

Effects of Calcium Carbonate as the Expanding Inhibitor on the Structural and Mechanical Properties of Expanded Starch/Polyvinyl Alcohol Blends

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ABSTRACT: In this study, expanded starch/PVA/CaCO₃ blends (ESPCs) were prepared using the pilot system composed of a supermixer and a twin-screw extruder to investigate the effects of CaCO₃ as the expanding inhibitor on the structural and mechanical properties of ESPCs. The pore ratio of ESPCs with the interconnecting open-cell structure decreased with increasing CaCO₃ content and the structure of ESPCs became more compact. The inhibiting process of CaCO₃ during the expansion of starch/PVA blends was proposed and certified by FTIR spectroscopy and X-ray diffraction. At least two parts of CaCO₃ were required to obtain a sufficient inhibiting effect on the expansion. The

mechanical properties of ESPCs such as tensile strength, elongation at break, modulus, and specific work of rupture were improved by the addition of CaCO₃ as the expanding inhibitor. As CaCO₃ content increased from one to four parts, the tensile strength increased 2.6-fold, from 70 to 180 kPa, whereas elongation at break increased about 1.5-fold. The moduli of ESPCs also increased with increasing CaCO₃ content. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1762–1768, 2004

Key words: expanded starch/PVA blends; modulus; mechanical properties; expanding inhibitor; FTIR

INTRODUCTION

The environmental pollution problem, attributed to the use of synthetic polymeric materials based on petroleum chemistry, has become increasingly serious and encouraged the worldwide legal restrictions on the use of synthetic polymeric materials and a number of research projects to develop environment-friendly biodegradable plastic materials as replacements for synthetic polymeric materials.

Various developments of environment-friendly polymeric materials are classified into two categories based on their raw materials: degradable synthetic polymers and renewable natural polymers. Among these, starch, a biodegradable natural polymer that exists abundantly in nature and very cheap, has been used as a replacement for synthetic polymeric plastics as well as in the food, textile, and paper industries after various modifications and processes.¹

Starch-based biodegradable plastic materials have been prepared by various methods: embedding the starch in synthetic polymer matrices,^{2–5} blending with hydrophilic polymers,⁶ using modified starch, foaming of starch within the extruder,⁷ and preparing ther-

moplastic starch.^{8,9} Among these, extrusion has been one of the most widely used methods. Altieri et al.⁸ reported that the loose-fill type of expanded starch, suitable for commercial uses such as packing material, could be made from starch with an amylose content of more than 70%. Another patent insisted that starch must contain more than 45% amylose to produce an expanded starch with excellent physical properties that is useful for packing material.⁹ Lim et al.,¹⁰ however, reported that the loose-fill type of an expanded starch could be made from ordinary starch under various conditions and that its physical properties were similar to those of expanded starch made from high amylose content starch.

Starch is extruded from the extruder by the following process. At first, the supply of starch into the barrel of the extruder rapidly increases the internal pressure of the barrel under high temperature. The mixture of water and starch then goes through the barrel at high temperature and pressure. When the mixture is extruded at the die face, it is expanded because of the difference between the external and internal pressures of the extruder. At that time, water plays a significant role as an expanding agent through its vaporization. After that, the expanded starch stiffens and maintains its expanded form, although the expanded starch had poor mechanical properties.

So, in this study, starch was blended with polyvinyl alcohol (PVA) during the extrusion process to im-

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TABLE I
Composition of ESPCs

Sample number	Notation of sample	Ingredient contents (part ^a)			Screw speed (rpm)
		Starch	PVA	CaCO ₃	
1	ESP20C1-150	100	20	1	150
2	ESP20C2-150	100	20	2	150
3	ESP20C3-150	100	20	3	150
4	ESP20C4-150	100	20	4	150
5	ESP30C1-150	100	30	1	150
6	ESP30C2-150	100	30	2	150
7	ESP30C3-150	100	30	3	150
8	ESP30C4-150	100	30	4	150
9	ESP20C1-300	100	20	1	300
10	ESP20C2-300	100	20	2	300
11	ESP20C3-300	100	20	3	300
12	ESP20C4-300	100	20	4	300
13	ESP30C1-300	100	30	1	300
14	ESP30C2-300	100	30	2	300
15	ESP30C3-300	100	30	3	300
16	ESP30C4-300	100	30	4	300

^a Part: relative quantity of ingredients to that of starch.

prove the flexibility of expanded starch suitable for packing material. CaCO₃ was used as the expanding inhibitor to restrict the excessive expanding supplemented by PVA. The effects of CaCO₃ on the structural and mechanical properties of the expanded starch/PVA blends were investigated.

EXPERIMENTAL

Materials

Native corn starch (Samyang Inc., Seoul, Korea) was used after being dried in a vacuum oven at 60°C for 20 h. Polyvinyl alcohol (PVA, DP = 1500; Dugsan Chemical Inc., Chungbuk, Korea), CaCO₃ (99+% A.C.S. reagent grade; Aldrich Chemical Co., Milwaukee, WI) and other reagents were used without further purification.

Preparation of expanded starch/PVA/CaCO₃ blends (ESPCs)

ESPCs were prepared using a twin-screw extruder composed of four sections whose temperatures were fixed at 215–210–90–50°C in sequence. At first, starch, PVA, and CaCO₃ were mixed in the supermixer; the resulting composition is shown in Table I. After being fed to the extruder, followed by the subsequent supply of a predetermined amount of water, the ingredient mixture was extruded to make ESPC under conditions of high pressure and temperature. The supply rates of the mixture and water were fixed at 500 g/min and 100–120 mL/min, respectively. The overall process is shown in Figure 1.

Scanning electron microscopy

The cross sections of ESPCs were examined using SEM (JSM 5410LV; JEOL, Tokyo, Japan) after being coated with gold. The image analyzer system (Bio-Med Devices Inc., Guilford, CT) was used to quantify the pore area, which was defined as the ratio of the total area of all pores to the total cross-sectional area.

FTIR spectroscopy

FTIR spectroscopy (M series, MIDAC Corp., Costa Mesa, CA) was used to observe the structural difference between ESPC and ingredients. After being dried in a vacuum oven at 60°C for 12 h, samples were prepared in the form of KBr pellets. FTIR spectra were obtained between 400 and 4000 cm⁻¹ at a resolution of 4 cm⁻¹.

X-ray diffraction

X-ray diffractograms of ESPCs were obtained by a DIP 2030 apparatus (MAC Science, Yokohama, Japan) using Cu-K_α radiation ($\lambda = 1.5405 \text{ \AA}$) at 2θ values ranging from 5 to 40°. The conditions were 40 kV, 30 mA, 100 mm of distance, and 120 s of beam time. The samples were used after being sufficiently dried in a vacuum oven at 60°C.

Mechanical properties

Mechanical properties of ESPCs [samples: 15 × 5 × 50 mm (width × depth × length)] were measured using a MiniMat (Rheometric Scientific, Piscataway, NJ) with a loading rate of 20 mm/min. Five specimens per sample were tested.

RESULTS AND DISCUSSION

Structural properties of ESPCs

The pilot system used for the preparation of ESPCs was composed of a supermixer and a twin-screw extruder. The experimental parameters that could affect the structural and mechanical properties of ESPCs were the composition of the raw material mixture, screw speed, supply rates of water and mixture, and

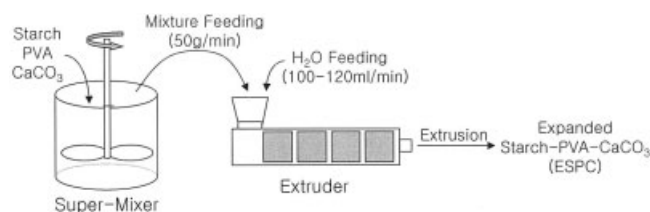


Figure 1 Preparation process of ESPC using twin-screw extruder.

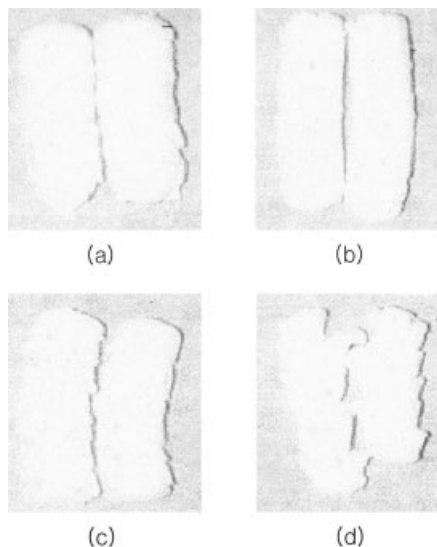


Figure 2 Appearances of expanded starch with 10 parts of PVA extruded at 150 rpm: (a) 1 part CaCO_3 ; (b) 2 parts CaCO_3 ; (c) 3 parts CaCO_3 ; and (d) 4 parts CaCO_3 .

sectional temperatures and pressures of the extruder. To obtain a flexible expanded starch/PVA blend using the extruder, the difference between the internal and external pressures of the extruder must be kept very high. Among those parameters, the supply rate of the mixture significantly affects the internal pressure of the extruder. So, the supply rates of the mixture and

water, which was added to improve the fluidity of the mixture in the extruder, were fixed at 500 g/min and 100–120 mL/min, respectively. The optimum sectional temperatures of the extruder were fixed at 215–210–90–50°C in sequence. Under the above-mentioned conditions, we could obtain a loose-fill type of ESPCs with various compositions of ingredients extruded at different screw speeds (Fig. 2).

Figure 3 shows the cross-sectional SEM micrographs of ESPCs extruded at a screw speed of 150 rpm. All ESPCs had the interconnecting open-cell structure, which became more compact with increasing CaCO_3 content. The pore size of ESPCs decreased with increasing CaCO_3 content. Figure 4 shows the pore ratio of ESPCs as a function of CaCO_3 content. The pore ratio was defined as the ratio of the total area of all pores to the total cross-sectional area and calculated using the image analyzer. As shown in Figure 4, the pore ratio of ESPCs, on the whole, decreased with increasing CaCO_3 content. In particular, the pore ratio decreased significantly with contents of calcium carbonate greater than two parts and this phenomenon appeared more clearly in ESPCs with higher PVA content.

Although the loose-fill type of expanded starch could be made from ordinary starch under various conditions, the expanded starch with low amylose content of 25% was still very brittle.¹⁰ PVA, which is a water-soluble and biodegradable crystalline polymer

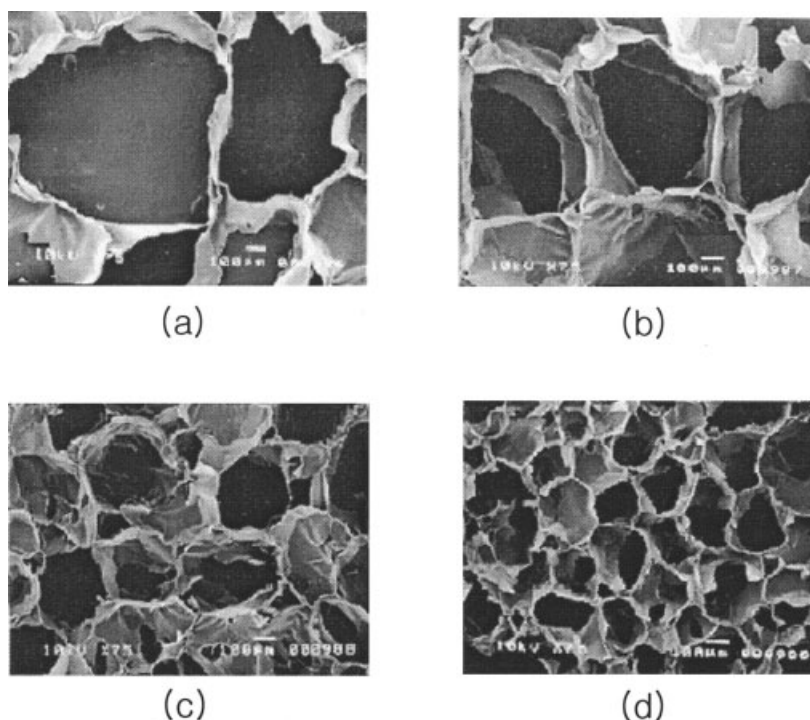


Figure 3 SEM micrographs of ESPC extruded at a screw speed of 150 rpm (PVA = 30 parts, $\times 75$): (a) 1 part CaCO_3 ; (b) 2 parts CaCO_3 ; (c) 3 parts CaCO_3 ; and (d) 4 parts CaCO_3 .

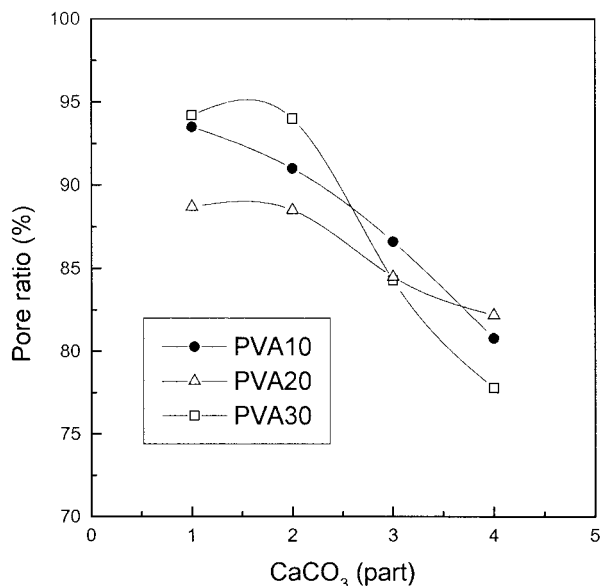


Figure 4 Pore ratio of ESPCs extruded at a screw speed of 150 rpm as a function of CaCO₃ content.

and also has flexible and expanding properties, has often been used in blending with other polymeric materials for improved mechanical and expanding properties, biodegradability, and biocompatibility.¹³⁻¹⁵ Thus, in this study, starch was blended with PVA during the extrusion to overcome the brittleness of the expanded starch. However, the expanded starch/PVA blend showed excessive expansion, supplemented by the expansion of PVA, followed by the rapid contraction because of the difference between the internal and external pressures of expanded starch/PVA blend at the moment of extrusion through the die face of the extruder. That contraction made the expanded starch/PVA blend unsuitable for a packing material because the blend lost the cushioning property. Thus an inorganic material, CaCO₃, was used as the expanding inhibitor. In low PVA content of 10 parts, the excessive expansion was low and CaCO₃ effectively inhibited the expansion even in its low content, increasing the inhibiting effect with increasing CaCO₃ content. However, at higher PVA content (20 and 30 parts), the excessive expansion was high and at least two parts of CaCO₃ were required to obtain the sufficient inhibiting effect on the expansion.

In this study, water (which was fed to improve the fluidity of the mixture in the extruder) concurrently functions as the expanding agent through its vaporization at high temperature and pressure. In addition, CaCO₃, generally known to degrade into calcium oxide and carbon dioxide at high temperature and pressure, can be thought to function as the expanding agent because carbon dioxide formed by the degradation of CaCO₃ also has an expanding ability. However, CaCO₃ actually inhibited the expansion of the blend.

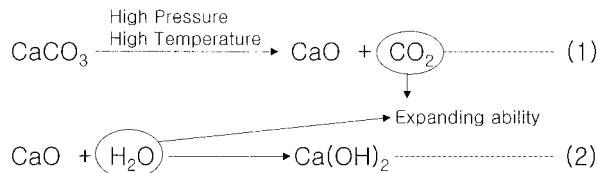


Figure 5 Proposed inhibiting process of CaCO₃ on the expansion of ESPC.

That result can be inferred from the following process, which was proposed in Figure 5. At first, CaCO₃ degrades into calcium oxide and carbon dioxide at high temperature and pressure in the extruder [Fig. 5, Reaction (1)]. Calcium oxide has the property to absorb water or carbon dioxide from air and to be solved in water and form calcium hydroxide, which has no expanding ability. Therefore, calcium oxide formed by the degradation of CaCO₃ can absorb carbon dioxide or react with water to form calcium hydroxide [Fig. 5, Reaction (2)]. Thus, it can be supposed that CaCO₃ functions as the expanding inhibitor because the calcium oxide formed by the degradation of CaCO₃ captures water and thereby prevents it from functioning as an expanding agent.

To ensure the above-mentioned inference, FTIR spectroscopy was carried out. In Figure 6, the specific peaks of starch (1638 cm⁻¹) and PVA (1247 and 1725 cm⁻¹) are shown in ESPC but those of CaCO₃ (2527,

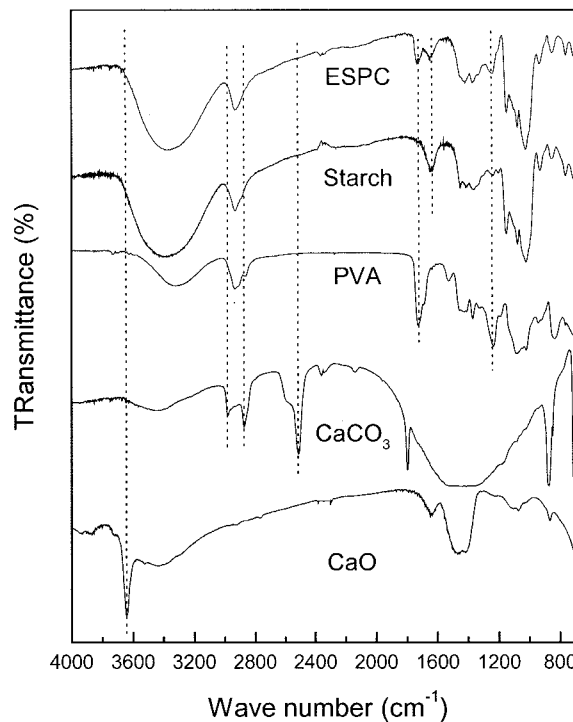


Figure 6 FTIR spectra of ESPC, starch, PVA, CaCO₃, and calcium oxide (ESPC: 30 parts PVA, 4 parts CaCO₃, 150 rpm).

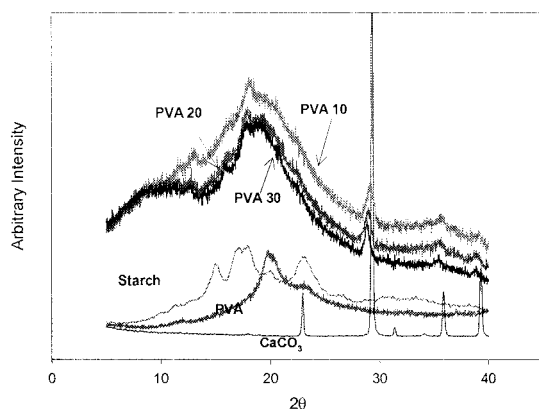


Figure 7 X-ray diffractograms of ESPCs, starch, PVA, and CaCO_3 .

2875, and 3005 cm^{-1}) and calcium oxide (3648 cm^{-1}) are not. In other words, neither CaCO_3 nor calcium oxide existed in ESPC. This is thought to be because CaCO_3 disappeared by the degradation into calcium oxide and carbon dioxide [Reaction (1)] and calcium oxide also disappeared by the reaction with water [Reaction (2)], as shown in Figure 5. Therefore, from the above results, it can be concluded that CaCO_3 functions as the expanding inhibitor during the expansion of ESPC by capturing and preventing water from functioning as the expanding agent.

In Figure 7, wide-angle X-ray diffractograms of ESPC, starch, PVA, and CaCO_3 are shown. It is generally known that starch has a different crystal structure according to its biological sources; that is, cereal starch has A-type crystal structure; tuber starch, B-type; and seed starch, C-type, respectively. V-type crystal structure appears in low molecular weight

starch or precipitated starch in solution.^{11,12} It is also known that the crystal structure of starch can be changed into a different crystal structure by extrusion at different temperatures. Generally, starch extruded at 135°C has a V-type crystal structure, whereas starch extruded over 185°C has a new crystal structure designated as E-type. This new structure, E-type, is characterized by three major peaks that are considered as peaks by the shift of peaks appearing in the V-type. Lim et al.,¹⁰ however, reported that the crystal structure of starch extruded at 180°C changes noncrystal structure by shear force during the extrusion. As shown in Figure 7, native corn starch has a typical A-type crystal structure with two singlet peaks and one doublet peak, whereas PVA shows two major peaks and CaCO_3 four major peaks. ESPC, however, shows no peaks attributed to starch, even though more peaks attributed to those of PVA and CaCO_3 appear.

Mechanical properties of ESPCs

To investigate the mechanical properties of ESPCs, tensile testing was carried out. ESPCs of the loose-fill type with circular cross section were cut in lengths of 50 mm and then deformed carefully into the rectangular cross-sectional specimen by slowly pressing to allow the structure of ESPCs not to be broken, and the dimension of the deformed specimens was about $15 \times 5 \times 50\text{ mm}$ (width \times depth \times length). The results of the tensile test are shown in Table II and Figures 8–10. The stress–strain curves of all ESPCs were linear and therefore the moduli of ESPCs could be calculated as the slope of the stress–strain curve. The specific work of rupture was defined as the work of rupture divided

TABLE II
Tensile Properties of ESPCs

Sample	Tensile strength (kPa)	Elongation at break (%)	Modulus (kPa)	Specific work of rupture (N/m)
ESP20C1-150	73.57	1.50	50.43	16.55
ESP20C2-150	83.73	1.96	42.76	24.62
ESP20C3-150	103.90	2.29	43.35	35.69
ESP20C4-150	140.00	2.96	47.33	62.16
ESP30C1-150	75.36	0.96	78.62	10.85
ESP30C2-150	86.22	1.72	50.07	22.24
ESP30C3-150	126.25	2.29	55.11	43.37
ESP30C4-150	134.40	1.96	68.64	39.51
ESP20C1-300	71.50	1.96	36.48	21.02
ESP20C2-300	98.12	2.29	42.85	33.70
ESP20C3-300	125.60	2.96	42.46	55.77
ESP20C4-300	180.70	3.62	49.86	98.12
ESP30C1-300	70.08	1.19	58.84	12.51
ESP30C2-300	95.59	2.29	32.96	32.84
ESP30C3-300	134.05	2.96	45.29	59.52
ESP30C4-300	168.50	3.29	51.22	83.15

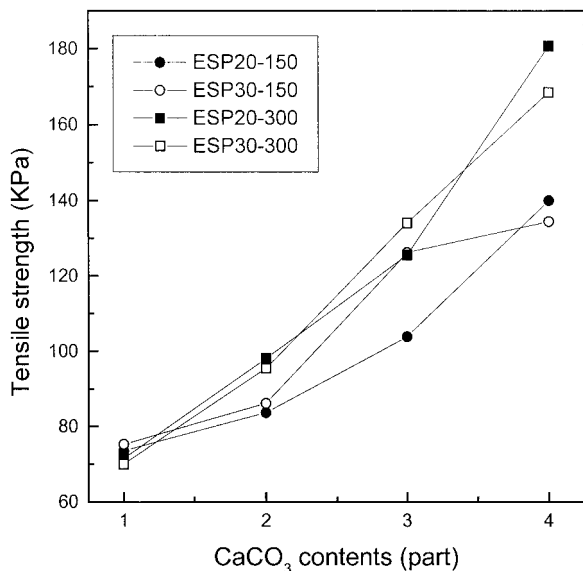


Figure 8 Tensile strength of ESPCs as a function of CaCO₃ content.

by the cross-sectional area of the specimen. As shown in Figure 8 and Table II, both tensile strength and elongation at break increased with increasing CaCO₃ content and those of ESPCs with lower PVA content extruded at higher screw speed were somewhat higher. In particular, as the CaCO₃ content increased from one to four parts, the tensile strength increased 2.6-fold, from 70 to 180 kPa, whereas elongation at break increased about 1.5-fold. Thus, the moduli of ESPCs calculated from the slope of the stress-strain

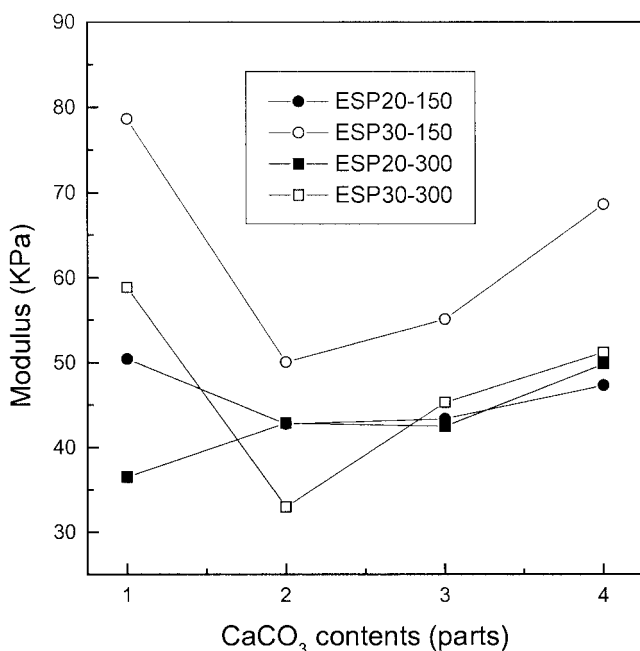


Figure 9 Moduli of ESPCs as a function of CaCO₃ content.

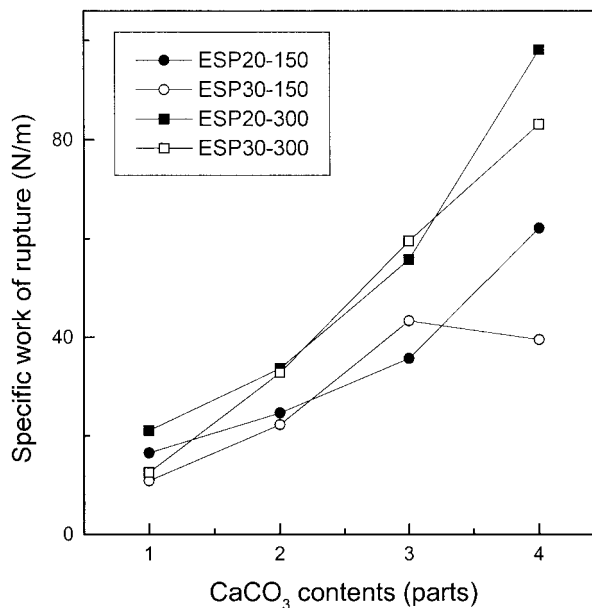


Figure 10 Specific work of rupture of ESPCs as a function of CaCO₃ content.

curves also increased with increasing CaCO₃ content. However, although having the lowest value of tensile strength, ESPCs with one part of CaCO₃ had the highest modulus (Fig. 9). In fact, the inhibiting effect of CaCO₃ on the expansion was trivial at the low CaCO₃ content of one part and ESPCs with this CaCO₃ content were extremely rigid and brittle. In addition, their elongation at break values were even lower compared with the low values of tensile strength. Thus, it was conjectured that the moduli of ESPCs with one part of CaCO₃ was very high, even though its tensile strength was lowest. Furthermore, the specific work of rupture of ESPCs, defined as the work of rupture divided by the cross-sectional area of each ESPC specimen, increased with increasing CaCO₃ content about four-fold. Therefore, it could be concluded that the mechanical properties of ESPCs were improved by the addition of CaCO₃ as the expanding inhibitor.

CONCLUSIONS

From the above results, it could be concluded that CaCO₃ functions as the expanding inhibitor during the expansion of starch/PVA blend because calcium oxide formed by the degradation of calcium carbonate captures and prevents water from functioning as the expanding agent. ESPCs were characterized by an interconnecting open-cell structure, which became more compact with increasing CaCO₃ content and the mechanical properties of ESPCs were improved by the addition of CaCO₃ as the expanding inhibitor.

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