Thus, WA after 26 h ($WA_{26h}$) for sample P6, which included 27.7% of albumin, was 87%, while for P4 sample (18.2% of albumin), it was 29%. The $WA_{26h}$ for sample P5, whose albumin content was intermediate, was 35%. After the water absorption test, the specimens became more elastic. This was already

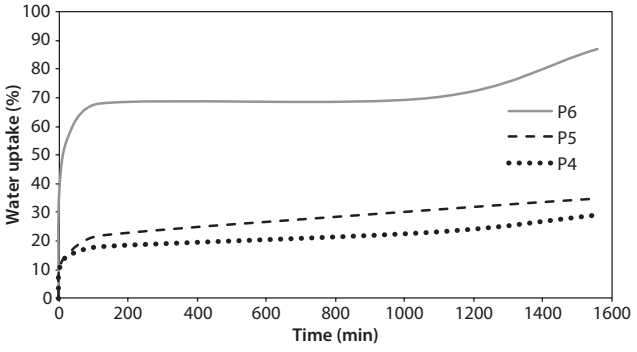


**Figure 2** Kinetics of water uptake for new albumin-based foams (samples P4, P5 and P6).

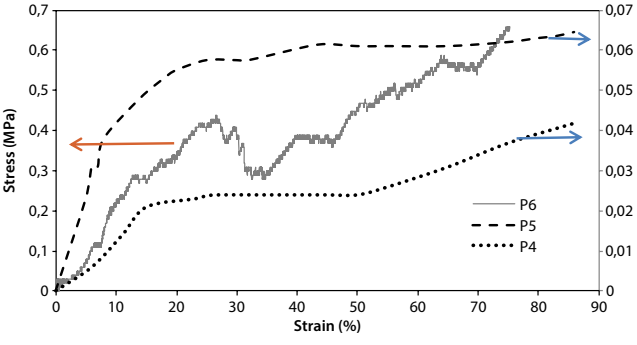


**Figure 3** Stress/strain curves of new albumin-based foams (samples P4, P5 and P6).

observed by Lacoste *et al.* [10] for previously described albumin foams. In order to reduce water absorption of foams, the partial or total replacement by glycerol of the water of the formulation should be envisaged. The utilization of one catalyst, in order to increase crosslinking of the materials, and/or the increase of DMC content (and concurrently of pentane), could represent other alternatives. Finally, the waterproofing of samples by post-treatment should be evaluated.

In order to compare the water resistance of new albumin foams, the same test was performed for a sample of albumin-DMC foam described previouly [13] and for a sample of natural tannin-furanic foam whose composition has already been presented [14, 22]. In these cases, $WA_{26h}$ was evaluated as 83% and 61% respectively. The behavior of these samples can be explained because their nearly total open porosity promoted water absorption, conversely to samples P4 and P5, whose closed-cell porosity was close to 50%. The same trends were established when WA was evaluated by complete immersion of samples.

Figure 3 presents the stress/strain curves obtained from compression tests of albumin-based samples P4, P5 and P6, and indicate that their structure was essentially rigid. As for several biobased foams, as for

example those derived from tannin, the compression curves show three typical phases, linear, elastic, collapse and densification; and compression resistance of materials was dependent on their density [18, 22]. Moreover, sample P6 behaved as typical brittle cellular solids and broke during compression tests, while P4 and P5 samples were squashed and yielded new compacted flexible materials which could be applied as shock absorbers (cushion), e.g., in packaging.

## 4 CONCLUSIONS

New foams have been developed from egg white albumin and DMC with neither aldehydes nor isocyanate in their composition. It was found that:

- The new foams presented very low densities in the range of 0.02–0.2 g/cm$^3$ and mechanical resistance between 0.023–0.34 MPa.
- These biofoams showed closed-cell content of up to 60% and good capacity for thermal insulation.
- Their residual pH was practically neutral: this enables their application in direct contact with lignocellulosic or metallic materials without any danger of substrate degradation.

These new natural foams were manifestly more environmentally friendly materials and exhibited very promising properties. In this way, the study exposed herein represents a substantial contribution to a future practical realization of protein-based foams.

## ACKNOWLEDGMENT

The authors would like to thank the Department of Physics of King Abdulaziz University for the technical contribution to the thermal and structural characterization of biobased foams.

The LERMAB is supported by a grant overseen by the French National Research Agency (ANR) as part of the Laboratory of Excellence (Labex) ARBRE.

This project was partially funded by the Deanship of Scientific Research (DSR), King Abdulaziz University Jeddah under grant No (7-130-36-HiCi). The second author, therefore, acknowledges with thanks DSR's technical and financial support.

## REFERENCES

1. L.J. Gibson and M.F. Ashby, *Cellular Solids, Structure and Properties*, Cambridge University Press, Cambridge, U.K (1997).
2. L. Pilato, *Phenolic Resins: A Century of Progress*, Springer-Verlag, Berlin Heidelberg (2010).
3. S.T. Lee, C.B. Park, and N.S. Ramesh, *Polymeric Foams: Science and Technology*, CRC Press, U.S. (2006).
4. D.L. Kaplan, Introduction to biopolymers from renewable resources, in: *Biopolymers from Renewable Resources*, D.L. Kaplan (Ed.), Springer, New York (1998).
5. J.M. Raqueza, M. Deleglise, M.F. Lacrampea, and P. Krawczak, Thermosetting (bio)materials derived from renewable resources: A critical review. *Prog. Polym. Sci.* **35**(4), 487–509 (2010).
6. W. Krische, and W. Spitteler, A process for manufacturing water resistant products from casein, US patent 646, 844 (1900).
7. B.E. Ralston and T.A. Osswald, The history of tomorrow's materials: Protein-based biopolymers. *Plast. Eng*. **64**(2), 36–40 (2008).
8. X. Li, A. Pizzi, M. Cangemi, V. Fierro, and A. Celzard, Flexible natural tannin-based and protein-based biosourced foams. *Ind. Crops Prod*. **37**(1), 389–393 (2012).
9. X. Li, A. Pizzi, M. Cangemi, P. Navarrete, S. Segovia, V. Fierro, and A. Celzard, Insulation rigid and elastic foams based on albumin. *Ind. Crops Prod*. 37(1), 149–154 (2012).
10. C. Lacoste, M.C. Basso, A. Pizzi, A. Celzard, and M.P. Laborie, Natural albumin/tannin cellular foams. *Ind. Crop. Prod*. **73**, 41–48 (2015).
11. G. Tondi, A. Pizzi, and R. Olives, Natural tannin-based rigid foams as insulation in wood construction. *Maderas Cienc. Tecnol*. **10**(3), 219–227 (2008).
12. M.C. Basso, S. Giovando, A. Pizzi, H. Pasch, A. Celzard, and V. Fierro, Tannin/furanic foam without blowing agents and formaldehyde. *Ind. Crops Prod*. **49**(17), 17–22 (2013).
13. M.C. Basso, A. Pizzi, and L. Delmotte, A new approach to environmental friendly protein plastics and foams. *BioRes*. **10**(4), 8014–8024 (2015).
14. G. Tondi, V. Fierro, A. Pizzi, and A. Celzard, Tannin-based carbon foams. *Carbon*. **47**(6), 1480–1492 (2009).
15. X.D. Zhang, C.W. Macosko, H.T. Davis, A.D. Nikolov, and D.T. Wasan, Role of silicone surfactant in flexible polyurethane foam. *J. Colloid Intersf. Sci*. **215**(2), 270–279 (1999).
16. M.C. Basso, M.C. Lagel, A. Pizzi, A. Celzard, and S. Abdalla, First tools for tannin-furanic foams design. *BioRes*. **10**(3), 5233–5241 (2015).
17. G. De Carvalho, J.A. Pimenta, W.N. dos Santos, and E. Frollini, Phenolic and lignophenolic closed cells foams: Thermal conductivity and other properties. *Polym. Plast. Tech. Eng*. **42**, 605–626 (2003).
18. A. Martinez de Yuso, M.C. Lagel, A. Pizzi, V. Fierro, and A. Celzard, Structure and properties of rigid foams derived from quebracho tannin. *Mater. Des*. **63**, 208–212 (2014).
19. F.A. Shutov, Phenolic foams in the USSR. *Cellular Polym*. **3**, 95–104 (1984).
20. A. Pizzi, R. Vosloo, F.A. Cameron, and E. Orovan, Selfneutralizing acid-set PF wook adhesives. *Holz Roh Werkst*. **44**(6), 229–234 (1986).

21. C. Lacoste, M.C. Basso, A. Pizzi, A. Celzard, E.E. Ebang, N. Gallon, and B. Charrier, Pine (*P. pinaster*) and quebracho (*S. lorentzii*) tannin-based foams as green acoustic absorbers. *Ind. Crop. Prod.*, **67**, 70–73 (2015).

22. C. Lacoste, M.C. Basso, A. Pizzi, M.P. Laborie, and A. Celzard, Pine tannin-based rigid foams: Mechanical and thermal properties. *Ind. Crops Prod.* **43**, 245–250 (2013).