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Microstructural and Physical Properties of Thermoplastic Corn Starch/Polystyrene Blend Foams Affected by Different Contents and Combinations of Plasticizers

Amirreza Zabihi¹ · Mohammad Fasihi¹ · Sajad Rasouli¹

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Abstract

A comprehensive study was performed on thermoplastic corn starch (TPS)/polystyrene (PS) blend foam to optimize the formulation from the aspects of plasticizer content and the blend ratio. Plasticization of native starch was implemented with various contents of plasticizer [water (W) + glycerol (G)], 21, 23, 25 and 29%, and *W/G* ratio of 1/2, 2/3, 3/2 and 2/1 using melt extrusion process. The influence of plasticizer loading content and also its combination on the microstructural and physical properties of the blend foam were investigated. The morphological consideration was also carried out by scanning electron microscopy to evaluate the distribution and regularity of the foam cells. The results showed that water had a desirable effect on the cell parameters in W + G = 21 and 29%. In the following, full factorial method in Minitab software was used to optimize the formulation according to the properties. Moreover, the effect of PS content on the moisture absorption and cell structure of TPS/PS blend foam was evaluated. In addition, the blend ratio of 20/80 was obtained as an optimum ratio for the TPS/PS blend foam. The addition of 20% PS to TPS caused to 6 times higher expansion ratio than PS and 60% higher than TPS, while 50% lower moisture absorption than TPS. This combination can be a good alternative candidate for warm food packing applications.

Keywords Thermoplastic starch (TPS) · Extrusion · Biodegradable · Foam · Microstructure · Physical properties

Introduction

In the recent decades, many reports have shown an increasing demand for plastic materials in various industrial and medical applications which have direct relationship with human health and the environment [1]. For example, plastic foams are widely used for diverse targets i.e. cushioning, insulation and warm food packaging [2]. Polystyrene (PS) is one of the most attractive plastics for foam industry, due to its low density, thermal insulation, good mechanical properties and low cost [3]. In spite of the desired properties, there are some challenges about the PS usage, i.e. that is indestructible, unsustainable and hazardous because of the release of toxic styrene, especially in hot applications [4]. Accordingly, many efforts were accomplished to replace PS with the environmentally friendly or biodegradable polymers by researchers [5–7]. In the recent years, starch as a bio-polymeric material from renewable resource has been attracted the attention of many researchers as a good candidate to alternate or blend with PS [8]. Starch is a low cost biodegradable polymer, and can also be used into soil as a compost organic fertilizer [9].

Starch is a semi-crystalline polysaccharide with polyhedral shape that includes of α -(1-4)-linked D-glucose, amylose with a linear molecular architecture, and a highly branched amylopectin with the myriad points of α -(1-6)-linked branch [10]. Starch in its native state is not able to process such as thermoplastic materials [11]. Therefore, to donate processability and flexibility to the starch, native starch has to transform to a moldable thermoplastic, thermoplastic starch (TPS) [12]. The homogeneous TPS melt is created via applying thermomechanical energy on native starch at the presence of water [13] and other plasticizers e.g. glycerol [14],

Mohammad Fasihi mfasihi@iust.ac.ir

¹ School of Chemical, Petroleum and Gas Engineering, Iran University of Science and Technology, 16846-13114 Tehran, Iran

poly(ethylene glycol) (PEG) [15], organic acids [16] and fatty acids [17]. In fact, the process leads to the reduction of intermolecular interactions between the starch chains, followed by the increment of the chains movements [18].

TPS foam manufactured by the extrusion-cooking technique, with various mechanical properties [19]. In general, TPS is blended with a synthetic polymer to improve the foamability, lower the density and increase the hydrophobicity [20]. So far, some studies were carried out to consider the influence of TPS on the TPS/PS blend foam properties [21–25]. Pushpadass et al. [23] examined the effect of talc as a nucleating agent, azodicarbonamide (ADC) and citric acid as blowing agents on the properties of TPS/PS foam at different blend ratios. Their results showed that 0.5% talc increased the expansion ratio of the foam, and citric acid led to a higher radial expansion and correspondingly lower density compared to ADC. Yayshahri et al. [26] evaluated the effect of glycerol as a plasticizer on the mechanical and degradation properties of high impact polystyrene (HIPS)/ starch blend via melt extrusion process. According to their results, increasing the starch and glycerol caused a faster degradation rate, a decrease in the values of impact strength and softening point of the TPS/HIPS blend. Mihai et al. [24] measured the impact of glycerol on the rheological properties of TPS/PS blend via in-line rheometry in an extrusion process. They found that the content of glycerol in TPS and also the TPS in the blend had a significant influence on the blend viscosity, and followed by the blend foamability.

Despite a few researches on the TPS/PS blend foam, nevertheless, there is a lack of a comprehensive study into the plasticizer combinations effect on the physical properties and cell morphology of the foam. Factually, finding an optimized TPS to blend with PS at an efficient ratio is a very important issue which has not been considered yet. In this study, we investigated the impact of various plasticizer contents of water and glycerol at different water/glycerol ratio as well as the PS/TPS ratio on the microstructural properties, cell morphology and moisture absorption of the TPS/PS blend foams in continuous extrusion process. Moreover, the effect of PS content on the cell morphology was discussed.

Materials and Methods

Materials

Corn starch with 10% moisture and the amylose/amylopectin ratio of 0.3 was supplied by Glucosan Inc. (Qazvin, Iran). General purpose polystyrene GPPS1160 with melt flow index (MFI) of 2.5 g/10 min at 200 °C, was purchased from Tabriz Petrochemical Co. Ltd. (Tabriz, Iran). Citric acid and sodium bicarbonate (SB) were obtained from DaeJung Corporation (Shiheung, South Korea). Talc as nucleating agent was also purchased from Omya Pars Co. (Tehran, Iran). Glycerol was supplied by a local company. Doubledistilled water was used to control the moisture content of starch in TPS preparation procedure, as well.

Fabrication of TPS/PS Blend FOAM

Preparation of TPS

TPS was prepared with different plasticizer amounts of G + W (glycerol and water were symbolized with G and W, respectively), i.e. 21, 23, 25 and 29 wt% at various W/G ratios, i.e. 1/2, 2/3, 3/2 and 2/1. For chemical modification of native starch, 2 wt% citric acid was used to partially esterify the starch for better heat stabilization [27]. The action was implemented to reduce the crystallinity degree of starch via the decrement of hydrogen bonding amount between the chains [28]. Because the crystals act as an obstacle against the starch processing [29] According to the presented formulations in Table 1, these materials were mixed in a highspeed dry mixer for 4 min. In order to facilitate the plasticizer penetration into starch, the mixed powders were kept for 48 h at ambient temperature. Afterwards, the mixtures were processed using a lab-scale single screw extruder, KEX series, L/D ratio of 26 made by KAJARAN Company (Iran). The barrel temperature for feeding to die zones were 95, 120 and 120 °C, respectively, and the screw speed was adjusted

Table 1 Designed formulations for TPS preparation

Sample	Starch (wt%)	$G^a + W^a (wt\%)$	Citric acid (wt%)	W ^a /G ^a
S21-1/2	77	21	2	1/2
S21-2/3	77	21	2	2/3
S21-3/2	77	21	2	3/2
S21-2/1	77	21	2	2/1
S23-1/2	75	23	2	1/2
S23-2/3	75	23	2	2/3
S23-3/2	75	23	2	3/2
S23-2/1	75	23	2	2/1
S25-1/2	73	25	2	1/2
S25-2/3	73	25	2	2/3
S25-3/2	73	25	2	3/2
S25-2/1	73	25	2	2/1
S29-1/2	69	29	2	1/2
S29-2/3	69	29	2	2/3
S29-3/2	69	29	2	3/2
S29-2/1	69	29	2	2/1

The TPS samples were symbolized with Sx-y, in which x is the G+W amount of 21, 23, 25 and 29%, and y is the W/G ratio of 1/2, 2/3, 3/2 and 2/1, respectively

^aG and W represent glycerol and water contents, respectively

30 rpm. The obtained TPSs were pelletized for better blending with PS.

Preparation of TPS/PS Blend Foam

First, the prepared Sx-y samples in Section "Preparation of TPS", were blended with PS at the TPS/PS blend ratio of 40/60 via the extruder. The temperatures for feeding, melting and die zones set equal to 95, 160 and 165 °C, respectively. In addition, the screw speed was 30 rpm. Then, in order to produce the TPS/PS blend foams, talc, and a combination of SB [30] and citric acid (as foaming agent) were added to the prepared pelletized blends. Next, according to the presented formulations in Table 2, the blend foams were manufactured by extruding pre-mixtures using the same extruder with the process conditions similar to the blend preparation.

Characterization Methods

Scanning Electron Microscopy (SEM)

SEM images were taken from the cross-sectional surface of the Fx-y samples by TESCAN Vega II, Czech Republic, using an accelerating voltage of 30 kV. All the Fx-y samples were firstly frozen in liquid nitrogen then snapped and followed by vacuum-dried. Before observations, the samples were coated with a thin layer of gold. The test was performed to quantitate the cell characteristics of the foams.

 Table 2
 Designed formulations for TPS/PS blend foam with the ratio of 40/60 by using the plasticized Sx-y samples (Table 1)

Sample	TPS/PS	FA ^a (phr)	Talc (phr)
F21-1/2	(\$21-1/2) 40/60	2	0.5
F21-2/3	(S21-2/3) 40/60	2	0.5
F21-3/2	(S21-3/2) 40/60	2	0.5
F21-2/1	(S21-2/1) 40/60	2	0.5
F23-1/2	(\$23-1/2) 40/60	2	0.5
F23-2/3	(\$23-2/3) 40/60	2	0.5
F23-3/2	(\$23-3/2) 40/60	2	0.5
F23-2/1	(\$23-2/1) 40/60	2	0.5
F25-1/2	(S25-1/2) 40/60	2	0.5
F25-2/3	(\$25-2/3) 40/60	2	0.5
F25-3/2	(\$25-3/2) 40/60	2	0.5
F25-2/1	(\$25-2/1) 40/60	2	0.5
F29-1/2	(S29-1/2) 40/60	2	0.5
F29-2/3	(\$29-2/3) 40/60	2	0.5
F29-3/2	(\$29-3/2) 40/60	2	0.5
F29-2/1	(\$29-2/1) 40/60	2	0.5

The samples of TPS/PS blend foams were symbolized by Fx-y, in which x and y belong to Sx-y

^aFA indicates the combination of SB and citric acid as foaming agents

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The volume expansion ratio (VER), cell density (N_c) and its wall thickness (δ) were calculated according to following equations: [31–33]

$$VER = \rho_p / \rho_f \tag{1}$$

$$N_{c} \cong \frac{10^{4}}{d_{a}^{3}} \left[1 - \frac{1}{VER} \right]$$
⁽²⁾

$$\delta = d_a \left[\frac{1}{\sqrt{1 - \frac{1}{\text{VER}}}} - 1 \right]$$
(3)

where ρ_f and ρ_p are the foam and pre-foamed densities for each sample, respectively.d_a is cell diameter which was obtained from SEM images for each sample.

Density Measurement

In this work, a basic method [33] was used to determine the density of each Fx-y and its pre-foamed blend, the sample's mass divided by its volume. The densities were obtained with an average on 5 different specimens for each foam and pre-foamed sample.

Moisture Absorption

To determine hydrophilicity level of the Fx-y foams, 5 predried specimens for each formulation were weighed with a sensitive scale and then were placed in the condition of 76% relative humidity (RH) for 192 h. After the period, the samples were again weighed, and moisture absorption amount (MA) was calculated.

Results and Discussions

Structural and Physical Properties of Foams

In this research work, the results were discussed with respect to the influence of G + W and W/G amounts on the microstructural and physical properties of Fx-y foams, to find an optimized formulation for TPS/PS blend foam. Fabricated Fx-y samples with various amount of plasticizers, x, at different y ratios were shown in Fig. 1.

SEM images of TPS/PS (40/60) blend foams with various plasticizer contents of G + W and ratios of W/G are demonstrated in Fig. 2. As seen in the figure, using lower amount of plasticizer at the TPS preparation helps to achieve a foam with better morphology. Moreover, increasing y from 1/2 to 2/1, caused a better distribution of the foams cells at the



Fig. 1 Fx-y blend foams with TPS/PS blend ratio of 40/60 at different x and y amounts

lower amount of x. Therefore, increasing and decreasing the contents of glycerol and water in the plasticizer combination, respectively, damaged the cells structure and led to a further cell collapse. Since, in spite of the plasticization role, evaporation of water has favorable influence on the extrusion foaming process, from blowing aspect. While, glycerol with a much higher boiling point [34] than the process temperature, acted as a plasticizer only, and caused the reduction of blend melt viscosity. The increment of plasticizer content (x) led to the collapse of foam cells. The worst effect of plasticizer on the blend foam belonged to F23-y and F25-y samples, which significant cell wall rupture was observed in them. It can be attributed to lower melt strength of the Fx-y blend foams as a result of high level of plasticizer. This issue causes the rupture of growing bubble walls during the foaming process, and subsequently the foam collapse. Accordingly, the effect of raising y had an opposite influence on the cells structure in the F23-y and F25-y samples, due to the surplus made internal pressure by water vapors, and followed by rupturing the cells wall.

According to Fig. 2, the cellular structure of Fx-y samples did not have any regularity, and included of large and small bubbles. In order to create a deep insight into the plasticizer effect on the microstructural properties of Fx-y, first, the cells diameter of each Fx-y sample was obtained by analyzing SEM images. After that, the probability density function (PDF) of the cells diameters was computed for all the foam samples and then were shown in Fig. 3. As discussed, increasing the y content in F21-y, F23-y and F25-y made higher cell size and wider cell size distribution (see Fig. 3). Whereas, this behavior was almost vice versa in the F29-y samples.

The achieved cell characteristics of each Fx-y sample are listed in Table 3. As seen in the table, the calculated results of cell size (d) and standard deviation (σ) have a good conformity with Figs. 2 and 3, and verifies the mentioned discussions on the irregularity of foam cells, clearly. According to the results, increasing the loading content of water in the plasticizer combination led to enhance the cell density in F29-y. Whereas, the behavior was inverse in F25-y sample. Besides, cell wall thickness did not have a specified variation. Moreover, the VER values of F21-y and F29-y samples nearly had an irrespective behavior to y, while, its evolution was uptrend in F23-y and F25-y. Since, the cell rupture occurred in the foams with x = 23 and 25% leading to increasing the cell size significantly (see Figs. 2, 3). This issue raised the volume of mentioned foams compared to the foams with x = 21 and 29%.

To create a better view into the density variation of Fx-y foams with changing the plasticizer contents and combinations, foam density at various x and water percentage in plasticizer combination (z) were reported in Fig. 4. As shown in Fig. 4a, density of F21-y and F29-y have a smooth change with increasing the z value, while this change is rapid in F23-y and F25-y. This issue is due to the uniform distribution, and integration of bubbles in the F21,29-y and F23,25-y foams, respectively. Therefore, a main factor of the decrement of foam density of F23,25-y was the cell rupture, which was followed by agglomeration of the bubbles. Additionally, Fig. 4b shows the density change versus plasticizer content at a same z. As shown, after engendering a minimum in the curve, the foam density increased with increasing x at diverse amount of z. higher amount of water content in plasticizer combination caused a lower value for $\rho_{\rm f}$.



Fig. 2 SEM micrographs of TPS/PS (40/60) blend foams with x of A 21%, B 23%, C 25% and D 29% at y amounts of a 1/2, b 2/3, c 3/2 and d 2/1, respectively

Water Absorption Property

TPS is a water soluble polymer due to its numerous hydroxyl groups [29], which leads to moisture attack and correspondingly, significant changes in its physical and mechanical properties [35]. Moreover, the hydrophilicity reduces the TPS tendency to its hydrophobic counterpart,

like PS, in polymer blending [36] Accordingly, this issue limits the TPS usage in industrial applications. In this work, we considered the effect of different plasticizer contents and combinations on the moisture absorption of TPS/PS blend foam with the ratio of 40/60. The obtained MA versus z and x for each Fx-y sample was reported in Fig. 5a and b, respectively. As exhibited in the figure, MA value reduced with increasing the z amount at each Fig. 3 Probability density function (PDF) of cells diameters, d, for Fx-y with A x = 21%, B 23%, C 25% and D 29% at the amount of a y = 1/2, b y = 2/3, c y = 3/2 and d y = 2/1, respectively



Table 3 Cell characteristics of Fx-y blend foams

Sample	$d\pm\sigma$ (mm)	VER	N _c (cell/mm ³)	δ (mm)
F21-1/2	0.283 ± 0.097	1.99	2.195×10^{5}	0.118
F21-2/3	0.339 ± 0.152	1.708	1.064×10^{5}	0.187
F21-3/2	0.197 ± 0.108	1.587	4.838×10^{5}	0.127
F21-2/1	0.197 ± 0.073	1.296	2.991×10^{5}	0.215
F23-1/2	0.873 ± 0.401	1.696	0.061×10^{5}	0.489
F23-2/3	0.577 ± 0.334	3.065	0.350×10^{5}	0.126
F23-3/2	0.402 ± 0.222	5.253	1.246×10^{5}	0.044
F23-2/1	0.678 ± 0.396	6.427	0.271×10^{5}	0.059
F25-1/2	0.119 ± 0.051	1.489	19.500×10^{5}	0.088
F25-2/3	0.230 ± 0.072	1.755	3.537×10^{5}	0.12
F25-3/2	0.323 ± 0.184	2.981	1.972×10^{5}	0.073
F25-2/1	0.491 ± 0.212	5.167	0.681×10^{5}	0.055
F29-1/2	0.254 ± 0.095	1.58	2.242×10^{5}	0.165
F29-2/3	0.326 ± 0.196	1.535	1.006×10^{5}	0.225
F29-3/2	0.196 ± 0.093	1.95	6.472×10^{5}	0.084
F29-2/1	0.124 ± 0.062	1.745	22.397×10^5	0.065

x, and raising the x content led to the reduction and then enhancement of MA at each z. Factually, the increment of z had an extreme effect on the hydrophobicity augmentation of the blend foam. Because, rising the water content in plasticizer caused a reduction of the intermolecular hydrogen bonding between the starch chains via frustrating the chains' OH groups [37]. In contrast, increasing glycerol in the plasticizer combination have an undesirable effect on the hydrophilicity reduction of the blend foam, due to its high water tendency [38].

Statistical Data Analysis

In order to find an optimized formulation for TPS/PS blend foam from the view point of the plasticizer content and combination, 4×4 full factorial design was used. This consideration was carried out to achieve a blend foam with the most desirable microstructural and moisture absorption properties. Design of experiment (DOE) and analysis of variance (ANOVA) were applied via utilizing MINITAB® 18 [39].



Fig. 4 Density of Fx-y samples against (a) water percentage in plasticizer combination and (b) plasticizer content, respectively



Fig. 5 Moisture absorption (MA) amount of Fx-y samples versus (a) water percentage in plasticizer combination and (b) plasticizer content, respectively

The plasticizer contents of x = 21, 23, 25, 29%, and water percentage in plasticizer combination of z = 33.3, 40, 60,66.7%, were evaluated as the independent factors. Cell diameter and water absorption amounts were also defined as the responses in DOE. Factually, all the microstructural properties and hydrophobicity behaviors of the blend foams are the functions of these two responses. The responses were investigated in five. After removing of non-significance items, the fitted models provided by the mentioned software for average cell diameter, d_a , and water absorption, MA. The results were reported in Table 4. The coefficients in each equation demonstrate the effect of the related term on that property. Positive and negative coefficients of the linear models indicate a synergistic and decreasing impact on the responses, respectively. In fact, the goal of optimization was to minimize cell diameter and foam ability to absorb moisture.

Response	Linear model
Cell diameter	$d=0.3483 - 0.09431 \text{ x } [21] + 0.2752 \text{ x}$ $[23] - 0.05756 \text{ x } [25] - 0.1233 \text{ x}$ $[29] + 0.02494 \text{ z } [33.3] + 0.01969 \text{ z}$ $[40.0] - 0.06881 \text{ z } [60.0] + 0.02419 \text{ z}$ $[66.7] + 0.004062 \text{ x} \times \text{z}$ $[21,33.3] + 0.06531 \text{ x} \times \text{z}$ $[21,40.0] + 0.01181 \text{ x} \times \text{z}$ $[21,60.0] - 0.08119 \text{ x} \times \text{z}$ $[23,33.3] - 0.06619 \text{ x} \times \text{z}$ $[23,30.0] + 0.03031 \text{ x} \times \text{z } [23,60.0] + 0.03031 \text{ x} \times \text{z} [23,60.0] + 0.03031 \text{ x} \times \text{z} [23,60.0] + 0.01111 \text{ x} \times \text{z } [25,40.0] + 0.10111 \text{ x} \times \text{z } [25,66.7] + 0.004063 \text{ x} \times \text{z}$ $[29,33.3] + 0.08131 \text{ x} \times \text{z}$ $[29,40.0] + 0.03981 \text{ x} \times \text{z}$ $[29,60.0] - 0.1252 \text{ x} \times \text{z } [29,66.7]$
Moisture absorption	MA = 4.6250 - 0.012 x [21] - 0.640 x [23] + 0.112 x [25] + 0.540 x [29] + 0.735 z [33.3] + 0.613 z [40.0] - 0.600 z [60.0] - 0.748 z [66.7]

x and z are the plasticizer content and water percentage in the plasticizer combination



Fig. 6 Optimization plot for the responses

Because, a TPS/PS blend foam with these characterizations show the best microstructural and hydrophobicity properties (see Section "Structural and physical properties of foams"). Further, desirability function approach (D) [40] was used at the optimization process of the results. It is based on transforming d and MA into a desirability values (minimum values), the combination of individual responses into a composite function and then its optimization [41]. The D values were so close to 1, which indicates the efficient settings to obtain desirable results for d and MA [42]. Finally, x=21% and z=66.7% (y=2/1) was obtained from optimization process (see Fig. 6) to produce the optimum level of microstructural and hydrophobicity properties for TPS/PS blend foam. Figure 6 represents a Minitab Response Optimizer tool that indicates how different experimental settings influence the predicted responses for a stored model.

Effect of PS Content on the TPS/PS Foam Properties

To investigate the impact of TPS content on the microstructural, physical and moisture absorption properties of the TPS/PS blend foams, the optimized TPS (x = 21%and z = 66.7% or y = 2/1) was used. For this purpose, TPS/ PS foam with the PS percentage of 0, 20, 40, 60, 80 and 100% was supplied via presented methodology in Section "Preparation of TPS/PS Blend Foam". The TPS/PS blend foam with different amount of PS was symbolized with Fr, in which r is the PS percentage. The formulations of these samples are given in Table 5. The created foam with different r was shown in Fig. 7.

To create a deep understanding into the impact of TPS content on the microstructural properties of the blend foam, SEM images were taken from the Fr samples. Moreover, cells diameter was estimated from the SEMs and their PDF was drawn for each sample. The SEM images and PDF analysis are represented in Fig. 8 together.

As shown in Fig. 8, the foam at the absence of PS had a good cell morphology and uniform distribution of cell diameter. While, increasing the PS content up to 40% led to widen the PDF curve and facilitate the cell wall rupture, which was followed by joining the bubbles together and then creation of very large cells. As seen in the figure, TPS/PS with the

 $\ensuremath{\text{Table 5}}$ The formulations of TPS/PS blend foam with different amount of PS

Sample	PS/TPS (wt %)	W/G ratio	W+G (wt%)	FA ^a (phr)	Talc (phr)
F0	0/100	3/2	23	2	0.5
F20	20/80	3/2	23	2	0.5
F40	40/60	3/2	23	2	0.5
F60	60/40	3/2	23	2	0.5
F80	80/20	3/2	23	2	0.5
F100	100/0	3/2	23	2	0.5

^aFA indicates the combination of SB and citric acid as foaming agents



Fig. 7 TPS/PS blend foam with the optimized formulation of TPS. **a** F0, **b** F20, **c** F40, **d** F60, **e** F80 and **f** F100

PS content of 60% has a good cell size, lower irregularity, and also probability density function with a slender distribution at a less amount of d. However, its expansion ratio was low. F100 (pure PS) had the slenderest PDF distribution and the furthest amount of probability at the least cell diameter, which was distinct already, due to the PS ability to foam [43]. To quantitate the cell and foams properties, d, N_c, δ , ρ_f and MA amounts were listed in Table 6. According to the table, F20 was an efficient foam from i.e. expansion ratio, physical and moisture absorption properties. This formulation has higher expansion ratio than TPS and PS with about half moisture absorption compared to TPS. This combination can be a good alternative candidate for pure PS foam packaging.

TPS had a negative effect on the cell growth and its diameter, which were randomly distributed. In fact, it can be attributed to the PS good response to the blowing agent in comparison with starch. In addition, the good melt strength of PS prevented the cell rupture, while this issue was vice versa in the TPS media.

Conclusions

In this research work, TPS/PS blend foam prepared by melt extrusion process was investigated at different plasticizer contents and combinations, and the blend ratio. The influence of content of water + glycerol as plasticizer and as well as water/glycerol ratio on the foam microstructural and physical properties were studied at a same TPS/ PS ratio of 40/60. Plasticizer content was varied between 21% up to 29% (21, 23, 25, and 29%) and water/glycerol ratios were 1/2, 2/3, 3/2 and 2/1. The results showed that the combination of plasticizer significantly affects the cell properties of the blend foams. Moreover, a decrease in foam density was observed at the increment of the water



Fig. 8 SEM images with the probability density function (PDF) of cells diameters for a F0, b F20, c F40, d F60, e F80 and f F100 samples

content in plasticizer combination. The lowest density of 0.189 g/cm^3 and moisture absorption of 3.3% was belonged to F23-2/1 sample. In addition, the influence of plasticizer contents and combinations on the hydrophilicity behavior of the blend foam also evaluated. Moisture absorption experienced a descending trend by increasing water content due to decreasing intermolecular hydrogen bonding between the starch chains via frustrating the chain's OH groups. Meanwhile, by rising plasticizer content, moisture absorption has increased because of glycerol water tendency. Moreover, the effect of various contents of PS in the blend showed the concentration of 20% PS resulted in highest expansion ratio which was about 6 times higher than PS and 60% higher than TPS.

Table 6 Cell and foam characteristics for each Fr sample

Sample	$d \pm \sigma(mm)$	N _c (cell/mm ³)	$\delta(mm)$	VER	MA (%)
F0	0.169 ± 0.063	17.90×10^{5}	0.012	7.36	9.77
F20	0.352 ± 0.247	2.10×10^{5}	0.015	12.17	5.02
F40	0.883 ± 0.569	0.11×10^{5}	0.0994	5.18	4.83
F60	0.197 ± 0.073	2.991×10^{5}	0.215	1.29	4.15
F80	0.426 ± 0.219	0.66×10^{5}	0.166	2.07	2.11
F100	0.112 ± 0.258	30.96×10^{5}	0.057	1.77	0

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