Foam Extrusion of High Density Polyethylene/Wood-Flour Composites Using Chemical Foaming Agents

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ABSTRACT: A one-way analysis of variance and thermal analysis were performed in this study to examine the influences of the contents, types (exothermic vs. endothermic), and forms (pure vs. masterbatch) of chemical foaming agents (CFAs), as well as the use of coupling agents, on the density reduction (or void fraction) and cell morphology of extrusion-foamed neat high density polyethylene (HDPE) and HDPE/wood-flour composites. The CFA types and forms did not affect the void fractions of both the neat HDPE and HDPE/wood-flour composites. However, a gas containment limit was observed for neat HDPE foams whereas the average cell size achieved in the HDPE/wood-flour composite foams remained insensitive to the CFA contents, irrespective of the foaming agent types. The experimental results indicated that the use of coupling agent in the formulation was required to achieve HDPE/wood-flour composite foams with high void fraction. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 3139–3150, 2003

Key words: wood-fiber/plastic composites; foam; extrusion; chemical foaming agents; thermal analysis

INTRODUCTION

In the past few years, scientific and industrial research has been increasingly focused on the study of composite materials comprising wood fibers in thermoplastic matrices.[1–14] Plastic/wood-fiber composite products are currently used in the building industry for siding, window and door frames, and decks as a replacement for conventional pressure-treated wood lumbers.[2–5] These products are resistant to moisture and insects and do not rot, split, warp, and splinter compared to traditional treated wood lumbers.[2–4] However, plastic/wood-fiber composites do not come without trade-offs. They are more brittle and have lower impact resistance than neat plastic products.[6,7,9,13–15] In addition, the density of plastic/wood-fiber composites is almost twice that of solid lumber.[10,11,14,16] These drawbacks may prevent plastic/wood-fiber composites from achieving their full potential in the conventional structural lumber market.

Substantial research efforts have been made to address the drawbacks of plastic/wood-fiber composites.[2,7–11] Recently, the concept of creating cellular foamed structures in the composites through batch or continuous extrusion processes has been successfully demonstrated to significantly improve the shortcomings of these composites.[10,11,17–21] Because of the presence of bubbles, the density of plastic/wood-fiber composites has been greatly reduced, and significant improvements in the ductility and impact resistance of the composites have also been achieved.[19]

However, most studies on the extrusion foaming of plastic/wood-fiber composites with chemical foaming agents (CFAs) have centered on the investigation of styrenics,[20] polypropylene,[11] and poly(vinyl chloride)[10] as matrices. There is currently a limited amount of information available on the extrusion foaming of polyethylene (PE)/wood-flour composites, although PE represents the largest portion of the wood–plastic composites market, accounting for almost 70% of plastics used in the manufacture of wood–plastic composites.[2] Consequently, it is of great importance to study the foamability of PE/wood-fiber composites through an extrusion process, and this was the goal of this study.

Background on CFAs and coupling agents

The CFAs used in the extrusion foaming process of unfilled thermoplastics can be divided into two major categories, endothermic and exothermic.[22–24] Endothermic CFAs absorb heat and usually generate CO_2 whereas the exothermic types release heat and produce mainly N_2 during their chemical decomposition reactions.[22,23] These CFAs influence the viscoelastic properties of the matrix and the cell morphology of

foamed plastics in different manners, because of the differences in their thermal decomposition behaviors.[23,24]

Endothermicity has been reported to be a desirable property because the foaming agent absorbs heat during its decomposition, which cools the polymer, increases the viscosity of the melt, stabilizes the cellular structure, and reduces cell coalescence.[23,24] By contrast, exothermic CFAs generate a lot of heat upon their decomposition. This heat may soften the polymer matrix and favor the occurrence of cell coalescence during the foaming process, resulting in a poor cellular structure with large bubbles.[23,24]

Despite the known effect of CFA types on the cell morphology of unfilled plastic foams, prior research has not extensively examined the effect of CFA types on the cell morphology of plastic compounds filled with wood fibers. Because the addition of wood fibers into the plastic matrix affects the viscoelastic properties of the matrix,[6,18] it is believed that the above-mentioned effect of CFA types on the cell morphology of unfilled plastic foams will change when incorporating wood fibers into the polymer matrix. Thus, it is necessary to examine the effect of CFA types on the foamability of wood-fiber filled plastic composites.

Besides the nature of gas given off upon their thermal decomposition, the CFAs used in the extrusion foaming process can be either in pure or masterbatch form (i.e., without or with polymer carriers). It has been reported that the polymer carriers of the CFAs can improve the compatibility between the active foaming agent and the polymer matrix, which may favor the production of foamed samples with fine cell morphology.[25] Nevertheless, the significance of the polymer carriers of the CFAs in the extrusion foaming of wood-fiber filled plastic composites has not been evaluated.

The use of coupling agents, which are important ingredients in the formulations of plastic/wood-fiber composites, also has a significant effect during the foaming process of the composites. Matuana et al.[17,18] reported that the surface modification of wood fiber with a coupling agent has strong effects on both the concentration of gas molecules absorbed by the composites and the cell morphology of the foamed composites produced through a batch foaming process. They showed that a microcellular-foamed structure was better developed in the composites with treated wood fibers than in the composites with untreated fibers because the addition of coupling agent into the formulation helped encapsulate the gas in the composites for the cell growth.

Despite this current state of knowledge, extrusion foaming of PE/wood-fiber composites has not received substantial attention in the open literature. Therefore, the main objective of this study was to develop high density PE (HDPE)/wood-flour composite foams through a continuous extrusion process using CFAs. Particular emphasis was placed on evaluating the effects of CFA contents, CFA types (endothermic vs. exothermic) and forms (with vs. without a polymer carrier), together with the effect of a coupling agent on the density reduction (or void fraction) and cell morphology of neat HDPE and HDPE/wood-flour composite foams.

EXPERIMENTAL

Materials

Petrothene LR 734001 (melt index = 0.38 dg/min, density = 0.954 g/cm^3), an HDPE from Equistar Chemicals, was used as the polymeric matrix. Commercial wood flour from hardwood maple was used as the filler. This wood flour was low specific gravity (0.54), standard grade (100-mesh size) supplied by American Wood Fibers. Three endothermic CFAs [BIH40, sodium bicarbonate (SB), and FP] and three exothermic CFAs (Celogen-OT, Celogen-AZNP, and EX210) were utilized in this study. The detailed information on all these CFAs is described in Table I. Among the CFAs used, BIH40 and EX210 had polymer carriers, whereas SB, FP, Celogen-OT, and Celogen-AZNP had no polymer carrier. Maleated PE with a melt flow rate of 5 dg/min and a percentage of functionality of 1.0 (Polybond 3009, Uniroyal Chemicals) was used as the coupling agent.

Thermal analysis of plastic and CFAs

The melting temperature (T_m) of the HDPE was determined using a Shimadzu differential scanning calorimeter (DSC) at a heating rate of 10°C/min in a nitrogen atmosphere. The peak melt temperature of the HDPE was 133.2°C (with the onset and end set at 123 and 143°C, respectively).

The thermal decomposition behaviors of CFAs (i.e., decomposition temperature, decomposition rate, and decomposition heat) were characterized using a high pressure DSC (Mettler Toledo Star System) at a heating rate of 10°C/min in a nitrogen atmosphere. The results are summarized in Table II.

The decomposition temperatures of the CFAs listed in Table II were characterized as the peak position of the decomposition of the CFAs. The decomposition rate of the CFAs was obtained by measuring the width of the decomposition peaks at half their height. The decomposition heat (ΔH) was determined from the area under the DSC curve (i.e., the amount of heat released or absorbed by the CFAs upon their decomposition reactions). A positive sign denotes the heat given off by the materials (exothermic), whereas a negative sign denotes the heat absorbed by the materials (endothermic). These thermal behaviors were

TABLE I
Specifications of CFAs Used in Study

Trade Names	Suppliers	Decomposition Reactions	Chemical Compositions	CFA/Carrier Masterbatch	Decomposition Gas
BIH40	Boehringer Ingelheim Chemicals	Endothermic	Sodium salt of polycarbonic acid + carbonate compounds	40/60[a]	CO_2
Sodium bicarbonate	Groupe Cantin, Beauport, Québec, Canada	Endothermic	Sodium bicarbonate	100/0	$CO_2 + H_2O$
FP	Reedy Chemicals	Endothermic	Encapsulated sodium salts of carbonic + polycarboxylic acids	100/0	CO_2
Celogen-OT	Uniroyal Chemicals	Exothermic	P,P'-Oxybis (benzenesulfonyl hydrazide)	100/0	N_2 + small amount of H_2O
Celogen-AZNP	Uniroyal Chemicals	Exothermic	Modified (nonplateout grade) azodicarbonamide	100/0	42% N_2, 21% CO, 21% NH_3, + 16% CO_2
EX210	Boehringer Ingelheim Chemicals	Exothermic	Azodicarbonamide	20/80[b]	N_2 + trace of CO_2 and NH_3

[a] The polymer carrier is polyethylene.
[b] The polymer carrier is polystyrene.

used to set up the extruder's processing temperature (temperature profile from the hopper to the die) during the foaming experiments.

Extrusion foaming

Wood flour, HDPE, CFAs, and coupling agent were dry blended in a high intensity mixer (TGAHK20, Papenmeier) for 5 min. Three different formulations were made in this study: HDPE alone, HDPE/wood-flour composites without coupling agent, and HDPE/wood-flour composites with coupling agent. The addition levels of CFAs, wood flour, and coupling agent are listed in Table III. After blending, the compounded materials were extruded through a 19.1-mm single-screw extruder (length/diameter ratio = 30/1, C.W. Brabender) to produce foamed samples. The rotational screw speed was set at 40 rpm.

As previously mentioned, the extruder temperature profile was set up based on the thermal analysis results of neat HDPE and CFAs. The neat HDPE matrix

used in this study melted at around 135°C and the decomposition temperatures of the investigated CFAs are in the range of 170–210°C (Table II). Based on these results, the extruder barrel's temperature profile was set as follows: zone 1: 170°C, zone 2: 180°C, and zone 3: 190°C. This barrel temperature profile was chosen to insure both the complete melting of the polymer matrix and the advanced degree of CFA decomposition during the experiments, while preventing the decomposition of wood flour that occurs at temperatures above 200°C.[26] The die temperature was set at 190°C during the experiments, unless mentioned otherwise.

Characterization of microstructure of foamed samples

After foaming, the extrudates were immediately dipped into a water bath to freeze the foam structure and minimize the deterioration of cells through cell coalescence during bubble growth.[11] The densities of

TABLE II
Data on Thermal Decomposition Heat (ΔH), Decomposition Temperature (Peak Max.), and Decomposition Rate (Peak Width) of CFAs as Determined by DSC

CFAs	Decomposition of Peak 1					Decomposition of Peak 2				
	ΔH (J/g)	Onset (°C)	End Set (°C)	Peak Max. (°C)	Peak Width (°C)	ΔH (J/g)	Onset (°C)	End Set (°C)	Peak Max. (°C)	Peak Width (°C)
BIH40	—	—	—	—	—	−422.2	178.1	191.9	185.3	9.3
Sodium bicarbonate	−134.7	170.7	181.0	174.5	6.1	−283.1	196.3	218.4	209.4	16.2
FP	—	—	—	—	—	−129.6	176.4	205.4	193.9	16.6
Celogen-OT	—	—	—	—	—	1066.7	161.8	179.6	171.7	11.2
Celogen-AZNP	—	—	—	—	—	635.0	205.1	211.1	209.4	3.7
EX210	—	—	—	—	—	1263.5	208.3	215.7	212.9	4.3

Ingredients	Neat Plastic (%)	Composites (%)
HDPE	100	60[a]
Wood flour	0	40[a]
CFA[b]	0–2	0–2
Coupling agent[c]	0	0 and 5

[a] The percentage is based on the total weight of the composites.

[b] The amount of active CFAs (not including the carrier) and the CFA content is based on the weight of neat HDPE.

[c] The coupling agent content is based on the weight of the wood flour.

the unfoamed (ρ_u) and foamed (ρ_f) samples were determined according to ASTM standard D792 using an Archimedes water displacement technique. Twenty replicates were used for each formulation. The void fraction (VF) or, equivalently, the density reduction, achieved in the samples was calculated according to the following equation[11,18]:

$$VF = \frac{(\rho_u - \rho_f)}{\rho_u} \cdot 100 \quad (1)$$

A Philips environmental scanning electron microscope (ESEM) was used to determine the average cell size developed in the foamed samples. Liquid nitrogen was used to freeze the samples before they were fractured to expose the internal features. The average cell size of the foamed samples was determined from the ESEM micrographs.

Statistical analysis

A one-way analysis of variance (ANOVA) was conducted to examine the differences in the mean void fraction among neat HDPE and HDPE/wood-flour composites foamed with various formulations. All analyses were performed using Design-Expert software version 6 (STAT-EASE, Corp.).

RESULTS AND DISCUSSION

Comparison of void fraction of neat HDPE and HDPE/wood-flour composite foams

The performance of various CFAs was examined to identify the most appropriate CFAs for foaming neat HDPE and HDPE/wood-flour composites. Figure 1 shows the effects of CFA types and the addition of coupling agent on the density reduction of neat HDPE and HDPE/wood-flour composite foams.

A single-factor ANOVA was performed on the data shown in Figure 1 to discern the effects of CFA types

and coupling agent on the void fraction of foamed neat HDPE and HDPE/wood-flour composites. The ANOVA results showed that the values of the predicted coefficient of regression (pred. $R^2 = 0.9601$) and adjusted R^2 (adj. $R^2 = 0.9622$) were both in agreement with that of the R^2 ($R^2 = 0.9641$). In addition, the value of the probability (p) $> F$ for the model (Fig. 1) was less than 0.0001, implying that the model was significant.

Note from Figure 1 that the incorporation of wood flour into the HDPE matrix significantly affected the void fraction of HDPE/wood-flour composite foams. The void fractions in the composites were far inferior to those in the unfilled neat HDPE counterparts, regardless of the use of the coupling agent (Fig. 1). This tendency was expected because the number of nucleated cells and their growth, which controls the void fraction during the foaming process, are strongly dependent on the amount of gas molecules dissolved in the material.[11,17,18] Because the amount of gas absorbed by the composite samples during foaming is much lower than that absorbed by neat plastic,[11,17,18] the void fractions in the composites were far inferior to those in the unfilled HDPE counterparts.

One can also notice that a slight but significant improvement in the void fraction could be achieved by utilizing a coupling agent in the composites (Fig. 1). As shown in this figure, the addition of coupling agent has significantly improved the void fraction of HDPE/wood-flour composites foamed with BIH40, Celogen-OT, and Celogen-AZNP foaming agents whereas no significant improvement was observed with SB, FP,
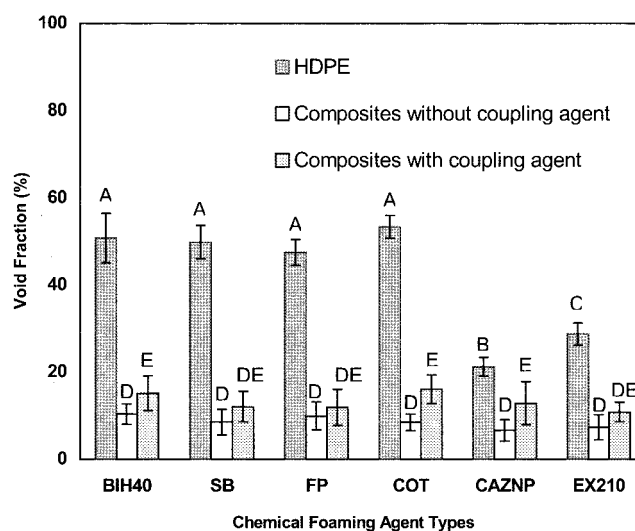

Figure 1 The effect of CFA types on the void fraction of foamed neat HDPE and HDPE/wood-flour composites with and without coupling agent. The letters in the graph represent the ANOVA results. The same letter denotes that the difference between these two treatments is not statistically significant ($p > 0.1$). Otherwise, the difference is statistically significant ($p < 0.05$).

TABLE IV
Comparison of Void Fraction and Average Cell Size of Neat HDPE and HDPE/Wood-Flour Composites Foamed with Celogen-AZNP and EX210 at Two Die Temperatures

| | Void Fraction (%) | | | | Average Cell Size (μm) | | | |
| | Celogen-AZNP | | EX210 | | Celogen-AZNP | | EX210 | |
Foamed Samples	190°C	220°C	190°C	220°C	190°C	220°C	190°C	220°C
HDPE	21.2 (2.2)	38.0 (1.4)	28.7 (2.1)	49.9 (3.0)	86.1 (6.7)	117.6 (32.8)	50.2 (5.0)	123.3 (33.8)
Composites without coupling agent	6.6 (2.4)	10.1 (2.2)	7.3 (2.9)	11.8 (2.2)	45.1 (10.0)	45.4 (13.0)	49.6 (5.0)	45.4 (10.0)
Composites with coupling agent	12.8 (0.1)	13.8 (3.0)	10.8 (2.3)	15.0 (2.2)	46.5 (8.4)	45.5 (12.3)	50.6 (4.8)	47.5 (6.4)

The values in parentheses represent the standard deviations.

and EX210 foaming agents. The increased void fraction of foamed composites with coupling agent may be attributed to the improved interfacial adhesion between the HDPE matrix and the wood flour. When the adhesion between the matrix and the filler is enhanced through the use of a coupling agent, more gas is dissolved in the samples and a foamed structure is better developed (i.e., higher void fraction). These results are in agreement with those reported in the literature.[17,18] However, the ineffectiveness of the coupling agent with certain foaming agents cannot be explained at the moment.

Figure 1 also shows that the void fractions of foamed neat HDPE and HDPE/wood-flour composites are not a function of the CFA types. Among the CFAs investigated, three endothermic CFAs (BIH40, SB, and FP) and one of the exothermic CFAs (Celogen-OT) produced foamed neat HDPE samples with similar void fractions and performed better than the other two exothermic CFAs (Celogen-AZNP and EX210). By contrast, both endothermic and exothermic CFAs produced HDPE/wood-flour composite foamed samples with similar void fractions.

The lower void fractions achieved in neat HDPE samples foamed with Celogen-AZNP and EX210 may be attributed to the incomplete decomposition of these two exothermic CFAs because of the lower processing temperature profile used during the experiments. This was expected because a large amount of gas molecules must be available in the polymer matrix for the cell growth to produce foams with a high void fraction.[11,17,18] Because the decomposition temperatures of the Celogen-AZNP and EX210 foaming agents are higher than the 190°C temperature set at the die (Table II), it is believed that the lower processing temperature at the die led to an incomplete decomposition of these two exothermic CFAs, resulting in a lesser amount of gas available for bubble growth. It is attributable to the lower content of gas that the void fractions achieved with Celogen-AZNP and EX210 exothermic CFAs were far inferior to those achieved with the other CFAs we investigated.

To validate the above-mentioned hypothesis, neat HDPE and HDPE/wood-flour composite samples were foamed at an elevated die temperature of 220°C using both Celogen-AZNP and EX210 exothermic CFAs. This high temperature was selected to increase the degree of decomposition of these two foaming agents. The results listed in Table IV clearly show that the void fractions of foamed neat HDPE and HDPE/wood-flour composite samples increased with the die temperature increase and almost reached the values achieved with other CFAs (Fig. 1). These results imply that the density reductions of foamed neat HDPE and HDPE/wood-flour composites are independent of the CFA types but are strongly influenced by the specific temperature profile used during processing. However, it should also be mentioned that a different trend was observed for SB, which also decomposes at a higher temperature (second peak at 209.4°C, Table II). A higher void fraction was achieved with SB, even after processing at a lower die temperature (190°C). It seems that a sufficient amount of gas for nucleation and growth of cells was generated during the first decomposition stage (at around 174.5°C) of this foaming agent.

Comparison of average cell size of neat HDPE and HDPE/wood-flour composite foams

The effects of the CFA types and forms on the cell morphology of foamed neat HDPE and HDPE/wood-flour composites is shown in Figures 2–4. Table V summarizes the average cell size measured from the ESEM micrographs.

Consider first the effects of the CFA types and the use of coupling agent on the average cell size of foamed HDPE/wood-flour composites as shown in Figures 2 and 3 and Table V. It is clearly seen that the foaming of the HDPE/wood-flour composite is not sensitive to the CFA types, independent of the use of coupling agent. All foamed HDPE/wood-flour composite samples had cells with finer average size than their neat HDPE counterparts, regardless of the CFA types. This was expected because the incorporation of
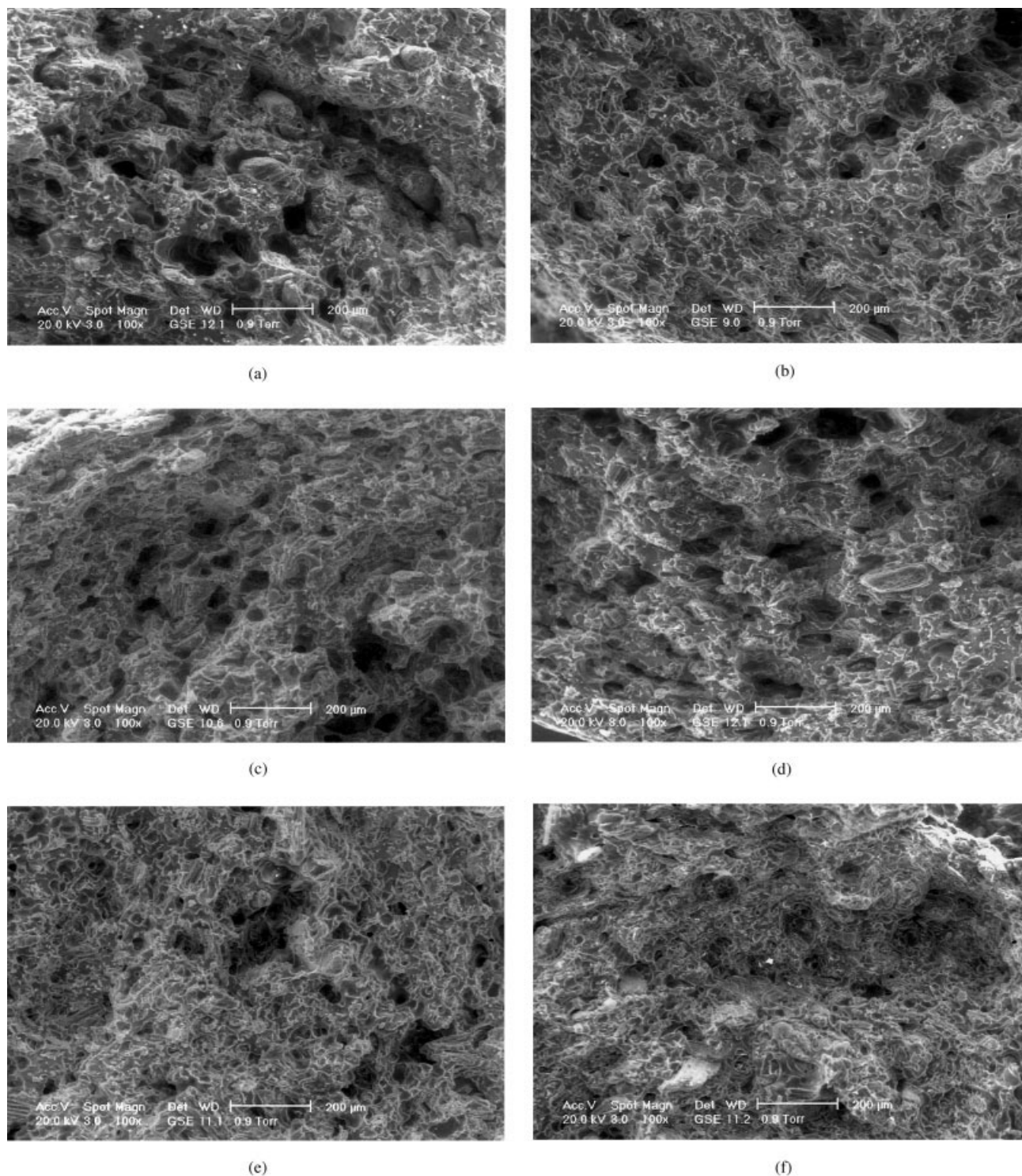
Figure 2 ESEM micrographs of HDPE/wood-flour composites (without coupling agent) foamed with endothermic CFAs (a) BIH40, (b) sodium bicarbonate (SB), and (c) FP and exothermic CFAs (d) Celogen-OT, (e) Celogen-AZNP, and (f) EX210.

wood flour into the HDPE matrix increased the melt viscosity of the matrix and made the composites stiffer than the unfilled HDPE, which provided high resistance to the cell growth in the polymer matrix.[10,11,18] One can also notice that the average cell size of composite foams with coupling agent was slightly larger

than that of the composites without coupling agent, as expected.

Next, consider the effect of CFA types on the average cell size of neat HDPE foams as shown in Figure 4 and Table V. It appeared that the cell morphology of neat HDPE foams was not a function of CFA type.
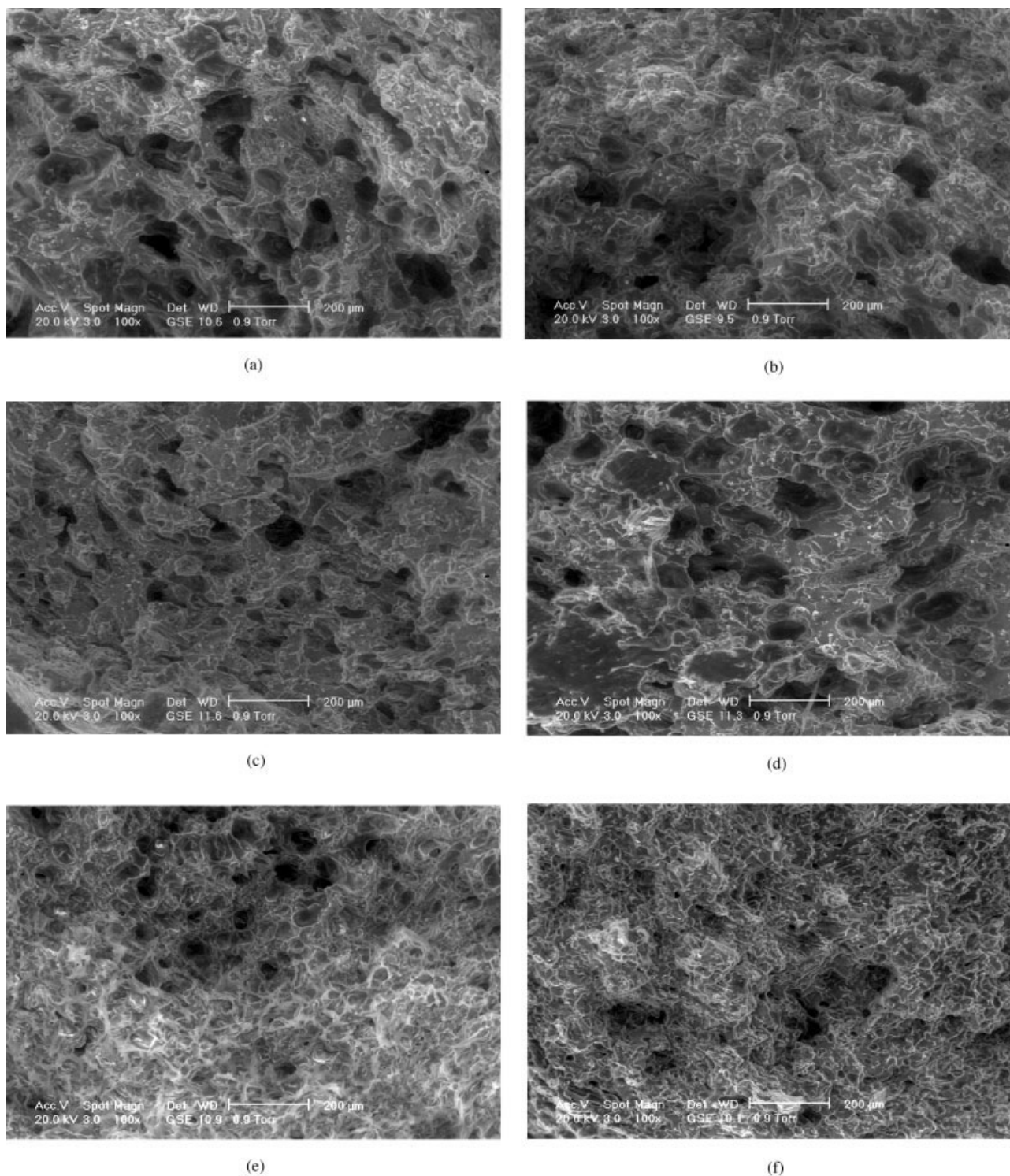
Figure 3 ESEM micrographs of HDPE/wood-flour composites (with coupling agent) foamed with endothermic CFAs (a) BIH40, (b) sodium bicarbonate (SB), and (c) FP and exothermic CFAs (d) Celogen-OT, (e) Celogen-AZNP, and (f) EX210.

When foamed at the same processing conditions, both endothermic (BIH40 and FP) and exothermic (Celogen-AZNP and EX210) CFAs produced neat HDPE foams with fine cell size (below 200 μm) whereas SB (endothermic) and Celogen-OT (exothermic) produced neat HDPE foams with large cell size (400–1300 μm).

The difference in the cell morphology of neat HDPE foamed with various CFAs may result from the different thermal decomposition behaviors of CFAs and/or the nature of gas given off upon their thermal decomposition. CFAs with a slow decomposition rate (i.e., a wide peak width) have been reported to initially nucleate a small number of bubbles.[23] As more gas is
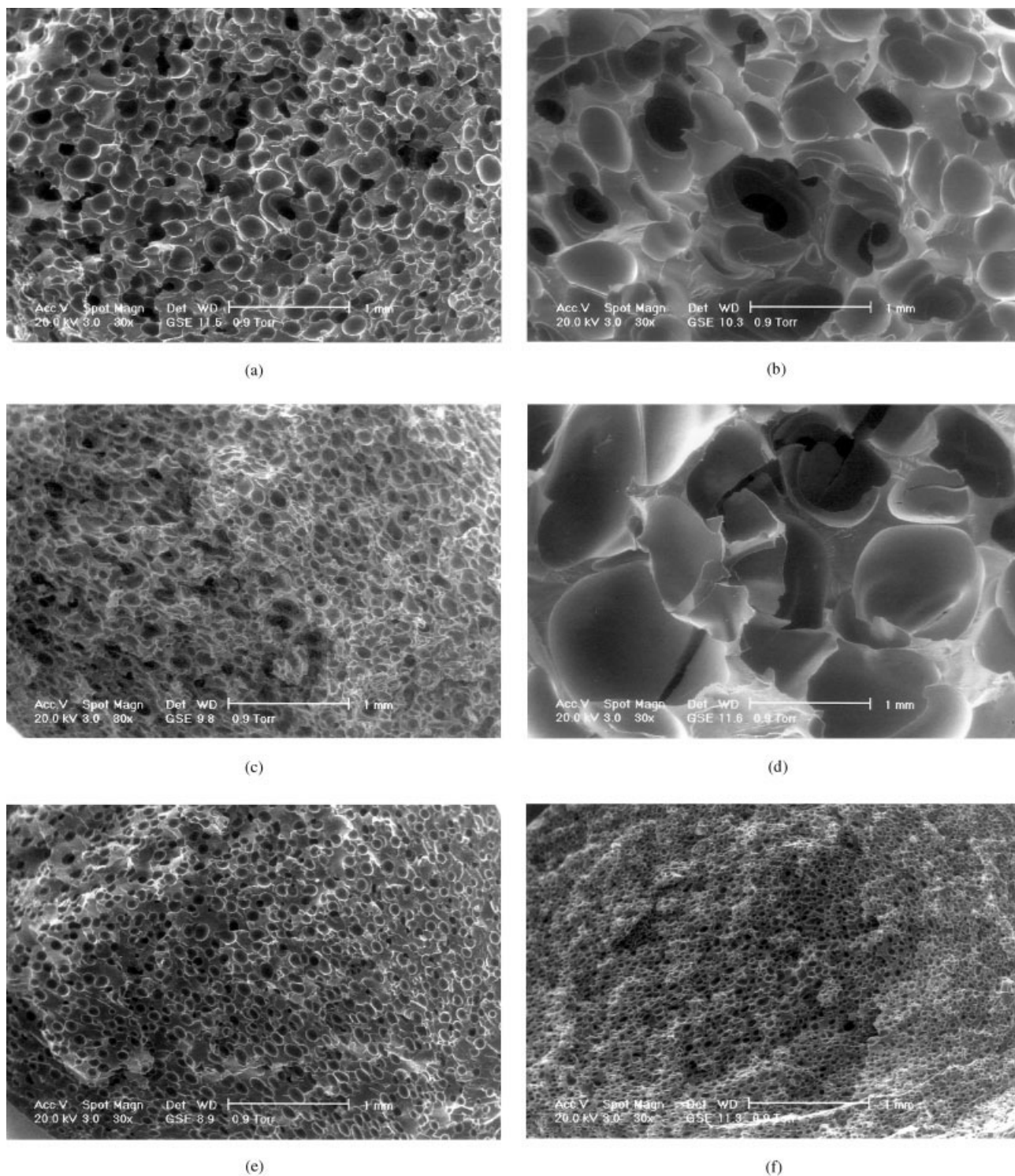
Figure 4 ESEM micrographs of neat HDPE foamed with endothermic CFAs (a) BIH40, (b) sodium bicarbonate (SB), and (c) FP and exothermic CFAs (d) Celogen-OT, (e) Celogen-AZNP, and (f) EX210.

generated, it migrates preferentially to the existing bubbles rather than nucleating new bubbles, leading to the growth of large irregular bubbles.[23] Based on these findings, the larger cell size of neat HDPE samples foamed with SB could be attributed to the slowest decomposition rate of the foaming agent. Table II

shows that SB has two decomposition peaks and its decomposition temperature range is much wider than that of the other CFAs investigated, which indicates a slower gas evolution rate (total decomposition rate of 22.25°C from both peaks). However, because an opposite trend was observed with other endothermic CFAs,

TABLE V
Average Cell Size of Neat HDPE and HDPE/Wood-Flour Composites Foamed with Various CFAs

CFAs	Average Cell Size (μm)		
	Neat HDPE	Composites Without Coupling Agent	Composites with Coupling Agent
BIH40	191 ± 23	52 ± 8	59 ± 7
Sodium bicarbonate	393 ± 54	55 ± 8	64 ± 13
FP	90 ± 11	46 ± 8	48 ± 8
Celogen-OT	1305 ± 285	52 ± 10	57 ± 9
Celogen-AZNP	86 ± 7	45 ± 10	47 ± 8
EX210	50 ± 5	50 ± 5	51 ± 5

the influence of the CFA thermal decomposition rate on the average cell size of neat HDPE foams could not be generalized. One can observe in Table V that neat HDPE samples foamed with FP had a finer average cell size compared to that achieved with BIH40, despite the slower decomposition rate of the FP foaming agent.

Along with the CFAs' decomposition rate, the decomposition heat of CFAs is also one of the important factors affecting the CFAs' performance. Contrary to the belief that endothermic CFAs usually produce thermoplastic foams with a fine cell structure and exothermic CFAs usually produce plastic foams with large cell size,[23,24] our experimental results show that the average cell size developed in neat HDPE foams is not governed by the type of CFAs. Even at elevated die temperature, EX210, an exothermic CFA, produced neat HDPE foams with smaller average bubble size (Table IV) than some of the endothermic CFAs (BIH40, SB) investigated (Table V), although it generates more heat upon its decomposition than the other CFAs (Table II). Conversely, SB, an endothermic CFA, produced neat HDPE foams with larger average size than exothermic CFAs (Celogen-AZNP and EX210). These results indicate that the cell morphology developed in neat HDPE foams is not a function of the

decomposition reaction type (endothermic vs. exothermic reaction) of the CFAs. Instead, some other factors such as the type of gas given off upon the decomposition of the CFAs may also be responsible for the cell morphology achieved in neat HDPE foams.

Cells with larger average size (above 400 μm) were produced in neat HDPE samples only when SB and Celogen-OT were used as the foaming agents. One can notice that these two CFAs give off water during their thermal decomposition, whereas the other CFAs investigated do not produce moisture (Table I). Because the solubility of water in a hydrophobic plastic matrix is very low, water molecules tend to aggregate together instead of evenly dispersing in the polymer matrix during the foaming process,[20] thus leading to the formation of cells of larger average size because water is an effective blowing agent.[10,20]

It is also necessary to mention that the CFAs used in this study differed from each other by the presence (masterbatch) or absence (pure) of polymer carriers. Foaming agents with polymer carriers may result in the development of fine cell morphology in the foamed samples because the polymer carriers can facilitate the dispersion of active foaming agents in the polymer matrix.[25] An opposite trend was obtained in this study because the experimental results indicated that the presence of polymer carriers was not a significant factor affecting the cell morphology of neat HDPE foams. Foamed neat HDPE samples with fine cells were produced even with FP and Celogen-AZNP foaming agents, although they do not have polymer carriers (Table I).

Effect of CFA contents on foamability of HDPE and HDPE/wood-flour composites

In previous sections, the effects of CFA types, CFA forms, and the use of a coupling agent on the foamability of neat HDPE and HDPE/wood-flour composites were examined by keeping the CFA content constant at 1% of the active blowing agent. Because the CFA addition levels affect the void fractions and the

TABLE VI
Effect of Active CFA Contents on Void Fraction of Neat HDPE and HDPE/Wood-Flour Composite Foams

Active CFA Contents (%)	Void Fractions (%)			
	Endothermic CFA (BIH40)		Exothermic CFA (Celogen-OT)	
	Neat HDPE	Composites	Neat HDPE	Composites
0	0	0	0	0
0.5	46.4 ± 1.6[A]	12.8 ± 3.3[D]	42.5 ± 2.2[A]	12.2 ± 3.8[D]
1	50.8 ± 5.7[B]	15.2 ± 4.0[D]	53.4 ± 2.6[B]	16.1 ± 3.3[D]
1.5	34.3 ± 1.6[C]	11.6 ± 3.9[D]	56.3 ± 1.5[B]	15.4 ± 3.5[D]
2	30.5 ± 1.6[C]	11.1 ± 2.6[D]	25.3 ± 3.3[C]	14.3 ± 3.7[D]

The composite samples contained 5% maleated polyethylene as the coupling agent. The superscript letters represent the ANOVA results. The same letter denotes the difference between these two treatments is not statistically significant ($p > 0.1$). Otherwise, the difference is statistically significant ($p < 0.05$).
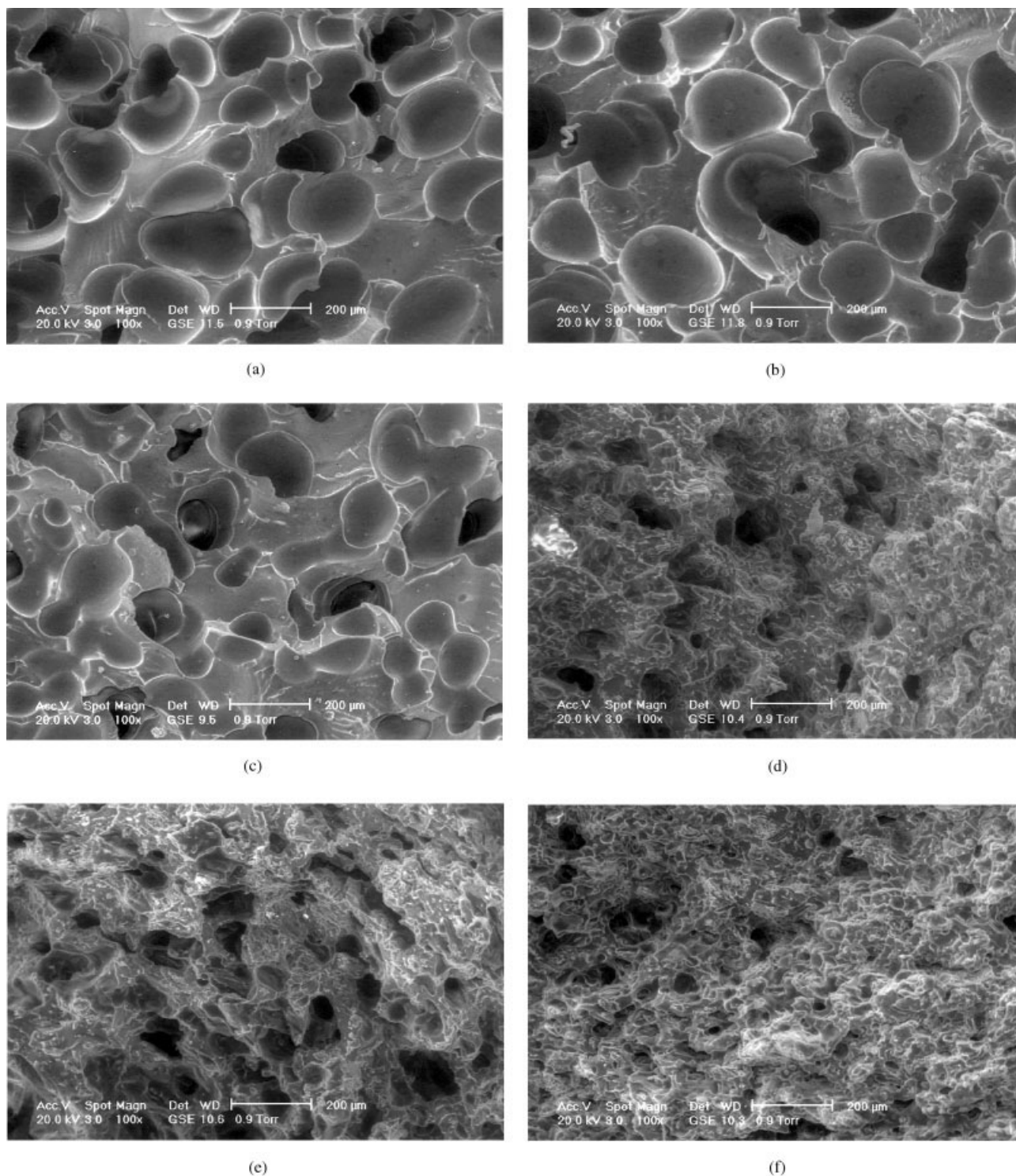
Figure 5 ESEM micrographs of neat HDPE foamed with (a) 0.5, (b) 1, and (c) 2% of BIH40 and HDPE/wood-flour composites (with coupling agent) foamed with (d) 0.5, (e) 1, and (f) 2% of BIH40 foaming agent.

cell morphology of extrusion-foamed materials,[10,11] the effect of the CFA concentrations was evaluated by quantifying the void fraction (Table VI) and average cell size (Fig. 5) of neat HDPE and HDPE/wood-flour composite samples foamed with endothermic (BIH40) and exothermic (Celogen-OT) CFAs.

A statistical analysis was performed on the data to distinguish the differences among the void fraction of samples foamed with various concentrations of both BIH40 and Celogen-OT foaming agents. The results listed in Table VII show that the models were statistically significant for both CFAs as indicated by $p > F$,

TABLE VII
Values of Coefficient of Regression (R^2) from ANOVA Analysis of Void Fraction Data of Neat HDPE and HDPE/Wood-Flour Composites Foamed with Endothermic (BIH40) and Exothermic (Celogen-OT) CFAs

ANOVA Parameters	BIH40	Celogen-OT
Model $P > F$	<0.0001	<0.0001
R^2	0.9564	0.9709
Adjusted R^2	0.9543	0.9695
Predicted R^2	0.9516	0.9677
Adequate precision	53.2	64.0

various R^2 parameters, and the values of adequate precision. The value of adequate precision measures the signal to noise ratio, and a ratio greater than 4 is usually desirable to navigate the design space.[27,28]

Several observations can be made from the results summarized in Table VI and Figure 5. Regardless of the CFA contents, the void fractions of neat HDPE samples were significantly higher than that of the composites. In addition, the average cell sizes developed in the foamed HDPE/wood-flour composites were much smaller than that developed in neat HDPE foams. These results were expected due to the greater stiffness and lower solubility of gas in the composites compared to unfilled polymer matrix.[10,11,17,18]

The void fraction of neat HDPE samples was significantly affected by the foaming agent's addition level. The void fraction of neat HDPE samples increased with the CFA content up to 1%. Above this concentration, the void fraction decreased with the CFA content, independent of the CFA type. This opposite trend in the void fraction could be attributed to the cell growth mechanism, which depends on the amount of gas dissolving in the polymer matrix during the foaming process.[18] As reported by Matuana et al.,[18,21] once the cells are nucleated, they continue to grow as long as there is enough gas for diffusion into the nucleated cells. The void fraction of the foamed sample will increase as the CFA content increases because of the cell growth.[18] However, once the nucleated cells are fully grown, cell coalescence and/or collapse may take place with a further increase in the CFA content. In particular, if cell collapse occurs, the average cell size will decrease and the void fraction of the resulting foamed samples will decrease.[18] This phenomenon is known as the gas containment limit[10,18,29] and is illustrated in Figure 5(a–c). In contrast, the gas containment limit was not observed for HDPE/wood-flour composite foams. One can notice from Table VI that the void fraction of the foamed composite samples was not affected by the CFA content. The void fraction of the foamed composite samples increased with the CFA content, reached the maximum value at around 0.5%, and leveled off. Other investigators have re-

ported similar behavior, which was attributed to the increased stiffness and melt viscosity of the composite, which offered a high resistance to cell growth.[10,11,18] Moreover, the average cell size shown in the ESEM micrographs clearly illustrate the absence of the gas containment phenomenon for the composites because the cell size remained almost insensitive to the increase in the CFA content [Fig. 5(d–f)].

CONCLUSIONS

This study examined the influences of the contents, types, and forms of CFAs, as well as the use of coupling agents, on the density reduction (or void fraction) and average cell size of extrusion-foamed neat HDPE and HDPE/wood-flour composites. The following conclusions can be made:

1. The CFA types (endothermic vs. exothermic) and forms (pure or masterbatch) did not affect the void fractions achieved in both neat HDPE and HDPE/wood-flour composite foams.
2. A gas containment limit was observed for neat HDPE foams whereas the average cell size achieved in the HDPE/wood-flour composite foams remained insensitive to the CFA contents, irrespective of the foaming agent types.
3. The use of a coupling agent in the formulation was required to achieve HDPE/wood-flour composite foams with high void fraction.
4. The optimum active CFA content (to maximize the void fraction) seemed to lie at around 1% for neat HDPE and 0.5% for HDPE/wood-flour composites, independent of the CFA type.

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