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Preparation and Cell Morphology of Ethylene-Vinyl Acetate Copolymer (EVA)/Wood-Flour Foams with Low Density

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ABSTRACT: The main objective of this study is to obtain ethylene-vinyl acetate copolymer (EVA)/wood-flour foams with low density (< 0.2 g/cm^3) using chemical blowing agent. Stearic acid was used as a compatibilizer to improve not only the compatibility between wood-flour and EVA but also the compatibility between moisture and EVA in this study. The effects of wood-flour content on the density and mechanical properties of EVA/wood-flour foams were studied. Also, the effects of content of stearic acid on the cell morphology of EVA/wood-flour foams were investigated. The shape of EVA/wood-flour foams with 20% wood-flour content becomes more uniform with increasing content of stearic acid. The most stabilized shape of the foams is obtained with 5 wt % stearic acid content. The density of EVA/wood-flour foams with 20% wood-flour and 5 wt % stearic acid is 0.11 g/cm^3. With increasing content of stearic acid, more gas remains in the EVA matrix and consequently, average cell size and density increase. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40894.

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INTRODUCTION

Because of the advantage of their light weight, buoyancy, cushioning performance, thermal and acoustic insulation, impact damping, and cost reduction, the markets for foams have been growing rapidly worldwide such as the automotive, packaging, construction, marine, sports, and leisure markets. The use of wood-flour in polymer foams has recently attracted great attention because of the growing environmental awareness.[1–21] The potential advantages of wood-flour, apart from their environmental gains, are the abundant availability of the raw materials from renewable resources and their low cost.

The main problem in the preparation of polymer/wood-flour foams is incompatibility between hydrophilic wood-flour and hydrophobic polymers. Also, incompatibility between the moisture released from wood-flour during foaming process and hydrophobic polymers generally leads to the nonuniform cell distribution. Therefore, many copolymers have been used as compatibilizers to improve the compatibility between hydrophilic wood-flour and hydrophobic polymer matrix. For example, maleic anhydride grafted polyolefins have been used as compatibilizers,[13–21] resulting in improvement of their physical properties. Compatibilizers also significantly influence the cell morphology. Several studies[3,4,14] have reported that compatibilizers prevent the gas from escaping during the foaming of polymer/wood-flour composites, resulting in higher void fraction.

Until now, most studies on polymer/wood-flour foams have centered on the investigation of polymer/wood foams with relatively high density (> 0.7 g/cm^3).[12,16–19] Even though low density is used for some applications of foams, there have been few studies on polymer/wood-flour foams with low density. Therefore, the main objective of this study is to obtain ethylene-vinyl acetate copolymer (EVA)/wood-flour foams with low density ($<$ 0.2 g/cm^3) using chemical blowing agent (CBA). EVA foams are extensively used for various purposes. In order to obtain low density of polymer foams, high melt strength is required in the foaming to enhance the resistance of the cellular material to thermal collapse. The high melt strength can be achieved by cross-linking EVA with dicumyl peroxide (DCP).

In this study, stearic acid was used as a compatibilizer to improve not only the compatibility between wood-flour and EVA but also the compatibility between moisture and EVA. The effects of wood-flour content on the density and mechanical properties of EVA/wood-flour foams were studied. Particular emphasis was placed on evaluating the effects of content of stearic acid on the cell morphology (average cell size and cell density) of EVA/wood-flour foams.

EXPERIMENTAL

Materials and Foam Preparation

EVA having 22% vinyl acetate content (melt index: 2 g/10 min, ASTM D1238) was provided by Hanwha Chem (South Korea).

Table I. Formulations of the EVA/Wood-Flour Foams Containing 5, 10, and 15 wt % Wood-Flour

Materials	Content (wt %)
EVA	100
Zinc oxide	3
Stearic acid	1
Wood-flour	5, 10, 15
DCP	1
JTR	5

The percentage is based on the weight of EVA.

Wood-flour (LIGNOCEL C20) was purchased from JRS (Germany). According to the provider, the size and bulk density of wood-flour are 70–150 μm and 0.1–0.135 g/cm^3, respectively.

DCP (Akzo Nobel, Netherlands) was used as a cross-linking agent. Zinc oxide (ZnO) from LG Chem (South Korea) was used as a cross-linking co-agent. Stearic acid with acid number 200–207 mg KOH/g from LG Chem (South Korea) was used as a compatibilizer. The CBA used was an activated azodicarbonamide, with a trade name of JTR from Kumyang (South Korea). This CBA decomposes in the temperature range of 130°C to 160°C, generating 160–180 cm^3/g of gas, most of which is nitrogen. Azodicarbonamide is odorless and easily dispersed. It is activated by organic acids, bases, and metal compounds.

Two different types of formulations are used for EVA/wood-flour foams as shown in Tables I and II. Stearic acid content was fixed at 1%, and three different contents of wood-flour were used: 5%, 10%, and 15% (Table I). Wood-flour content was fixed at 20%, and four different contents of stearic acid were used: 1%, 2%, 3%, and 5% (Table II). The percentage is based on the weight of EVA.

Wood-flour was dried at 80°C in an air circulating oven for 24 h (moisture content $<$ 1%) before mixing. However, it reabsorbed some moisture from the environment as the experiment has been done in the summer season (relative humidity $>$ 65%). As a result, the moisture content of wood flour is 1% before mixing with EVA. EVA, wood-flour and other additives were melt-mixed in a bench kneader PBV-03 (Irie Shokai, Japan) at 110° and 20 rpm. The glass transition temperature of EVA is around −30°C. However, EVA used in this study is a semicrystalline polymer and T_m is around 81°C. Therefore, to melt EVA completely, 110°C is used in the kneader. EVA was firstly melted for 2 min followed by the addition of wood-flour, ZnO, and stearic acid. Mixing was continued for 8 min to ensure the homogeneous dispersion of wood-flour and other additives in the matrix. Then, the obtained EVA/wood-flour mixtures were mixed with CBA and DCP in a two roll-mill at 90°C for 5 min. After being mixed in a two roll-mill, the mixture was put in a mold and was cross-linked at155°C under 14.7 MPa for 40 min in an electrically heated hydraulic press. After removal of the pressure, expansion took place immediately.

Foam Testing

A Universal Testing Machine (Model 4466, Instron, USA) was used to obtain the tensile strength of the foams at room temperature. The crosshead speed was 500 mm/min. The tensile strength was measured according to ASTM D412. All measurements were performed for five replicates of specimens and averaged to get the final result. The densities of the EVA/wood-flour foams were measured with a gravimeter (Ueshima MS-2150, Japan) using an Archimedes water displacement technique.

The rebound resilience was measured according to DIN 53512. The sample was placed in the sample holder and the pendulum was released from a horizontal position. The pendulum rebounded after impacting the sample and the angle of rebound was read. As the scale is graduated into 100 equal divisions, the percent rebound resilience is read directly from the scale.

Compressions set measurements were performed according to ASTM D395. The foams were compressed by 50% for 6 hours at 50°C and then the pressure was removed and the foam was allowed to recover for 30 minutes at ambient temperature. The final sample thickness was measured and the compression set was calculated using the following equation. The spacer thickness is the thickness to which the sample is compressed at the beginning of the test, which is 50% of the original sample thickness.

$$\text{Compression set } (\%) = [(T_o - T_f)/(T_o - T_s)] \times 100 \quad (1)$$

where T_o is the original sample thickness, T_f the final sample thickness, and T_s the spacer thickness.

Compression set is the reduction in thickness after a material is aged in compression. The lower the compression set is, the better the elastic recovery of the foam.

To investigate cellular structure, the cross sections of the EVA/wood-flour foams were cryogenically fractured and were examined with field emission gun-Scanning Electron Microscope (SEM, FEI Quanta 200, USA). All the cells in each SEM image were analyzed to obtain the average cell size and cell density. The cell size was determined by measuring the maximum diameter of each cell using Kanscope 3.0 (Mirero Co. Korea). The cell density (N_f), the number of cells per unit volume, is determined from the following equation[22]:

$$N_f = \left(nM^2/A\right)^{3/2} \quad (2)$$

where n is the number of cells on the SEM micrograph, M the magnification factor, and A the area of the micrograph (cm^2).

Table II. Formulations of the EVA/Wood-Flour Foams Containing 20 wt % Wood-Flour

Materials	Content (wt %)
EVA	100
Zinc oxide	3
Stearic acid	1, 2, 3, 5
Wood-flour	20
DCP	1
JTR	5

The percentage is based on the weight of EVA.

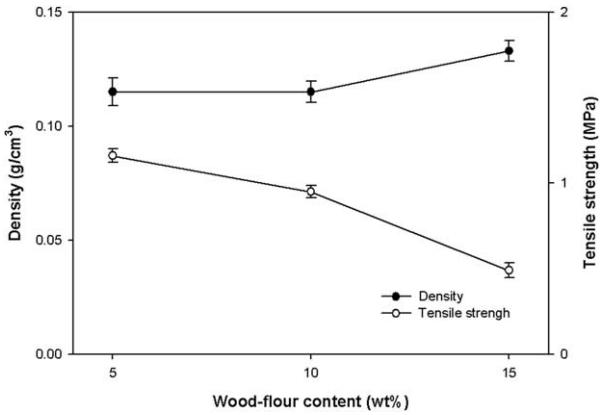

Figure 1. Effect of wood-flour content on density and tensile strength of EVA/wood-flour foams with 5%, 10%, and 15% wood-flour content.

RESULTS AND DISCUSSION

Table I shows the formulations of EVA/wood-flour foams containing 5%, 10%, and 15% wood-flour. Figure 1 shows the effect of wood-flour content on their density and tensile strength. The density of EVA/wood-flour foams increases with increasing content of wood-flour. This is because of the increased melt viscosity of EVA/wood-flour foams with increasing wood-flour content. The increased melt viscosity was confirmed by increased torque during melt-mixing. The increase in the melt viscosity restrains growth of cells during foam processing, leading to the increase of density. The tensile strength of EVA/wood-flour foams decreases with increasing content of wood-flour even though the density of the foams increases. This is because of poor compatibility between hydrophobic EVA and hydrophilic wood-flour.

Figure 2 shows the effect of wood-flour content on the compression set and rebound resilience of EVA/wood-flour foams with 5%, 10%, and 15% wood-flour content. Compression set is the reduction in thickness after a material is aged in compression. The lower the compression set value is, the better the elastic recovery of the foam. With increasing content of wood-flour, the compression set of EVA/wood-flour foams decreases. This decrease is because of the increased density. This result is also confirmed by increased rebound resilience of EVA/wood-flour foams with increasing content of wood-flour. The percent rebound resilience measured is inversely proportional to the hysteretic loss. The higher rebound resilience value is, the better the elastic recovery of the foam.

Even though the foaming of EVA/wood-flour composites with wood-flour content up to 15% was successful using 1% stearic acid, the foaming of EVA/wood-flour composites with 20% wood-flour content was not successful using 1% stearic acid as shown in Figure 3(a). During the foaming, water in 20% wood-flour can be released as a significant amount of moisture. As the solubility of hydrophilic moisture in hydrophobic polymer matrix is very low, moisture could aggregate together in the polymer matrix. Therefore, when the pressure is removed, cells developed by moisture could be coalesced and become large cells. Also, the gas from the smaller neighboring bubbles developed by CBA tends to diffuse into these large cells, and these large cells could be easily ruptured, resulting in large cavities and loss of gas.[13] The loss of gas and the resultant foam contraction lead to irregular-shaped EVA/wood-flour composite observed in Figure 3(a).

To improve not only the compatibility between wood-flour and EVA but also the compatibility between moisture and EVA, 1% stearic acid is used as a compatibilizer for the foams in Figures 1 and 2. However, for the foams with 20% wood-flour, 1% stearic acid is not enough amounts as shown in Figure 3(a). Therefore, more amounts of stearic acid are used as a compatibilizer for the foams as shown in Table II and Figure 3(b–d).

Stearic acid used in this study has hydrocarbon groups (C14: 2–5%, C16: 28–33% and C18: 58–63%) and COOH end groups. Hydrocarbon groups have interactions with EVA, and COOH end groups have interactions with wood-flour and moisture. Therefore, more amounts of stearic acid lead to a reduced agglomeration and better dispersion of wood-flour and moisture in the EVA matrix. As a result, the shape of EVA/wood-flour foams with 20% wood-flour content becomes uniform with increasing stearic acid content as shown in Figure 3. The most stabilized shape of EVA/wood-flour foams is obtained with 5 wt % stearic acid content. The density of EVA/wood-flour foams with 20% wood-flour and 5 wt % stearic acid is 0.11 g/cm^3.

Figure 4 shows the typical SEM images of the cellular structure of EVA/wood-flour foams with 20% wood-flour content. With 1% stearic acid content, only large cavities are observed as shown in Figure 4(a). With increasing content of stearic acid, more uniform closed-cell structures are observed as shown in Figure 4(b–d). This could be because of the improvement in the dispersion of wood-flour and moisture in EVA matrix.

Figure 5 shows the effect of stearic acid content on the average cell size and cell density of the EVA/wood-flour foams. As only large cavities are observed with 1% stearic content, average cell size and cell density for 1% stearic acid content are not included in Figure 5. EVA/wood-flour foams with 2% stearic content have an average cell size of 25 μm, and a cell density of 0.03×10^6 cell/cm^3. With 5% stearic acid content, the average

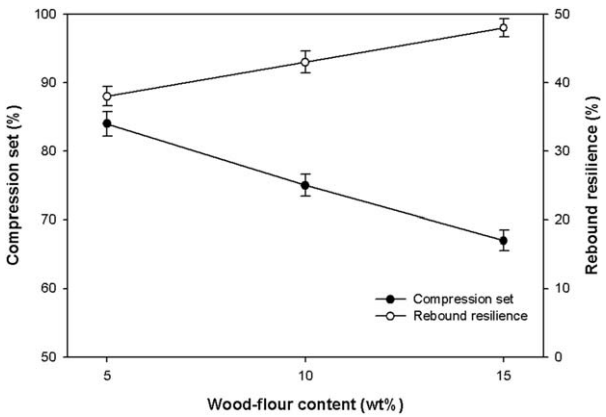

Figure 2. Effect of wood-flour content on compression set and rebound resilience of EVA/wood-flour foams with 5%, 10%, and 15% wood-flour content.

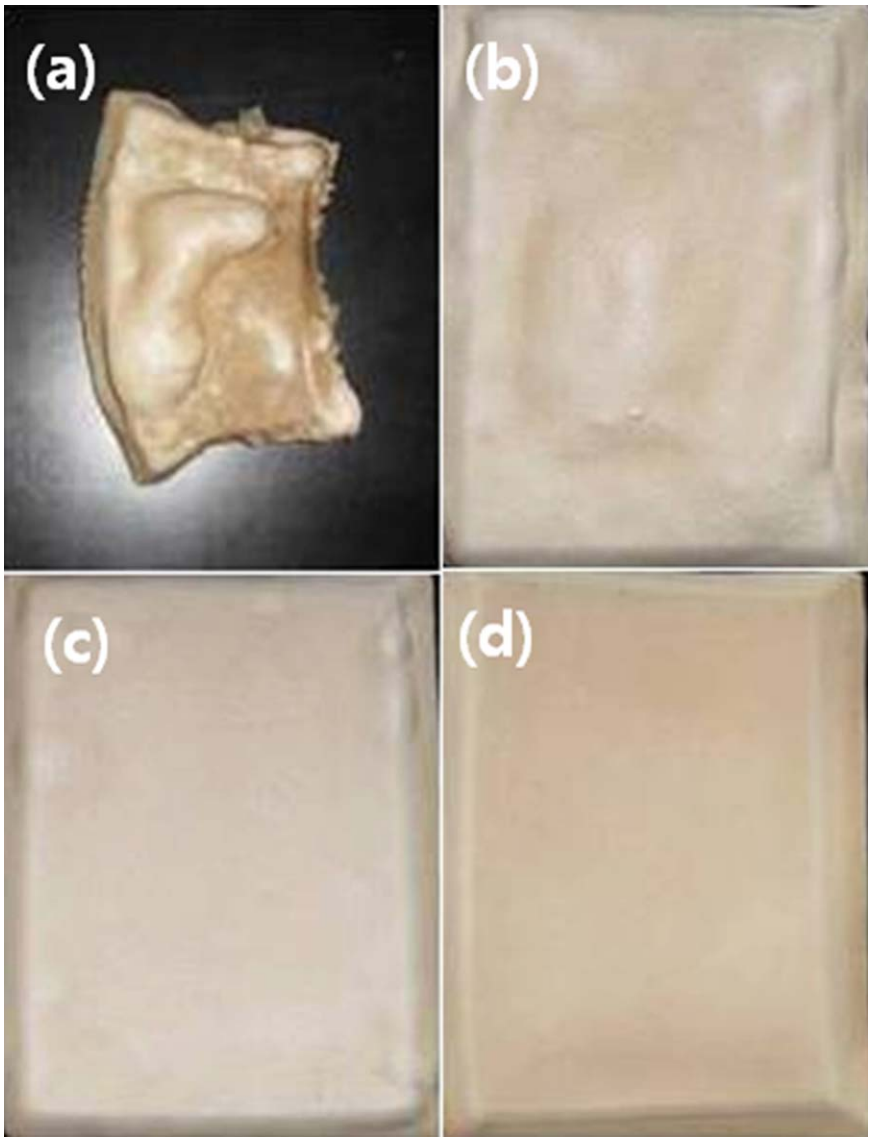

Figure 3. EVA/wood-flour foams with 20% wood-flour content and (a) 1% stearic acid content, (b) 2% stearic acid content, (c) 3% stearic acid content, and (d) 5% stearic acid content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cell size increases to 70 μm, and the average cell density increases to 4.15×10^6 cell/cm^3.

Increasing content of stearic acid not only improves the dispersion of wood-flour in EVA matrix, but also prevents the gas from escaping. With increasing content of stearic acid, more gas remains in the EVA matrix, and the amount of gas available for cell nucleation and growth increases. As a result, average cell size and cell density increase. Other investigators[14] have also reported that compatibilizers prevent the gas from escaping during the foaming of polymer/wood-flour composites, resulting in the increase of average cell size.

To evaluate the effect of CBA content on density of EVA/wood-flour foams with 20% wood-flour content, six different contents of CBA were used: 1%, 2%, 3%, 4%, 5%, and 6%. The content of stearic acid was fixed at 5%. The density of EVA/wood-flour foams with 20% wood-flour content continuously decreases with increasing CBA content in Figure 6. Matuana et al. reported[14] that void fraction of HDPE/wood-flour foams increased with CBA content up to 1% but slightly decreased as CBA content further increased. Void fraction is inversely proportional to density. Therefore, the density of HDPE/wood-flour foams cannot continuously decrease with increasing content of CBA. However, for EVA/wood-flour foams with 20% wood-flour content, their density can continuously decrease with increasing CBA content up to 6% in this study.

CONCLUSIONS

Even though the foaming of EVA/wood-flour composites with wood-flour content up to 15% was successful using 1% stearic acid, the foaming of EVA/wood-flour composites with 20% wood-flour content was not successful using 1% stearic acid. In order to improve the compatibility between moisture and EVA

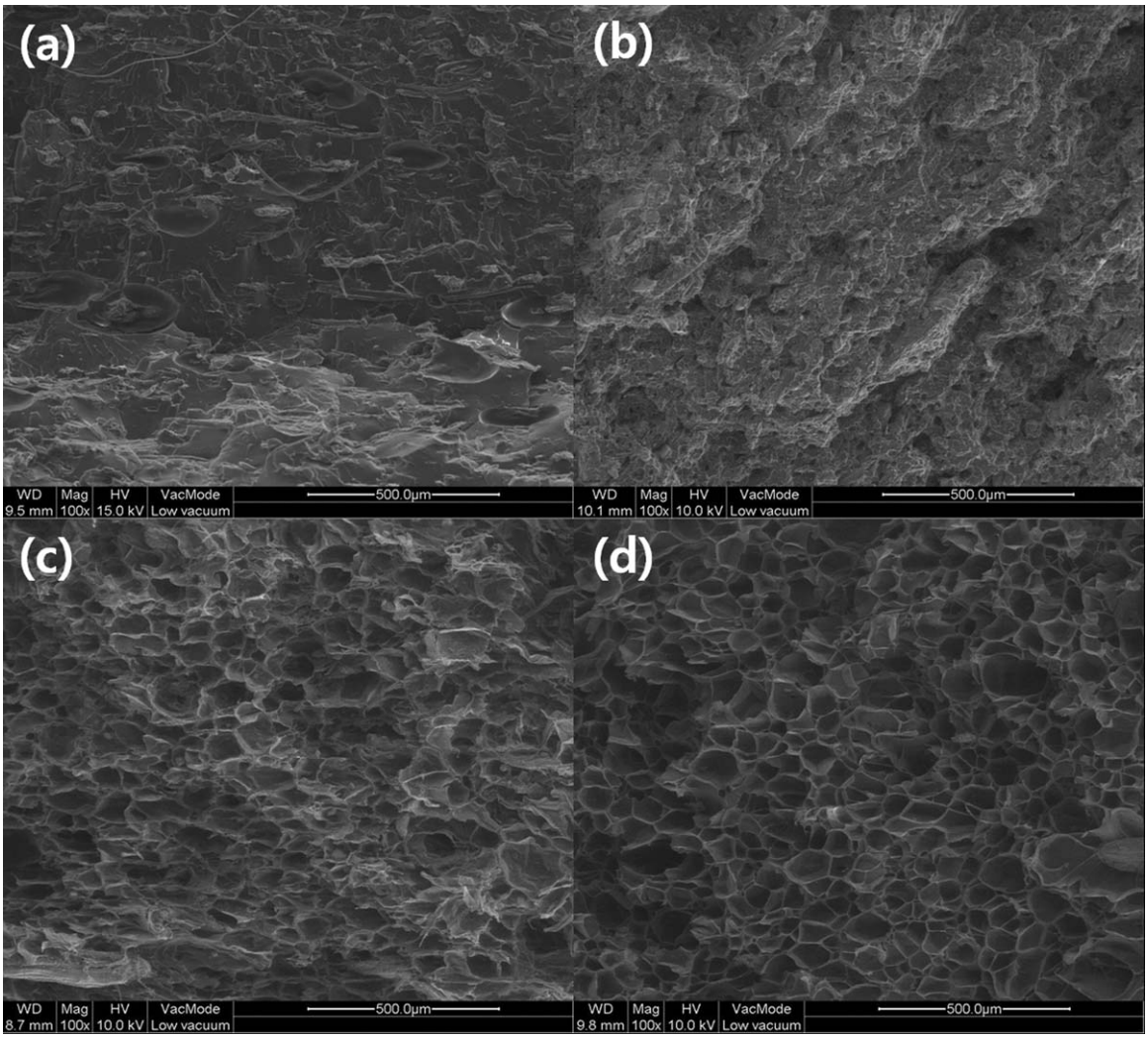

Figure 4. SEM images of the cellular structure of EVA/wood-flour foams with 20% wood-flour content and (a) 1% stearic acid content, (b) 2% stearic acid content, (c) 3% stearic acid content, and (d) 5% stearic acid content.

as well as the compatibility between wood-flour and EVA, stearic acid is used as a compatibilizer for EVA/wood-flour foams. However, 1% stearic acid is not enough for EVA/wood-flour composites with 20% wood-flour content. Therefore, more amounts of stearic acid are used for the foams with 20% wood-flour because it could lead to a reduced agglomeration and better dispersion of wood-flour and moisture in the

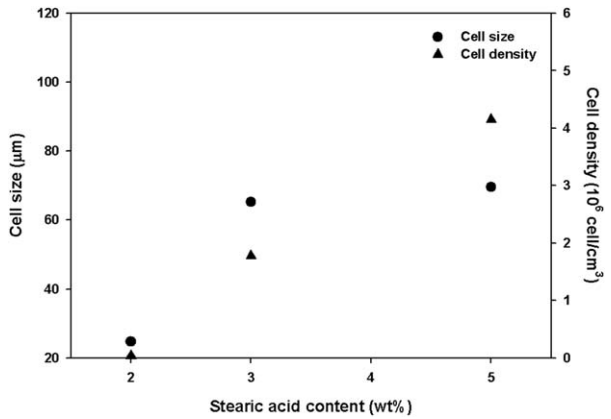

Figure 5. Effect of stearic acid content on average cell size and cell density of the EVA/wood-flour foams with 20% wood-flour content.

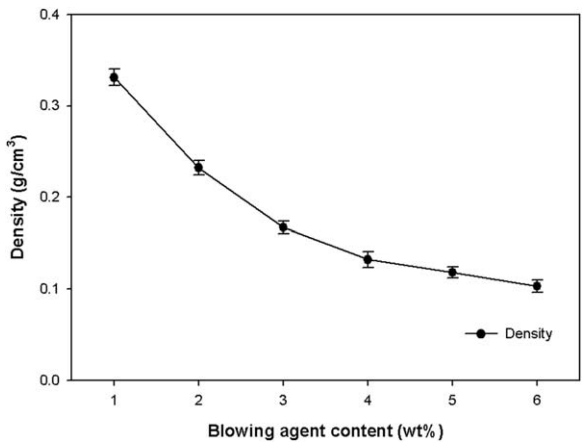

Figure 6. Effect of CBA content on density of EVA/wood-flour foams with 20% wood-flour content.

EVA matrix. As a result, the shape of EVA/wood-flour foams with 20% wood-flour content becomes more uniform with increasing content of stearic acid. The most stabilized shape of the foams is obtained with 5 wt % stearic acid content. The density of EVA/wood-flour foams with 20% wood-flour and 5 wt % stearic acid is 0.11 g/cm^3.

Increasing content of stearic acid prevents the gas from escaping as well as improves the dispersion of wood-flour in EVA matrix**.** With increasing content of stearic acid, more gas remains in the EVA matrix and the amount of gas available for cell nucleation and growth increases. Consequently, average cell size and cell density increase.

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