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Foaming of Synthetic and Natural Biodegradable Polymers*

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ABSTRACT: Biodegradable polymers, both synthetic and natural, often show poor foamability, in terms of the ability to form a fine-celled structure and to retain it. In fact, foams with high density and/or non uniform morphology are generally obtained with these materials. Poor rheological properties, poor solubility and inadequate diffusivity of the ordinary foaming agents, and insufficient setting mechanisms (e.g., crystallization kinetics), are the possible reasons. In this work different approaches, tuned to the different materials, have been investigated to improve the foamability of biodegradable materials, such as polyesters, polysaccharides, vegetal and animal proteins. This comprehensive analysis allows one to gain a wide and clear picture of the relevance and efficiency of the available strategies: process optimization, macromolecular design, choice of blowing agent, and use of additives.

KEY WORDS: foams, biodegradable material, nanocomposites.

INTRODUCTION

Owing to their peculiar properties, polymeric foams find wide applications when good mechanical properties and reduced density need to be coupled as is the case, for example, of acoustic insulation and damping, thermal insulation, and impact resistance [1–3].

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Figure 8 appears in color online: <http://cel.sagepub.com>

The large and increasing volume of foamed materials has stimulated interests in developing innovations related to environmentally friendly processes and materials that can be utilized in these high-volume applications. Biodegradation can be considered a possible approach to solve the disposal problem, especially when recycling is difficult or costly or when biodegradation is a functional requirement of the product [3].

Biodegradable synthetic polymers are already utilized in many biomedical applications, such as biodegradable sutures, wound dressing, bio-resorbable implants, and drug delivery systems, where the high cost of the materials is justified [4]. However, their use in commodity applications, such as packaging or agriculture, is still limited either for economical reasons or for difficulties related to their processing, often due to their poor thermal stability.

Natural polymers are emerging, recently, for their ability to form plastic materials after 'plasticization'. Plasticization consists in the de-structurization of the secondary and tertiary structures of natural macromolecules, like proteins, which have complex hierarchical (helix) arrangement. Properties of these 'plastics' depend strongly on several factors and, despite large availability and low cost, their use is still very limited [5].

Suitable materials for industrial foaming must display adequate properties, and their manufacture process must be relatively simple and inexpensive. The foamability is mainly related to the rheological characteristics of the melt [6,7] and to the ability of the polymer to set the newly formed cellular structure. In particular, the strain-induced hardening behavior is a fundamental characteristic for the foaming process, since it allows the polymer to withstand the stretching forces at the latter stage of the bubble growth.

Macromolecular design can be a way for improving the foamability of materials. With synthetic polymers this can be carried out by inducing some branching on linear molecules, by increasing the molecular weight or by enlarging the molecular weight distribution [8]. With natural polymers, instead, macromolecular design can simply mean selection of the proper material within the widest and richest polymer source, i.e., nature.

In this work, several criteria have been used to improve foamability of different biodegradable polymers, both synthetic and natural. Effect of processing, blowing agent selection, macromolecular modification, use of additives, nucleants, plasticizing agents, and natural polymer selection on foaming are herein discussed.

RESULTS AND DISCUSSION

Effect of Process Parameters on Foamability of PCL

Foaming of a thermoplastic polymer is a three-parameter process: gas concentration, foaming temperature, and pressure drop rate [9,10]. Foaming temperature can be considered the most important since it influences the crystallization/vitrification of the polymer and cell coalescence [11]. Pressure drop rate is, instead, correlated to the thermodynamic instability necessary to generate the nuclei [12] and, mainly, affects foam morphology while gas concentration is directly correlated to the availability of gas necessary to inflate the bubbles, influencing the final density [13]. By opportunely choosing these parameters it is possible to tailor both foam density and cellular structure to the desired properties/applications. This optimization becomes critical when dealing with not-easy-foamable materials.

As an example the batch expansion of the poly(ϵ -caprolactone)/N₂ system conducted by using the protocol reported in [14] is illustrated here. The effect of temperature on final foam density was investigated in the range of 44–55°C, in which the system under investigation became foamable. In this range when increasing the temperature, the foam density initially decreases, then it reaches a minimum value (0.15 g/cm³) in correspondence with 51°C and, finally, it increases again for higher foaming temperatures. Fine morphologies, with cell dimension of the order of 100 μ m were obtained. Furthermore, to fine-tune structures and properties, further analysis was performed in a smaller range of process variables. Table 1 reports results on the combined effect of the aforementioned process parameters in this narrow experimental range. Scanning electron micrographs (SEM) (Figure 1) show the cellular structure of the corresponding foams. It can be noted that Samples A and B are characterized by the same cell dimension but different densities while Samples A and C have approximately the same

Table 1. Process parameters and final characteristic of PCL foams.

	Sample A	Sample B	Sample C
Saturation pressure (bar)	200	200	140
Pressure drop rate (bar/s)	320	380	260
Foaming temperature (°C)	44.5	46.5	44.5
Foam density (g/cm ³)	0.231	0.192	0.227
Cells dimension (μ m)	64	58	183

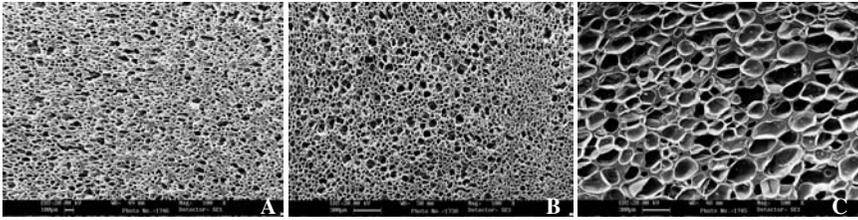


Figure 1. SEM of PCL foams obtained with different foaming conditions, as reported in Table 1.

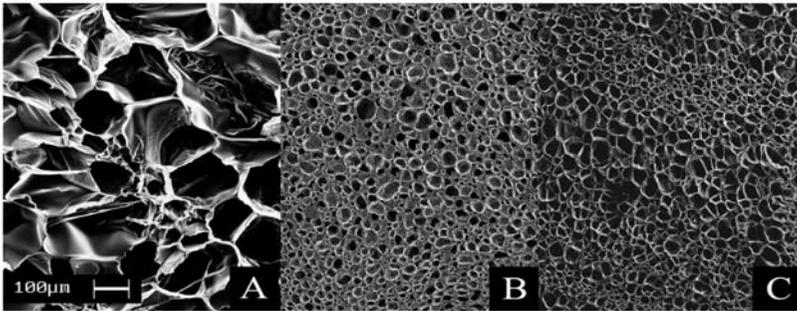


Figure 2. SEM analysis of PCL extrusion-foamed with CO₂ (A), N₂ (B), and 20/80% CO₂/N₂ mixture (C).

density but different dimension of cells, to demonstrate how process parameters can effectively be used to control the final foam structure.

Effect of Blowing Agent on Foamability of PCL

Foaming agent and its interaction with polymeric matrix play an important role in the foaming process. Plasticization induced by the blowing agent results in a reduction of the viscosity and the characteristic temperatures. This effect depends on the kind of blowing agent used and its concentration [15]. Different blowing agents determine different processing windows, as a consequence. This effect on poly(ϵ -caprolactone) foaming, achieved both by a batch and by an extrusion system [16], using two different gases, N₂ and CO₂, is presented here. The latter gas plasticizes PCL more extensively, as evidenced by lower melt viscosity, lower foaming temperatures, measured at the same gas concentration. Furthermore, solubility of CO₂ in PCL is higher than N₂, while mutual diffusivity is lower [16]. As a result, foams with lower densities can be expected by using CO₂, but with coarser morphologies. In Figure 2, the SEM of foams

expanded with CO₂ (A), N₂ (B), and their 20–80% vol mixture (C) are reported. Foam A had a density of 0.03 g/cm³ and 250 μm mean cell diameter, Foam B had a density of 0.2 g/cm³ and 20 μm mean cell diameter, and Foam C had a density of 0.07 g/cm³ and 50 μm mean cell diameter. In effect, the use of the mixture led to the optimal use of the two blowing agents, with a synergic effect.

Effect of Molecular Architecture Modification on Foamability of PLA

Foaming occurs after a thermodynamic abrupt instability is imposed on the polymer–gas solution, leading to cell nucleation, which is then followed by the growth of the newly formed nuclei and the subsequent stabilization of the foamed cellular structure. The latter two steps are strictly related to the rheological characteristics of the melt. During the bubbles growth, in fact, the viscosity of expanding matter should be low enough to allow the elongational deformation of the melt while, during the stabilization of the cellular structure, the strain-induced hardening behavior of polymer should be sufficient to withstand the stretching force at the latter stage of the bubble growth, avoiding the collapse of the newly foamed structure.

There are basically two possibilities to tune the rheological properties of the melt: (i) to optimize the molecular weight and molecular weight distribution of the polymer and/or (ii) to induce branching of the macromolecules [8].

As an example, the effect of chemical modification of batch foamed poly(lactic acid) (PLA) is shown here. Two chain extenders were used to treat PLA in melt state: 1,4-butanediol (BD) and 1,4-butane diisocyanate (BDI) [17]. BD was employed as the first coupling agent and acid value reducer to link carboxyl groups of PLA, and then BDI was added to let it react with hydroxyl end groups of PLA to achieve chain extended PLA. Two modified PLA samples were obtained by using different ratios of BD to BDI: modified Sample 1 (M1): COOH/BD = 2:1, OH/BDI = 2:1, i.e., equimolar amount of BD and BDI relative to end groups COOH and OH of PLA, where COOH and OH contents were calculated from the acid values determined by titration; Sample 2 (M2): COOH/BD = 2:1, OH/BDI = 1:1, i.e., BDI amount was excessive compared to M1. The original PLA was also processed in the same conditions for comparison purposes.

The more complex macromolecular structure of the modified materials, as shown in Figure 3, plays an important role in giving rise to higher viscoelastic moduli. Moreover, during the foaming process,

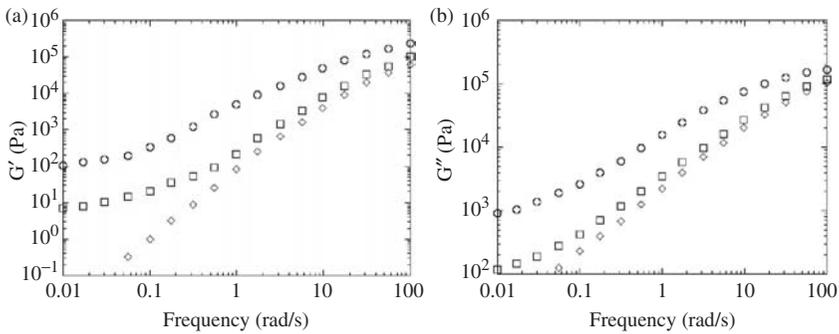


Figure 3. Rheological behavior for neat and chemically modified PLA samples, G' (a) and G'' (b) vs frequency, 170°C, for M2(○), M1(□) and plain PLA (◇) samples.

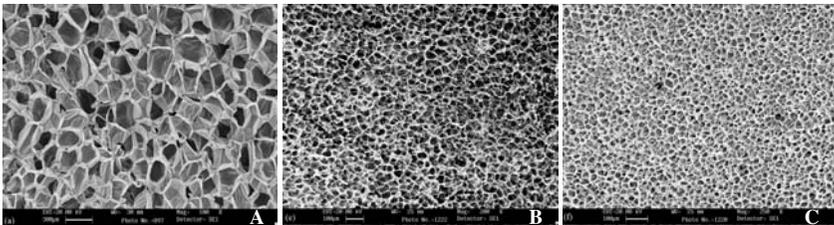


Figure 4. SEM for foams of neat PLA (A, magnification factor 100) and chemically modified PLA samples M1 (B, magnification factor 200) and M2 (C, magnification factor 250).

the improved rheological properties hinder the excessive cell growth, avoiding cell walls rupture and collapse between adjacent cells and allowing a cell density increase and a final foam density decrease. As a confirmation, Figure 4 shows the cellular structure of neat PLA foam (A, 7.7×10^5 cells/cm³, 0.12 g/cm³), M1 foam (B, 1.8×10^8 cells/cm³, 0.067 g/cm³), and M2 foam (C, 6.7×10^8 cells/cm³, 0.092 g/cm³), obtained in the same process conditions.

Suitable macromolecular architecture modification has proved to have great influence on the viscoelastic properties of the PLA matrix, resulting, therefore, in an efficient method to enhance PLA foamability, allowing a finer control of the final foam cellular structure and, at the same time, a reduction of the final foam density.

Effect of Fillers on Foamability of PLA

The presence of inorganic particles in a polymeric matrix affects its properties, mainly, in terms of thermal and rheological properties.

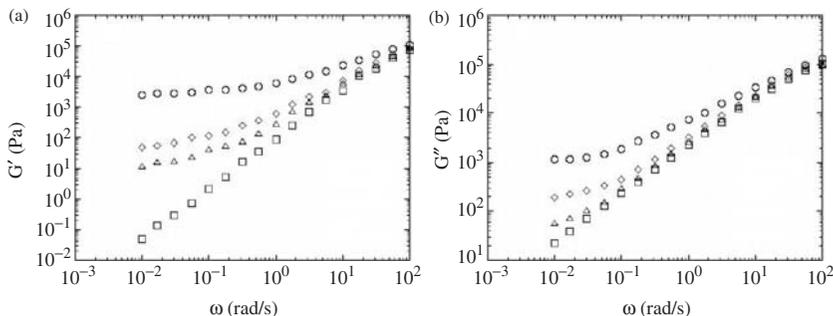


Figure 5. Rheological behavior of neat PLA (\square) and PLA nanocomposites containing 2(Δ), 5(\diamond) and 10(\circ) wt.% of Cloisite 30B, G' (a) and G'' (b) vs frequency, 170°C.

This effect becomes more evident when the filler has, at least, one nanometric dimension [18]. In fact, the aspect ratio of these particles is very high and, as a consequence, the interaction between macromolecules and inorganic particles are enhanced to a great extent. Furthermore, when considering the foaming process of a polymeric matrix, these particles can act as heterogeneous bubble nucleation sites, increasing greatly the number of nuclei [19]. According to the classical nucleation theory [9] the heterogeneous bubble nucleation rate is a function of the heterogeneous nucleation sites concentration (defined as the number of particles per cubic centimeter). Therefore the particle's concentration is very important because it sets the upper limit for heterogeneous nucleation sites.

In this section the effect of a modified montmorillonite, Cloisite 30B, on the thermal and rheological properties of the PLA matrix and on its foamability is presented as a case study. As reported by many authors for different polymer–filler systems [20,21], the presence of Cloisite 30B in the PLA matrix causes a great increase in the rheological properties, if compared with the neat polymer (Figure 5). This effect is dependent, for the investigated system, on the nanofillers content (2 and 5 wt%). The presence of nanofillers modified the crystallization behavior of PLA. As shown in Figure 6, a small percentage of nanoclay promoted crystal nucleation, increasing the crystallization kinetics.

Bearing in mind these results, it is possible to understand the contribution of the nanofiller in obtaining finely dispersed cells in foams of PLA nanocomposite (5 wt% of filler) with respect to neat PLA foams, obtained with the same foaming condition. As reported in the SEM (Figure 7) the foamed neat PLA shows larger cell size (250 μm) while 5 wt% filled PLA shows cells of about 30 μm . This behavior can be

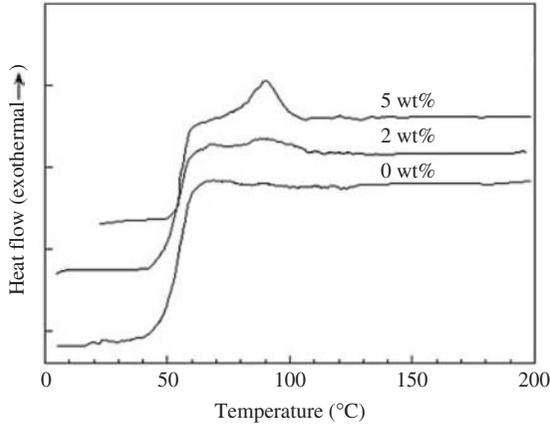


Figure 6. DSC cooling thermograms at $-10^{\circ}\text{C}/\text{min}$ for PLA and PLA/30B nanocomposites with different weight fractions nanofiller.

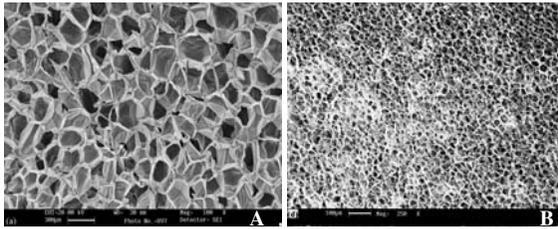


Figure 7. SEM for foams of neat PLA (A) and 5 wt% filled PLA (B).

ascribed both to increased cell nucleation, due to the presence of the heterogeneous bubble nucleation sites, and to the intrinsically high viscosity and elasticity, caused by organoclay exfoliation and chain extension/branching, which reduce the cell growth. Finally, the fast crystallization rate for PLA nanocomposite is also helpful for stabilizing the cell structure during the foaming process.

Foams from Vegetal Proteins

Zein is a protein that can be extracted from maize, is not water-soluble, and has potential applications in edible (more than biodegradable!) packaging. Plastic characteristics out of this material can be achieved by extruding, for example, a 75%–25% wt mixture of zein-PEG400, at temperatures of 80°C , 80 rpm with a lab-scale extruder.

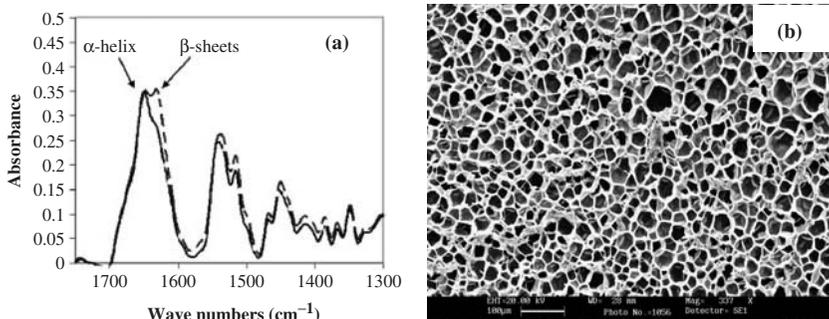


Figure 8. FTIR analysis of two lots of zein (a) and SEM of foamed zein (b).

Properties of these materials are strongly dependent on primary and secondary structures of the proteins. Figure 8(a) reports, for example, FTIR analysis on two lots of zein, received from the same producer, same extraction technique but, probably, grown in different conditions, revealing small differences in the secondary structure. In particular, one protein contained more β -sheets (dashed line) than the other (continuous line). This, as also reported in the literature [22], resulted in plasticized materials with completely different mechanical properties. In particular, the protein with less β -sheets was much more deformable (more than 40 times) than the other, which was fairly brittle. The two zein lots were subsequently batch foamed at 70°C, after saturation at 70°C and at a pressure of 180 bar of a 25–75% vol mixture of CO₂ and N₂, for 6 h. The less deformable material, with more β -sheets, gave collapsed foam, not being able to withstand elongational deformation during foaming, while a fine-celled, low density foam resulted from the other, deformable plastic material. The SEM of the latter foam is presented in Figure 8(b). The selection of the proper macromolecular system, within a very narrow group (same class of protein), allowed the achievement of a foamed material with very interesting properties for packaging applications.

CONCLUSIONS

This study illustrates some possibilities to improve the foamability of biodegradable polymers, both synthetic and natural. Proper choice of the main processing parameters can be helpful for obtaining tailored foams, in terms of cellular structure and final foam density. Different types of

foaming agent show a different interaction with the polymeric matrix, affecting gas molecules' solubility and diffusivity, polymer viscosity and its characteristic temperatures, greatly influencing, therefore, the foaming process of the analyzed biodegradable material. Molecular modification can be used to enhance viscoelastic properties of the polymer and, therefore, can reduce cell rupture and/or collapse during cell growth. The presence of nanoparticles in a polymeric matrix offers additional cell nucleation sites and affects both the rheological and thermal properties, allowing a better control of the final foam structure. Finally, the foaming process of a vegetal protein (zein) is possible and it can be influenced by the hierarchical structure of the natural polymers.

REFERENCES

1. Throne, J.L. (1996). *Thermoplastic Foams*, Sherwood Publisher, Hinckley, OH.
2. Gibson, L.J. and Ashby, M.F. (1988). *Cellular Solids: Structure and Properties*, Pergamon Press, Oxford.
3. Klempler, D. and Sendjarevic, V. (2004). *Polymeric Foams and Foam Technology*, Hanser Gardner, Munich.
4. Wise, D.L., Trantolo, D.J., Altobelli, D.E., Yaszemski, M.J. and Gresse, J.D. (1996). *Human Biomaterials Applications*, Humana Press Inc., Totowa, NJ.
5. Cuq, B., Gontard, N. and Guilbert, S. (1998). Proteins as Agricultural Polymers for Packaging Production, *Cereal Chemistry*, **75**(1): 1–9.
6. Siripurapu, S., Gay, Y.J., Royer, J.L., DeSimone, J.M., Spontak, R.J. and Khan, S.A. (2002). Generation of Microcellular Foams of PVDF and its Blends using Supercritical Carbon Dioxide in a Continuous Process, *Polymer*, **43**(20): 5511–5520.
7. Spitael, P. and Macosko, C.W. (2004). Strain Hardening in Polypropylenes and its Role in Extrusion Foaming, *Polymer Engineering and Science*, **44**(11): 2090–2100.
8. Xanthos, M., Young, M.W., Karayannidis, G.P. and Bikiaris, D.N. (2001). Reactive Modification of Polyethylene Terephthalate with Polyepoxides, *Polymer Engineering and Science*, **41**(4): 643–655.
9. Colton, J.S. and Suh, N.P. (1987). The Nucleation of Microcellular Thermoplastic Foam with Additives: Part I: Theoretical Considerations, *Polymer Engineering and Science*, **27**(7): 485–492.
10. Lee, J.S.W., Wang, K. and Park, C.B. (2005). Challenge to the Extrusion of Low-density Microcellular Polycarbonate Foams using Supercritical Carbon Dioxide, *Industrial Engineering Chemistry Research*, **44**(1): 92–99.
11. Krause, B., Mettinkhof, R., Van der Vegt, N.F.A. and Wessling, M. (2001). Microcellular Foaming of Amorphous High- T_g Polymers using Carbon Dioxide, *Macromolecules*, **34**(4): 874–884.

12. Arora, K.A., Lesser, A.J. and McCarthy, T.J. (1998). Preparation and Characterization of Microcellular Polystyrene Foams Processed in Supercritical Carbon Dioxide, *Macromolecules*, **31**(14): 4614–4620.
13. Naguib, H.E., Park, C.B. and Reichelt, N. (2004). Fundamental Foaming Mechanisms Governing the Volume Expansion of Extruded Polypropylene Foams, *Journal of Applied Polymer Science*, **91**(4), 2661–2668.
14. Marrazzo, C., Di Maio, E., Iannace, S. and Nicolais, L. (2006). Process-Structure Relationships in PCL Foaming, accepted for publication on *Journal of Cellular Plastics*.
15. Van der Vegt, N.F.A., Briels, W.J., Wessling, M. and Strathmann, H., (1999). The Sorption Induced Glass Transition in Amorphous Glassy Polymers, *Journal of Chemical Physics*, **110**(22): 11061–11069.
16. Di Maio, E., Mensitieri, G., Iannace, S., Nicolais, L., Li, W. and Flumerfelt, R.W. (2005). Structure Optimization of Polycaprolactone Foams by using Mixture of CO₂ and N₂ as Blowing Agent, *Polymer Engineering and Science*, **45**(7): 432–441.
17. Di, Y., Iannace, S., Di Maio, E. and Nicolais, L. (2005). Reactively Modified Poly (Lactic Acid): Properties and Foam Processing, *Macromolecular Materials and Engineering*, **290**(11): 1083–1090.
18. Ray, S.S. and Okamoto, M., (2003). Polymer/Layered Silicate Nanocomposites: A Review from Preparation to Processing, *Progress in Polymer Science*, **28**(11): 1539–1641.
19. Ramesh, N.S., Rasmussen, D.H. and Campbell, G.A. (1994). The Heterogeneous Nucleation of Microcellular Foams Assisted by the Survival of Microvoids in Polymers Containing Low Glass Transition Particles. Part II: Experimental Results and Discussion, *Polymer Engineering and Science*, **34**(22): 1698–1706.
20. Shen, J., Zeng, C. and Lee, L.J. (2005). Synthesis of Polystyrene-Carbon Nanofibers Nanocomposite Foams, *Polymer*, **46**(26): 5218–5224.
21. Fujimoto, Y., Ray, S.S., Okamoto, M. and Ogami, A. (2003). Well-controlled Biodegradable Nanocomposite Foams: From Microcellular to Nanocellular, *Macromolar Rapid Communications*, **24**(7): 457.
22. Gao, C., Taylor, J., Wellner, N., Byaruhanga, Y.B., Parker, P.L., Mills, E.N.C. and Belton, P.S. (2005). Effect of Preparation Conditions on Protein Secondary Structure and Biofilm Formation of Kafirin, *Journal of Agricultural And Food Chemistry*, **53**(2): 306–312.