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# The simultaneous effect of nucleating and blowing agents on the cellular structure of polypropylene foamed via the extrusion process

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**Abstract:** The current work presents the preparation of polypropylene (PP) foams by the extrusion process, focusing on the influence of the foaming agent and nucleating agent on the microstructure of the foams. Sodium bicarbonate alone and also its mixture with citric acid were used as the chemical blowing agents. Expanded graphite nanoparticle and talc were also used as the nucleating agents. Great differences were found in terms of the foam structure depending on the type of nucleating and blowing agents. Using expanded graphite nucleating agent instead of talc resulted in foams with higher cell densities and more uniform cellular structures. Moreover, the foams including the mixed blowing agents exhibited higher cell densities and upper expansion ratio.

**Keywords:** blowing agent; extrusion; foam; nucleating agent; polypropylene.

## 1 Introduction

Nowadays, polyethylene (PE) and polystyrene (PS) foams are widely used in packing, building, and automotive industries because of their admirable properties such as excellent insulation properties and high energy absorption besides their low material cost. Moreover, they can be easily produced continuously by the extrusion process. Recently, polypropylene (PP) foams have been considered as a substitute for other thermoplastic foams such as PE and PS owing to some superior properties, e.g. higher stiffness than PE, higher impact strength than PS and

higher service temperature range than both of them (1). However, poor foamability because of its intrinsic weak melt strength caused PP foams not to have been developed in industrial applications as much as PE and PS foams. Its low melt strength results in the quick rupture of cell walls during bubble growing under extensional force. Consequently, produced PP foams typically have a high open cell content and non-uniform cell distribution which are undesirable for many applications (1).

The foaming behavior of PP and its influencing factors have been investigated in some studies. The cell nucleation, bubble growth and the final cell morphology of extruded PP foams have been studied extensively (2–6). Earlier studies attempted to enhance the melt strength by partial crosslinking of PP (7). Although, this method made a substantial improvement in volume expansion and cell uniformity, the accurate control of the crosslinking process was a major problem. Other efforts have also been made to produce branched PP usually by grafting a kind of long chain molecule onto linear PP such that, in turn, its melt strength increased dramatically (8–10). Improved melt strength was also observed in the PPs with a wide molecular weight distribution. Alteppep et al. improved foamability of PP by blending the two types of PP with different viscosities (11). In other different research, for foaming linear PP, it was blended with polymers such as high density polyethylene (HDPE) (12, 13), low density polyethylene (LDPE) (14, 15), propylene-ethylene copolymer (PER) (16) or ethylene-octene copolymers (17). These studies tried to enhance the melt strength of PP by blending it with a high melt strength polymer which caused the prevention of cell coalescence and therefore resulted in finer cell foam with a better cell uniformity. Besides the kind of the matrix, nucleating and blowing agents also an enormous effect on the final cell structure. Talc is usually used as a nucleating agent in many types of foams. However, it was reported that some nanofillers like nanoclay (18), nanosilica (19) and nano-calcium carbonate (20) had better nucleation efficiency than talc in PP foams. Nanofiller nucleating agents can simultaneously improve the melt strength of PP and thus suppress cell coalescence (19, 21). Very

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recently, it was observed that adding thermoplastic elastomers like styrene-ethylene-butylene-styrene (SEBS) (22) into PP can enhance nucleation sites and cell distribution uniformity. It was stated that the nanoscale soft segments in the thermoplastic elastomers could act as a template for the bubble nucleation and growth (22, 23). Nanocellular foams were successfully produced from these kinds of blends.

The type of blowing agent also has a great impact on the foam structure. A blowing agent can be either a physical or chemical type. A physical blowing agent dissolves into the polymer at a high pressure. While, a chemical blowing agent releases gas by decomposition at a certain temperature and the released gas is dissolved in the polymer melt. Park and co-workers studied extrusion foaming of PP using CO<sub>2</sub>, isopentane and butane as the blowing agents (24, 25). Fine cell foams were obtained through optimizing the process parameters. They reported finer cell and lower density foams in which a blowing agent with lower diffusivity was used (24).

Extrusion foaming of PP is under development and a general applicable and economic way to produce PP foams especially by the extrusion process is not yet available. In this study, the PP foams were produced by the extrusion process using different nucleating and blowing agents. Random copolymer PP, branched PP and their mixture were used as matrices. The efficiency of expanded graphite as a nucleating agent was considered and compared with talc. Moreover, the effects of using a single blowing agent (sodium bicarbonate) and a mixture of two blowing agents (citric acid and sodium bicarbonate) on the morphology of foams were studied comparatively.

## 2 Materials and methods

### 2.1 Materials

The PPs used in this study were linear random copolymer PP (RG 3212E, MFI=0.25 g/10 min) supplied by the Regal Petrochemical Company (Isfahan, Iran) and branched homopolymer PP (Daploy W130 HMS, MFI=2.1 g/10 min) supplied by Borealis GmbH (Vienna, Austria). Talc (Persitalc 20-SW, average size=3.5 μm) from Omya Pars Co. (Tehran, Iran) and expanded graphite (EC1500, average size=7 μm) from Ito Kokuen Co. (Kuwana, Japan) were applied as nucleating agents. Sodium bicarbonate (SB) and citric acid anhydrous (CA) from Daejung Co. (Shiheung, South Korea) were used as blowing agents.

### 2.2 Sample preparation

In preparing PP foams first PP with 15 wt% of a blowing agent and 1 wt% of a nucleating agent were premixed by a high speed mixer at room temperature. The matrix was a linear copolymer PP or branched homopolymer PP or a mixture of equal weights of each one. The chemical blowing agent was either sodium bicarbonate alone or a 56/44 mixture of sodium bicarbonate and citric acid (by weight). The premix was subsequently melt extruded using a single screw extruder (Brabender Extrusiograph, D=19 mm, L/D=25). The extruder was fitted with a cylindrical die with an inside diameter of 2 mm. The zone temperature profile of the extruder, starting from the feeding zone to the die was set to be 140°/170°/190°/210°/170°C, respectively. The die temperature was chosen as the optimal temperature in which maximum expansion with minimum collapse was observed (3). The screw rotating speed was also maintained fairly constant at 50 rpm. The compositions and the nomenclature of the samples are presented in Table 1. The samples were coded as follows: the first letter denotes the foaming agent component (S for sodium bicarbonate and C for citric acid/sodium bicarbonate), the second letter denotes the nucleating agent component (T for talc and G for expanded graphite), and the third numeral denotes the matrix type (1 for branched PP, 2 for linear PP and 3 for their 50/50 blend).

### 2.3 Characterization methods

Melting behavior of samples was evaluated by a differential scanning calorimeter (DSC1, Mettler Toledo, Greifensee, Switzerland) at a scanning rate of 10°C/min under a nitrogen purge. The crystallinity percentage ( $X_c$ ) was then calculated by:

**Table 1:** Compositions of the samples.

Sample	Linear PP	Branched PP	Sodium bicarbonate	Citric acid	Talc	Expanded graphite
ST1	84	0	15	0	1	0
ST2	0	84	15	0	1	0
ST3	42	42	15	0	1	0
SG1	84	0	15	0	0	1
SG2	0	84	15	0	0	1
SG3	42	42	15	0	0	1
CG1	84	0	8.4	6.6	0	1
CG2	0	84	8.4	6.6	0	1
CG3	42	42	8.4	6.6	0	1
CT3	42	42	8.4	6.6	1	0

$$X_c = \frac{\Delta H}{\Delta H^o} \times 100 \quad [1]$$

where  $\Delta H$  is the measured specific heat from the endothermic peak and  $\Delta H^o$  is the melting enthalpy of 100% crystalline PP.  $\Delta H^o$  was obtained from the literature and was equal to 209 J/g (23).

The morphology of the foamed samples was observed by using scanning electron microscopy (SEM, Vega II XMU, Tescan, Kohoutovice, Czech). Prior to SEM characterization, a thin coating of gold was applied to the surface of samples to improve image resolution. The average cell size and size distribution were then determined by analyzing the SEM images using the aid of the ImageJ software program (NIH, Bethesda, MD, USA). Bulk density of neat PP and foams was determined via water displacement in accordance with ASTM D792.

## 3 Results and discussion

### 3.1 Thermal properties

The melting behavior of the samples prepared with different matrices was studied using differential scanning calorimetry and the measured results are shown in Figure 1. The melting point of ST1, ST2 and ST3 were 163°C, 145°C and 155°C, respectively. Melting point of linear PP was about 18°C less than branched PP because linear PP was a random copolymer of propylene and ethylene and so its melting point was lower than homo PP. The melting

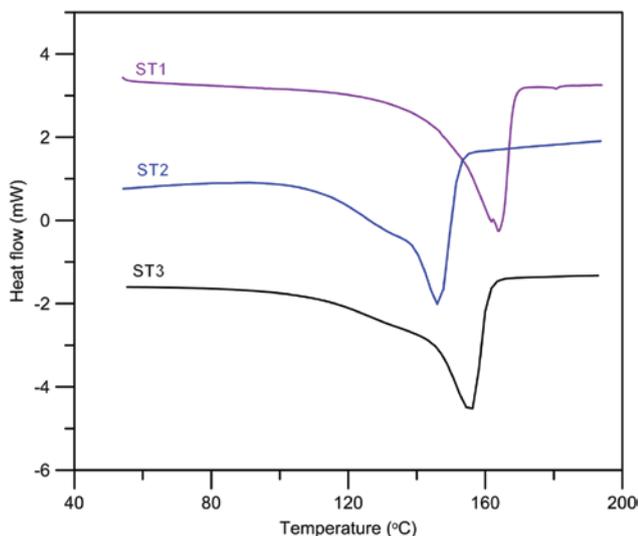


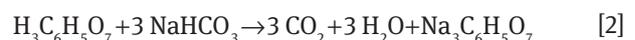
Figure 1: DSC heating curve of some samples.

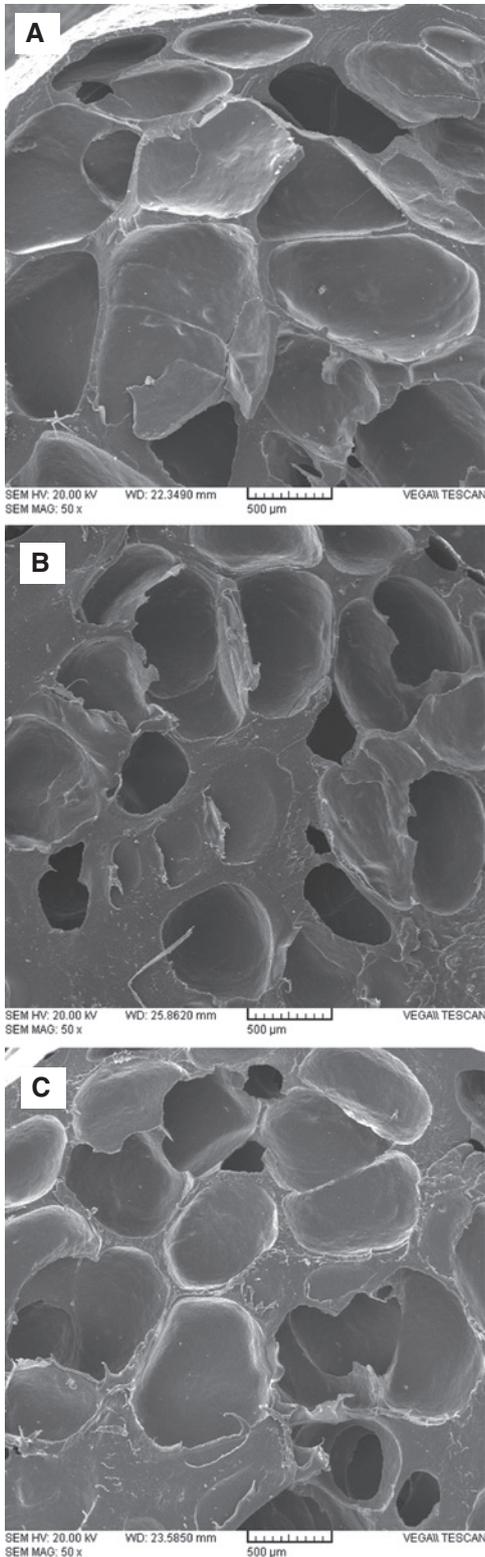
curve of the blend just showed one peak in between two melting points of pure components as a result of complete miscibility and co-crystallization of two kinds of PPs. The overall crystallinity of the three samples was in the range of 42–45%. It was known that foams from more crystalline materials usually made a lower cell concentration and lower cell size than foams from less crystalline materials (26). However, the close crystallinity percent of the samples revealed that the possible difference in the foam structure of samples cannot be known from their crystallinity percent difference. Moreover, the blending of the two PPs caused broadening of the melting range, which is desirable for some applications.

### 3.2 SEM microscopy

The microstructure of the STi samples (including talc nucleating agent and SB blowing agent) was observed by SEM, as shown in Figure 2. A big cell size and non-uniform cell distribution were observed in these samples which can be attributed to the cell coalescence and possible poor cell nucleation during the foaming process. The average cell sizes of these samples were about 600  $\mu\text{m}$ . However, the average cell size in ST1 was a little higher than in ST2 and ST3 due to lower viscosity of branched PP (or higher MFI) than linear PP. By using expanded graphite instead of talc as a nucleating agent (SGi samples), a clear decrease in cell size and an increase in cell density were observed (Figure 3).

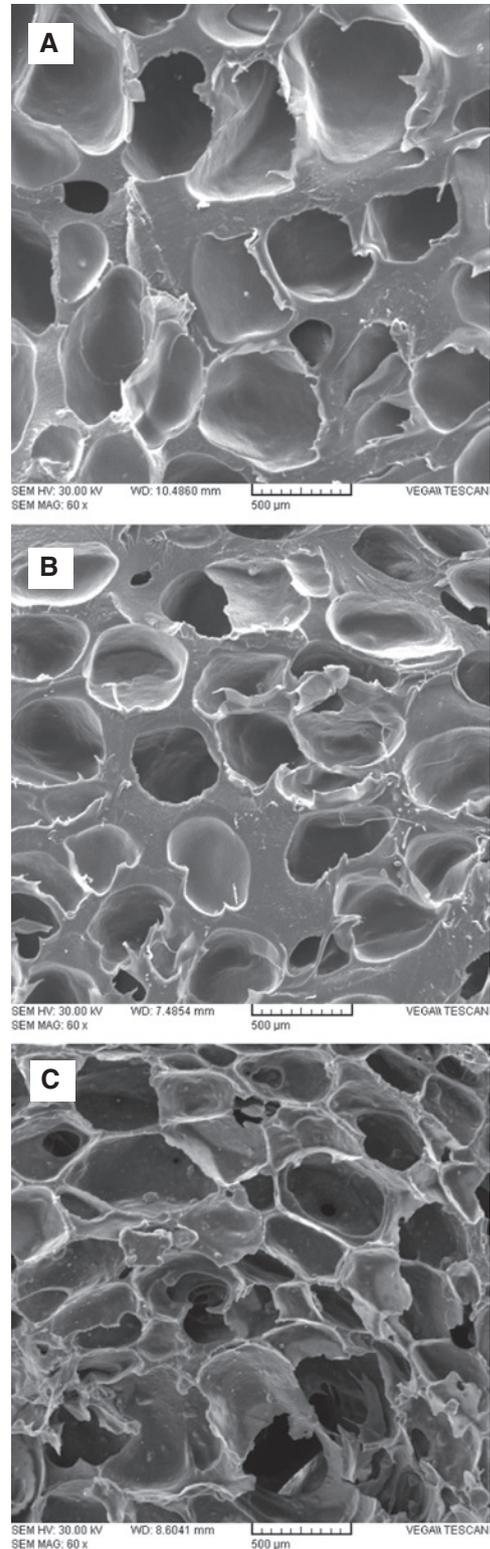
Dispersed expanded graphite consists of tactoids with each one composed of several layers. The thickness of these tactoids is in the range of 20–50 nm (27, 28). While talc particle thickness size is in the scale of microns. The lower particle thickness of expanded graphite than talc leads to higher specific surface area which has a direct effect on the heterogeneous nucleation phenomenon. The improvement in the microstructure was more noticeable when the mixture of SB and CA was used as a blowing agent. In these cases (CGi samples) the cells were seen in all areas of foams and the form of the cells turned from circular to hexagonal shape with a thin wall thickness. While, in other samples, cell walls were thick and a large number of unfoamed areas were detected. This observation cleared that the mixed blowing agents or one of their chemical reaction by-product is an effective nucleating agent for the foaming process. The mixed SB/CA blowing agent is known by the commercial name of Hydrocerol and its chemical decomposition reaction under heating is:





**Figure 2:** SEM images of (A) ST1, (B) ST2 and (C) ST3.

In this reaction, trisodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ) is a reaction by-product which constitutes about 58% of total blowing agent. It seems that this material strongly acts as a bubble nucleating agent in CGi series samples.



**Figure 3:** SEM images of (A) SG1, (B) SG3 and (C) CG3.

The values of cell diameters in the samples with different combinations of nucleating agent/blowing agent for branched homo-PP (W130), linear co-PP (RG) and their blend (W130/RG) are illustrated in Figure 4. As seen, the

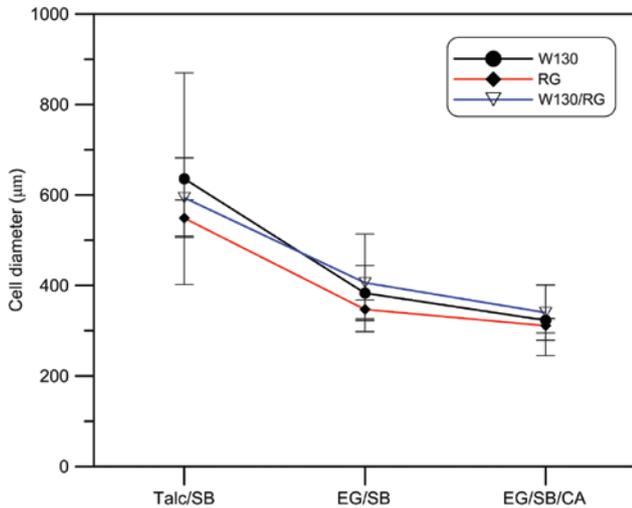


Figure 4: Cell diameter of different foamed samples.

trend of changing the cell diameter was almost similar for different matrix types. A large average cell size with a broad distribution was observed in the PP/talc/SB foams. The average cell diameter decreased from about 600  $\mu\text{m}$  to about 400  $\mu\text{m}$  and cell size distribution became more uniform when EG was used instead of talc as a nucleating agent for any type of matrix. Moreover, using a combination of CA and SB as a blowing agent significantly resulted in the better cell size uniformity and smaller cell diameter under the same foaming conditions. The average cell diameters of copolymer PP-based foams were a little lower than two other types of matrices because of higher viscosity of this PP which made a higher retarding force against bubble growth during foaming formation. The cell density ( $N_0$ ), i.e. the number of cells per cubic centimeter of samples was determined by (29):

$$N_0 = \left[ \frac{nM^2}{A} \right]^{1.5} \left( \frac{\rho}{\rho_f} \right) \quad [3]$$

where  $n$  is the number of cells in the SEM micrograph,  $M$  is the magnification factor,  $A$  is the area of the micrograph (in  $\text{cm}^2$ ),  $\rho$  is the density of the unformed and  $\rho_f$  is the density of the foamed sample. The calculated results of cell densities are represented in Figure 5. Random copolymer-based foams experienced slightly higher cell densities because of their lower cell sizes. If only better melt strength were the difference between matrices, the branched PP should show a higher cell concentration, as it would have less cell coalescence. But, it appears that fewer nuclei are nucleated in the branched PP vs. the linear PP. It can be moderately attributed to its lower shear viscosity as stated in other research (29). However, the combination of nucleating agent/blowing agent had the main effect on the cell

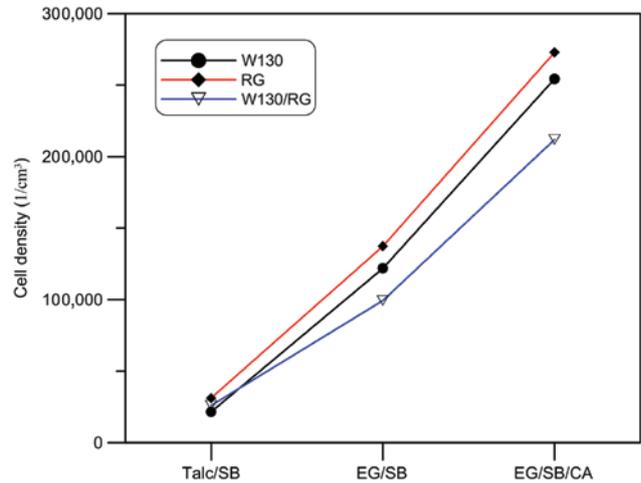


Figure 5: Cell density of different foamed samples.

density parameter. The cell density of SGI foams increased up to 4–5.5 times in comparison with STi foams that confirmed the higher efficiency of expanded graphite as a nucleating agent when compared with talc. Furthermore, using a mixture of blowing agents instead of single SB along with EG nucleating agent practically enhanced the cell densities up to two-fold. The cell wall thickness ( $\delta$ ) was also estimated as (18):

$$\delta = d \left( \frac{1}{\sqrt{1 - \frac{\rho}{\rho_f}}} - 1 \right) \quad [4]$$

The calculated cell densities and cell wall thicknesses of different foams are listed in Table 2. The average cell wall thickness of ST1, ST2 and ST3 was in the range of 215–262  $\mu\text{m}$ . As mentioned previously, the cell size and distribution was not uniform in these foams and a large number of unfoamed areas were partially observed

Table 2: Summary of characteristics of the foamed samples.

Sample	Cell diameter ( $\mu\text{m}$ )	Foam density ( $\text{kg}/\text{m}^3$ )	Cell wall thickness ( $\mu\text{m}$ )	Cell density ( $1/\text{cm}^3$ ) $\times 10^{-4}$
ST1	636 $\pm$ 205	406 $\pm$ 45	219	2.2
ST2	549 $\pm$ 105	440 $\pm$ 38	215	2.1
ST3	594 $\pm$ 77	472 $\pm$ 18	262	2.3
SG1	383 $\pm$ 53	287 $\pm$ 19	80	12.2
SG2	347 $\pm$ 38	388 $\pm$ 18	111	13.7
SG3	406 $\pm$ 95	305 $\pm$ 41	92	9.9
CG1	323 $\pm$ 68	130 $\pm$ 30	26	25.4
CG2	311 $\pm$ 59	163 $\pm$ 14	32	27.3
CG3	340 $\pm$ 53	152 $\pm$ 18	33	21.2
CT3	357 $\pm$ 53	282 $\pm$ 17	73	15.1

(Figure 1). While SG1, SG2 and SG3 displayed lower than half cell wall thickness as well as more uniformity in the cell size and its distribution in comparison with the series of STi foams (Figure 2). Moreover, the foams prepared by the mixed SB and CA blowing agents along with EG nucleating agent formed a meaningfully thinner cell wall thickness which was in the range of 30  $\mu\text{m}$ . This result revealed that simultaneous using the mixed blowing agents and expanded graphite nucleating agent, can significantly improve the foam structure in the extrusion process. In addition, in CGi samples the expansion ratio was 5.5–7 while when single blowing agent used, the expansion ratio was in the range of 2–3. It might be for that using citric acid caused the decomposition temperature of blowing agent to decrease and more part of blowing agent to participate in the bubble growing. Nevertheless, the branched PP had the higher expansion ratio, which was expected. For more comparison of talc and EG nucleating agents, the CT3 formulation designed similarly to CG3 with only a difference in which talc replaced by EG. The SEM structure of CT3 and CG3 are presented in Figure 6. Cell density dropped

from  $2.1 \times 10^5$  cells/ $\text{cm}^3$  for CG3 to  $1.5 \times 10^5$  cells/ $\text{cm}^3$  for CT3 at the same conditions. Besides, cell wall thickness increased from 33  $\mu\text{m}$  for CG3 to 73  $\mu\text{m}$  for CT3. This result elucidated that the better cell structure and higher cell density in CG3 was not just due to using mixed blowing agents, but, the presence of expanded graphite advanced this modification more.

## 4 Conclusions

In this work, PP foams by the extrusion process were successfully prepared using different chemical blowing agents and nucleating agents. Random copolymer PP, branched homopolymer PP and their blend were used as matrices. Regarding the cellular structure of the foams, the incorporation of expanded graphite resulted in finer cellular structures, thinner cell wall thicknesses and higher cell densities. More improvement in the cell structure was observed when the mixture of sodium

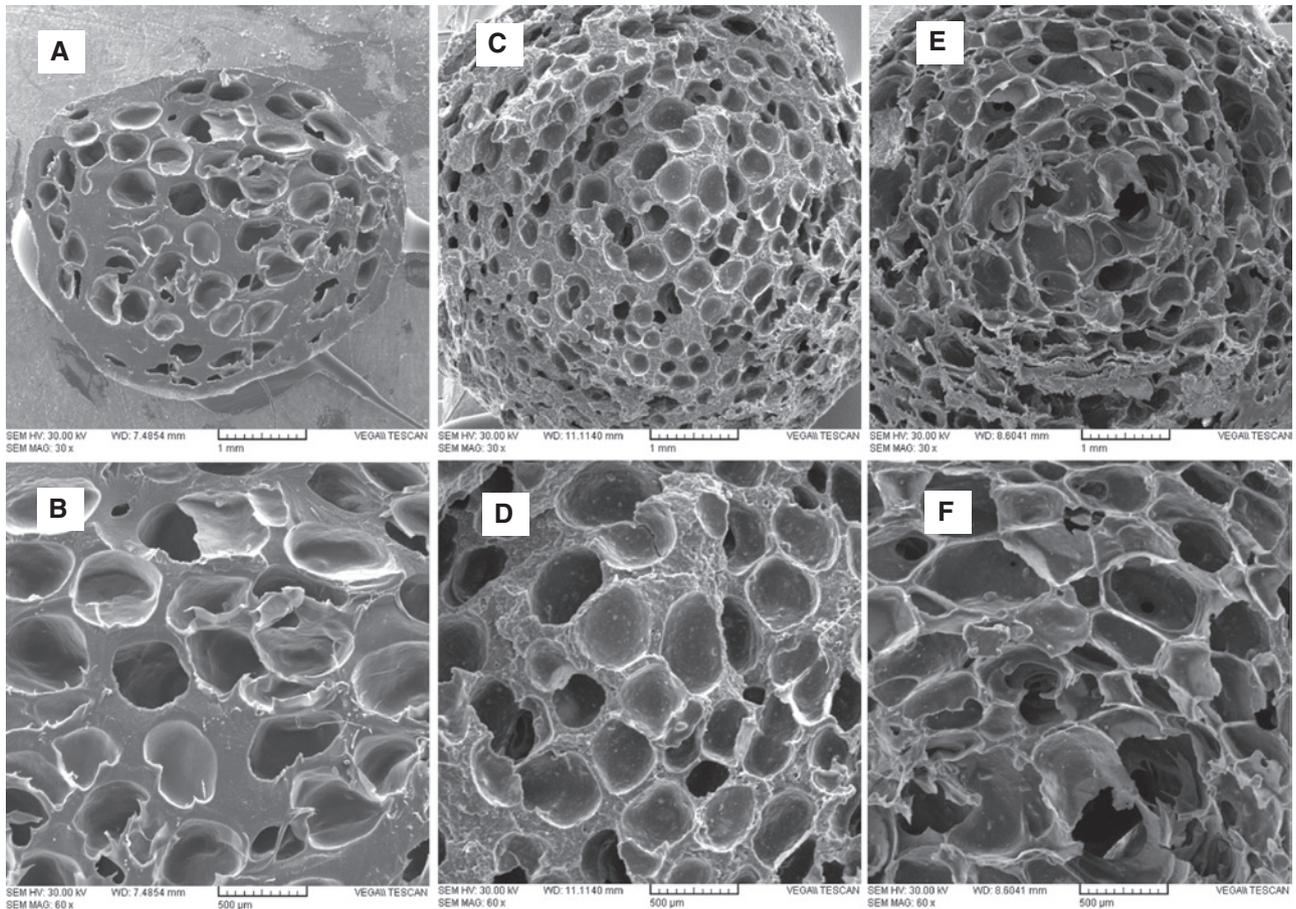


Figure 6: SEM images of (A,B) SG1, (C,D) CT3 and (E,F) CG3.

bicarbonate and citric acid was used as a blowing agent instead of sodium bicarbonate alone. In these cases, the foam density was reduced to 130 kg/m<sup>3</sup> and cell wall thickness of 30 μm was reached. It seems that the by-product of chemical decomposition reaction of mixed blowing agents could act as an effective nucleation agent. The foams obtained by linear PP experienced higher cell density, while the expansion ratio was higher for the ones produced with branched PP.

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