New Breathable Films Using a Thermoplastic Cross-Linked Starch as a Porogen

Bo Shi, Mike Shlepr, James H. Wang, Greg Wideman

Kimberly-Clark Corporation, 2100 Winchester Road, Neenah, Wisconsin 54956
Correspondence to: M. Shlepr (E-mail: mshlepr@kcc.com)

ABSTRACT: Breathable films, which find in variety of product applications, are conventionally made using mineral porogens such as calcium carbonate ($CaCO_3$). This article addresses a novel biodegradable and highly breathable film without inorganic porogens. Unexpectedly, a thermoplastic cross-linked natural polymer (corn starch) was used successfully to create tortuous passages for film breathability. This concept was demonstrated using two types of thermoplastic cross-linked corn starches as porogens and contrasted to control samples: native corn and chemically cross-linked starches, respectively. The films discussed had increased breathability and mechanical properties relative to the control samples. The film morphology reveals that filler was irregular when thermoplastic starch or $CaCO_3$ was used. The difference in filler from chemically modified cross-linked starch and thermoplastic cross-linked starch was observable as well. It is believed that spherical particles provided by thermoplastic cross-linked starch helps film debonding and porosity during the film stretch processes. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41016.

INTRODUCTION

In the natural environment, all plants and animals require a mechanism to inhale and exhale gases such as oxygen or carbon dioxide. For example, leaf bearing plants such as trees complete air exchange via stomata. Earthworms, on the other hand, rely on their body skin to achieve breathability. When the soil is filled with water on a rainy day, earthworm has to come closer to the soil surface to breathe because heavy water content does not allow oxygen to diffuse through its skin. This case is especially true during spring and summer when the atmospheric temperature is relatively high whereas gas solubility in water is low. Additional examples can be found from the article by Hinton who described respiratory systems of insect egg shells.[1] It seems that gas exchange is accomplished through a fine structure of the shell of *Leptohylemyia*. In human, we would like to wear shoes and sports clothing that provide breathability for comfort and hygiene. To achieve this purpose, non-woven fabrics and thin breathable films in some cases such as those of the diaper application are needed. This article is about how to fabricate thin breathable film using organic filler such as starch.

Plastic films find a wide variety of applications such as light weight and low cost material to separate the good from the bad (i.e., barrier films). Indeed, good and bad are dependent on the application and selective transmission is usually the more desired barrier. Breathable films and fabrics are designed to increase the transmission rate of gases without loss of other barrier properties, such as liquid transmission. Breathability can be improved by polymer selection (e.g., polyether block amides), microporosity (e.g., meltblown non-wovens), or microperforations (e.g., laser perforations). Conventional high-breathability films widely used in disposable goods (e.g., diapers) are made of polyethylene together with an inorganic porogen such as calcium carbonate ($CaCO_3$), or zeolite with and without stearic acid coating.[2] The film breathable functionality is due to the presence of micropores (Figure 1) created by film stretching under either ambient or heated condition. Stretched, breathable films play a significant role in high volume consumer health and personal hygiene products such as diapers and incontinence articles, wound dressing, surgical drape, garments, and highly absorbent foam with breathable film for fluid management.[3–6]

In recent years, there is a sustainability concern to continuously use non-biodegradable and non-renewable materials for consumer products—mostly related to raw material availability and supply, as well as post use disposal and carbon footprint—although cost-effective, polyolefin-based breathable films are mostly based on petroleum-derived polyolefins, which is not renewable or sustainable. Consequently, a significant amount of effort is placed on development of breathable films that are biodegradable. For example, Bastioli et al. made breathable and biodegradable film bags and ventilated systems for organic waste
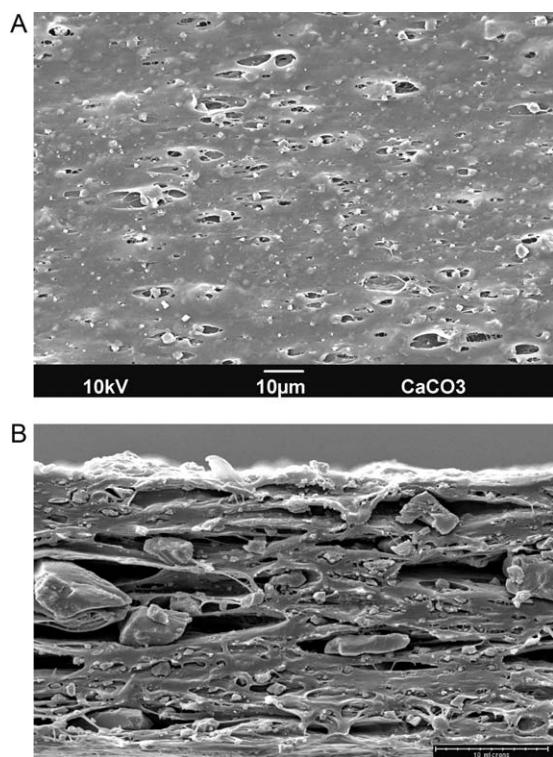
Figure 1. Conventional CaCO$_3$-filled breathable film. Scanning electron micrographs of a stretched, breathable film (**a**) surface (**b**) a cross-section through the thickness.

collection, respectively.[7,8] The film consisted of starch and co-polyester such as Ecoflex® or Eastar-Bio® polymer. Film breathability was below 1000 g m^{-2} day^{-1} without using any porogen and stretch, which served the intended applications as high breathability was not needed for garbage bags. Biodegradable and highly breathable films such as those constructed by Topolkaraev et al. and Kaufman et al. relied on inorganic porogens such as CaCO$_3$ from OMYA, Inc. (Proctor, VT), where matrix polymers were biodegradable polyesters such as Ecoflex® from BASF (Mt. Olive, NJ) or Bionolle from Showa Highpolymer (Japan).[9,10] The filler level may range from a few percent to over 50% by weight in order to produce high-film breathability.[11] However, the use of inorganic porogen is relatively expensive due to high density and has disadvantages during processing because the porogen tends to accumulate around the lip of the extrusion die. In some cases, organic porogens such as polystyrene-based material were used to create breathable films.[9,12] However, the organic porogen is not compatible with matrix polymers and a compatibilizer must be used to achieve a porogen particle size distribution suitable for producing breathable films. The film breathability using this organic porogen was fairly low, around 1200 g m^{-2} day^{-1}.

Starch and its derivatives such as cross-linked starch are well known and widely used in food industry (viscosity modifier, thickener, etc.), and many industrial applications such as those in papermaking.[13,14] Starch is a natural polysaccharide and contains about 25 wt % amylose and about 75 wt % amylopectin. The exact ratio of these two moieties is dependent on plant ori-

gin and species (i.e., corn, wheat, potato, etc.). A variety of starch modification techniques such as esterification and cross-linking have been documented.[15,16] For example, Van Soest et al. disclosed a method of preparing for cross-linked starch particles.[17] The particle size is dependent on starch and cross-linking agent type, concentration, reaction time, and the character of the solvent used during a particular method of manufacturing. Wildi et al. utilized extrusion technology to produce the cross-linked starch at a rate ≥1.0 metric ton per hour.[18] This thermoplastic cross-linked starch is reportedly used as a petroleum-based latex replacement with applications focused in the paper industry.[19] However, its use for thermoplastic applications, particularly for breathable films, has not been previously reported. Figure 2 conceptually summarized the breathable film production processes described above and its fate in the environment.

This work set out to explore if thermoplastic cross-linked starch could produce highly breathable films without traditionally relying on the use of inorganic porogens such as CaCO$_3$. In addition, the desired films should be highly biodegradable so a biodegradable poly(butylene adipate terephthalate) was chosen. It is also an objective of this article to provide compositions, steps, and processing conditions to produce the highly breathable and biodegradable films. Several excellent citations are available to detail biodegradability of materials used in this work and, while not addressed further here, research on the biodegradability of the composite would continue under separate covers.[20–22]

EXPERIMENTAL

Materials

About 99.7 wt % food and flavoring grade glycerin was purchased from Cognis Corporation (Cincinnati, OH) and used as a plasticizer. The 100% food grade Excel P40S (mono-diglyceride) was purchased from Kao Corporation (Tokyo, Japan) and used as a surfactant, which facilitates the conversion of native starch into thermoplastic starch. Porogen A is a 100% food grade native corn starch (Cargill Gum™ 03460) purchased from Cargill Inc. (Minneapolis, MN). Porogen B is a 100% food grade chemically cross-linked corn starch (National 4302) purchased from Ingredion™ (Bridgewater, NJ). It was derived from native corn starch by a chemical modification using phosphorus trichloride oxide (POCl$_3$) and supplied as off-white powder. Porogens C and D were another type of thermoplastic cross-linked starches (Ecosphere 2202 and 92240) produced by a process that differs from that of Porogen B.[23] Both were 90–99% modified food grade starches with the balance being water. They were purchased from EcoSynthetix® (Ontario, Canada). The aliphatic–aromatic copolyester, branded as Ecoflex® F BX 7011, which is poly(butylene adipate terephthalate), was obtained from BASF (Mt. Olive, NJ) as the 100% extrusion resin.[24]

It was necessary to convert the starch porogens A and B to thermoplastic starch (TPS) and thermoplastic cross-linked starch (TPXS) before blending with the copolyester (see "Thermoplastic Starch Preparation," "Thermoplastic Chemically Cross-Linked Starch Preparation," and "Film Casting" sections).
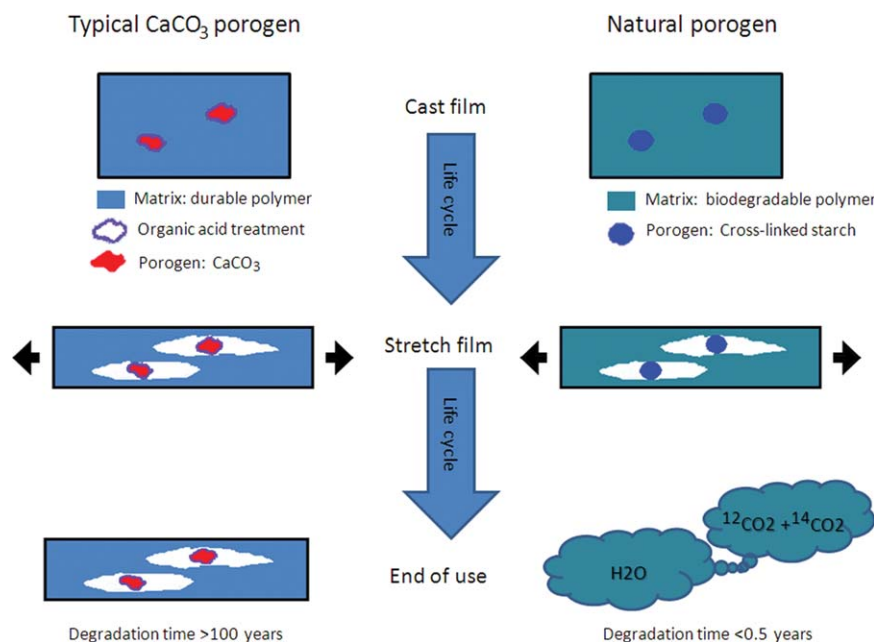
Figure 2. Breathable film production and fate. Schematic of a few parts of the life of diaper outer covers that compares the production and end of use of typical- (left half) and natural- (right half) porogenic films. The concentration of the natural isotope carbon 14 will be proportional to the amount of contemporary organics present, which for petrochemical-based plastics will be zero. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

This additional step was not required for the starch porogens C and D, as they were supplied in a plasticized state suitable for extrusion processing.

Thermoplastic Starch Preparation

Native corn starch (Porogen A) was converted into TPS using Thermo Prism USALab16 extruder (Thermo Electron Corporation, Stone, England). Porogen A (98 wt %) was premixed with Excel P40S (2 wt %) using a kitchen aid mixer (Hobart, Troy, OH). The mixing time was 2 min. When the extruder temperatures were heated to 90°C, 100°C, 115°C, 125°C, 130°C, 130°C, 130°C, 125°C, and 120°C from zones 1 to 9, and the die temperature was 115°C; the extruder motor was turned on and set screw rotational speed at 2.5 Hz. The mixture of Porogen A and surfactant was loaded to K-Tron feeder (K-Tron North America, Pitman, NJ) and fed into the extruder throat at 17 g min^{-1}. Glycerin was pumped into zone 1 at 3.4 g min^{-1} using a gear pump (Bodine Electric Company, Grand Island, NY), which produced a TPS with 20 wt % glycerin. At these conditions, the extruder torque ranged from 55% to 60%, and the die pressure was 900–1000 kN m^{-2}. When the strand was formed, it was cooled down with a series of fans through a convey belt (Bondie Electric Company, Chicago, IL), pelletized using a pelletizer (Emerson Industrial Controls, Grand Island, NY) and saved in a plastic bag. TPS pellets were used to blend with copolyester (Ecoflex® F BX 7011) for making breathable and biodegradable films.

Thermoplastic Chemically Cross-Linked Starch Preparation

Porogens C and D were supplied as converted TPXS and were used directly for the film casting in this study. Steps to convert the cross-linked starch (Porogen B) into TPXS were similar to those for thermoplastic starch Porogen A above. Porogen B was premixed with Excel P40S at a weight ratio of 98/2 using a kitchen aid mixer. The mixing time was 2 min. When the extruder temperatures were heated to 90°C, 110°C, 130°C, 145°C, 150°C, 150°C, 150°C, 140°C, 130°C, and 125°C from zones 1 to 9, and the die temperature was 115°C, the extruder motor was powered and set screw rotational speed at 2.5 Hz. The mixture of Porogen B and surfactant was loaded to K-Tron feeder and fed into the extruder throat at 15 g min^{-1}. Glycerin was again pumped into zone 1 using a gear pump at a rate to produce TPS with 20 wt % glycerin. When the run was stable, the extruder torque was 60%–65% and the die pressure was 2000–2500 kN m^{-2}. TPXS strand was cooled using a moving belt with a series of fans, pelletized, and saved in a plastic bag. In comparison, extruder torque and die pressure are higher than those for TPS making, indicating there is a strong binding at molecular level for the cross-linked starch. TPXS pellets were used to blend with the copolyester for making breathable and biodegradable films.

Film Casting

The film making was carried out also using Thermo Prism USALab16 extruder, which is a twin screw extruder that provides extensive mixing for direct film casting. Ecoflex® F BX 7011 copolyester was fed by one K-Tron feeder and the cross-linked starch was fed by another K-Tron feeder. The films casting was accomplished using a 10 cm film die and run through a Haake TP-1 chilled roller press (Haake Karlsruhe, Germany). The roller speed on the press was adjusted to reduce the film thickness to approximately 0.03–0.05 mm. The material feeding rate, processing temperatures and other operating parameters are shown in Tables I and II for four starch samples blended

Table I. Copolyester and Film Processing Conditions; Composition

Sample No.	Blend composition (wt %)				
	TPS A	TPXS B	TPXS C	TPXS D	Ecoflex®
1	30				70
2		30			70
3			10		90
4			20		80
5			30		70
6				30	70
7					100

with the copolyester, respectively. Sample preparation was documented by Wang and Shi[25] and Kaufman et al.[10]

Sample No. 1 is 30 wt % TPS made from Porogen A and 70 wt % Ecoflex® F BX 7011 copolyester. Sample No. 2 is 30 wt % TPXS made from Porogen B and 70 wt % copolyester. The die pressure is significantly different whereas other processing conditions (temperatures, torque, and screw rotational speed) are very similar. This is due to the differences in the type of starch by chemistry of cross-linking. Filler A is the native corn starch and Filler B is the cross-linked corn starch.

The processing temperatures were adjusted according to the ratio of Ecoflex® F BX 7011 copolyester to the cross-linked starch in order to result in good films for stretching. The good processing temperature window for the specific blend ratio is about 10°C–15°C. For example, the film processing for the copolyester and Porogen C blend was also good at the highest barrel temperature of 200°C. It is likely to observe unmelted gels if the temperature is lower than the stated range.

The neat Ecoflex® F BX 7011 copolyester film (Sample No. 7) was also made as a control in order to compare its mechanical properties to those of films made from blends (Sample No. 1–6).

Stretching the Precursor Films for Breathability
Samples with 70/30 Ecoflex® F BX 7011copolyester/porogen were stretched to levels in which high breathability is typically achieved. According to the film elongation data shown in Table III, the film stretch was performed in the cross direction for all samples under ambient conditions. The film stretch was accom-

plished using Sintech 1/D tester. The film was cut into 12.5 cm in length before stretching. The gauge length was 5 cm after the film was secured on clamping units. The film stretching speed was 127 mm min⁻¹.

Test Methods
Tensile Property. The mechanical tensile properties of the unstretched films were determined using Sintech 1/D tensile tester (Sintech Corporation, Cary, NC) using ASTM D638-08 Standard Test Method for Tensile Properties of Plastics as protocol. The tensile tester was equipped with TestWorks 4 software from MTS Systems Corporation (New Castle, DE). After conditioning for 24 h at 21°C at 50% humidity the film samples were cut into dog bone shapes with a center width of 3.0 mm before testing. The dog-bone film samples were held in place by rubber grips on the Sintech set to a gauge length of 18.0 mm. During the test, samples were stretched at a crosshead speed of 127 mm min⁻¹ until breakage occurred. The computer program TestWorks 4 collected data during the test and generated a stress (MPa) versus strain (%) curve from which a variety of properties were calculated by the TestWorks 4 program: for example, modulus, peak stress, and elongation. Five samples were tested in both the machine direction (MD) and the cross direction (CD) and average values for each parameter are reported.

Breathability Testing. The film breathability was tested using a Mocon Permatran-W Model 101K system for measuring high water vapor transmission rates of sheet goods. A reference film of known water vapor transmission rate was used to verify system calibration and accuracy before collection of data on unknowns. Test samples were cut by a die-press to avoid film damage.

Structure. Scanning electron microscopy (SEM) was used to characterize the surface and internal structure of films before and after film stretching. Several representative samples were mounted with conductive tape, sputter coated with gold, and examined for surface structure. For study of the internal structure, several representative samples were immersed in Formula 19 denatured ethanol, frozen by immersion in liquid nitrogen, and impact-sectioned with a single edge razor blade while in the liquid nitrogen. Sections were removed from the liquid nitrogen and placed on a metal surface to reach room temperature. Sections were either directly examined or phases were decorated by an oxygen plasma.[26] For decoration, an Emitech

Table II. Copolyester and Film Processing Conditions; Extrusion Conditions

Sample No.	Extruder temperature profile (°C)										P_{melt} (kN m⁻²)	Torque (%)
	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8	T_9	T_{die}		
1	120	130	140	150	160	160	160	155	150	145	900–1000	60–65
2	110	120	130	145	160	160	160	155	150	145	3000–4500	65–75
3	120	130	170	180	200	200	200	190	180	140	4100–4300	72–76
4	120	130	210	240	240	240	240	240	240	140	4000–4100	65–70
5	120	130	210	230	230	230	230	230	230	140	3400–3600	60–64
6	120	130	180	210	210	210	210	210	210	140	3600–3800	70–75
7	120	130	140	155	155	160	155	155	155	150	1400–1500	70–75

Table III. Mechanical Properties for Neat Copolyester (Ecoflex® F BX7011) and Breathable Film Precursors (i.e., before stretch)

Sample No.	Sample description	Composition (wt %)	Film thickness (mm)		Peak stress (MPa)		Elongation (%)		Modulus (MPa)		Energy at break (J cm^{-3})	
			MD	CD	MD	CD	MD	CD	MD	CD	MD	CD
1	Ecoflex®/TPS-A	70/30	0.04 (0.004)	0.05 (0.001)	25.7 (2.1)	15.3 (3.1)	691 (54)	598 (118)	106 (24.4)	112 (56.5)	102 (13.5)	57.1 (18.2)
2	Ecoflex®/TPXS-B	70/30	0.04 (0.002)	0.04 (0.001)	35.2 (1.6)	25.3 (3.2)	329 (31)	776 (46)	25.3 (3.1)	68.9 (19.2)	75.0 (9.4)	77.5 (11.6)
3	Ecoflex®/TPXS-C	90/10	0.05 (0.002)	0.04 (0.001)	24.6 (1.6)	24.9 (1.1)	356 (26)	879 (8.4)	69.2 (3.6)	81.9 (5.3)	59.0 (6.8)	100 (4.1)
4	Ecoflex®/TPXS-C	80/20	0.04 (0.001)	0.04 (0.000)	26.2 (1.1)	23.4 (1.7)	334 (25)	817 (39)	99.7 (3.0)	120 (9.3)	61.4 (6.7)	98.1 (8.8)
5	Ecoflex®/TPXS-C	70/30	0.03 (0.002)	0.04 (0.002)	29.0 (1.3)	19.9 (1.7)	323 (22)	708 (41)	166 (12.4)	189 (12.8)	69.0 (6.2)	87.8 (10.6)
6	Ecoflex®/TPXS-D	70/30	0.03 (0.001)	0.03 (0.001)	22.2 (2.1)	15.7 (2.2)	107 (12)	563 (113)	128 (14.5)	164 (17.8)	17.0 (3.4)	72.2 (15.5)
7	Ecoflex®	100	0.03 (0.005)	0.03 (0.001)	42.1 (6.5)	35.3 (6.7)	443 (88)	744 (98)	74.8 (3.1)	83.5 (4.9)	118 (35.7)	134 (31.0)

Mean and (Standard Deviation) for five samples.
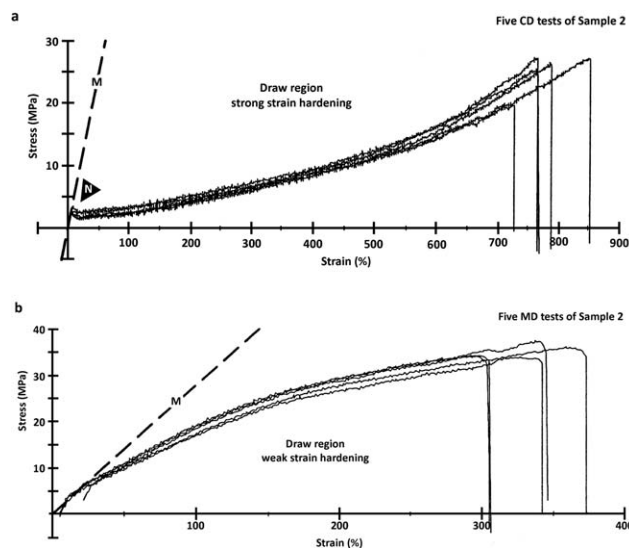
Figure 3. Stress–strain data. Examples of stress–strain data obtained from five breathable film precursors of Sample 2 stretched in the CD (**a**) and MD (**b**) film orientations. M, dashed line of measured Modulus; N, arrowhead pointing to onset of Necking. Sintech 1/D tensile frame; 127 mm min^{-1}.

K1050X barrel reactor operated at 40 W with an oxygen flow of 50 mL min^{-1} was sufficient to produce the blue-white plasma indicative of an oxygen-rich plasma. Both undecorated and decorated sections were vertically mounted, sputter-coated with gold at 20 mA for 60 sec, and examined in a JSM-6490LV. Illustrative micrographs of surface and internal structure were digitally captured.

RESULTS AND DISCUSSION

Tensile Property

Melt blending of the copolyester and each of the starch porogens was carried out on a laboratory scale extruder and film casting equipment (see Experimental section). Tensile stress–strain curves of the films followed those typical of ductile, extruded plastic films with features indicative of elastic yield, initiation of draw, draw propagation, and break (Figure 3). Films differed in the specifics of the onset of these regions (Table III) and the degree of strain hardening evident in the draw region. The transition from the elastic to plastic response was more pronounced in CD tests as a sharp decrease in stress was present indicating the onset of necking. With the exception of Sample No. 1, strain hardening was more pronounced when films were tested against (CD) than with (MD) the extrusion direction. Sample No. 1 exhibited stain hardening similar to that of the CD elongation of all the films but a distinction in CD and MD elongation was not evident.

As shown in Table III, the mechanical properties of the blend films generally had lower peak stress and greater modulus than the neat copolyester (Ecoflex® F BX 7011), but film elongation and energy-at-break were in comparable ranges. In some cases, the film CD elongation for Sample No. 2, 3, and 4 is about 5–18% greater than the neat copolyester film.
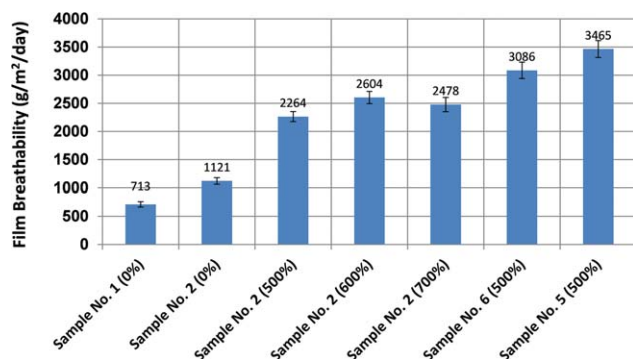
Figure 4. Summary of film breathability with different levels of stretching. Average ($n = 5$) breathability of the samples at various levels of stretch (percent in parenthesis). Error bars are plotted using one standard deviation values. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The film comprising of copolyester and TPS Porogen A was a comparative material to those comprising cross-linked starches. The differences in the film mechanical property for Sample No. 1 were not significant from Sample No. 2 to Sample No. 6 except for film MD elongation and energy at break. As shown in Table III, the film CD peak stress for all samples was weaker than film MD peak stress. Anisotropic mechanical properties displayed from Sample No. 2–6 may be due to starch cross-linking effect, whereas Sample No. 1 is closer to isotropy in film elongation.

Within TPXS-C for Sample No. 3, 4, and 5, the film MD elongation started to decrease from 879% to 708% as TPXS filler in the blends changed from 10% to 30%. However, the film CD elongation, including the film peak stress and energy at break, was not significantly altered. However, the film MD and CD modulus for Sample No. 3, 4, and 5 is significantly increased. For example, the film MD modulus for Sample No. 5 is increased 140% in comparison to Sample No. 3, and the film CD modulus for Sample No. 5 is increased 131% in comparison to Sample No. 3.

Breathability

Film breathability was determined before and after stretching to various levels of elongation (percentage in parenthesis) for samples with thirty percent filler (Figure 4). The film breathability for an unstretched film of Sample No. 1 was 713 g m^{-2} day^{-1} and remained at that level even after 500% stretching. For samples containing TPXS, breathability was at least doubled when stretched to 500%. These values were in the range of 3100–3500 g m^{-2} day^{-1} reported by Kaufman et al. for Ecoflex®-based films using 40 wt % CaCO$_3$ as the porogen and stretched to 500%.[10] Stretching beyond 500% appeared to produce modest gains in breathability. Wu et al. used polycaprolactone (PCL) and destructured starch of Mater-Bi AF05H (Novamont, Italy) to make breathable film.[27] The film breathability was around 410 g m^{-2} day^{-1}, much lower than the comparative sample (Sample No. 1) from this study. It is not known if this difference might be accounted for by lower bulk permeability of PCL relative to Ecoflex® F BX 7011 copolyester or lower porosity at the interface of the PCL matrix and filler. However, no porosity

at the copolyester (Ecoflex® F BX 7011) and TPS interface was apparent by the study methods to be discussed next.

Structure

Structural study was performed on both stretched and unstretched films in order to elucidate the mechanism of the film breathability. Figure 5 compares a sectional profile for Sample No. 1 before (a) and after (b) the film was stretched to 500%. Examination of several sections showed TPS domains before stretching were in the size range of sub-micrometer to upward of five micrometer domains. As with all the porogens examined here, this size range is typical of the CaCO$_3$ commonly used in mass production of breathable films. There are no tortuous air passages or micropores present in either film. Rather the TPS was deformed to a wave-like structure by a mechanical tension during the film stretch. These structures are reminiscent of the wave-like structure produced during laminar flow of immiscible polymers with dispersion predicted by the capillary number.[28] This suggests adhesion between the copolyester matrix and TPS was sufficiently high for stress transfer without interface failure and the modulus of the TPS was sufficiently low that plastic deformation occurred. TPS and copolyester molecules were mobile and could pass each other rather than form micropores during the film stretch. Therefore, increased film breathability cannot be created in blends of polyester and TPS without the presence of inorganic porogens such as CaCO$_3$ or using native corn starch alone.[7,8,27]
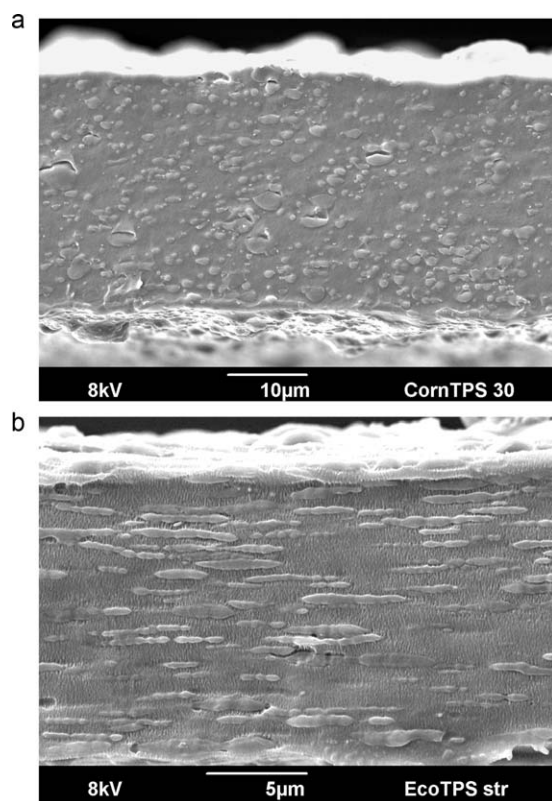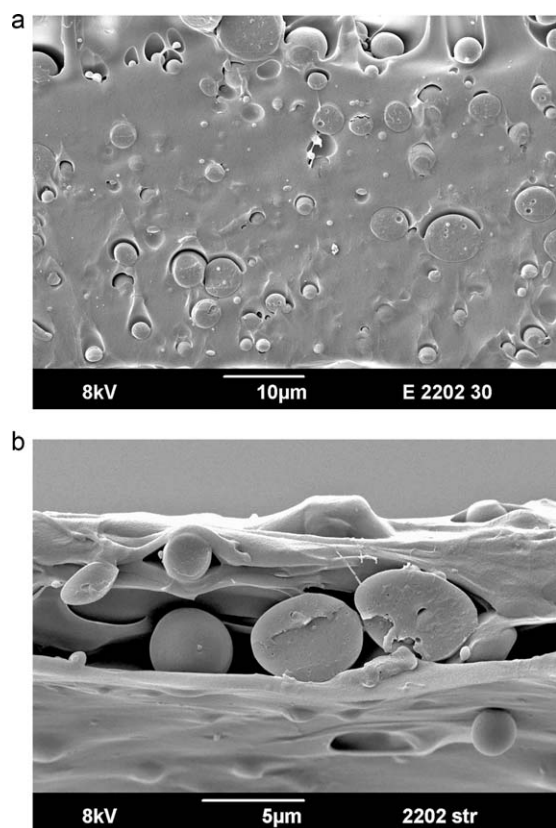

Figure 5. Structure of Ecoflex®/TPS-A (70/30) film. Scanning electron micrographs of cross-sections through the thickness of the film (**a**) before stretching and (**b**) after stretching to 500%.

Figure 6. Structure of Ecoflex®/TPXS-D (70/30) film. Scanning electron micrographs of cross-sections through the thickness of the film (**a**) before stretching and (**b**) after stretching to 500%.

In fact, starch in its native form has granular sizes less than 100 micrometers with elliptical, spherical, or circular shapes. Starch is destructured when it is converted into TPS under high temperature and shear during extrusion. To overcome the inferior mechanical properties of TPS, it is commonly blended with a synthetic polymer for the intended applications. In this comparative example, starch aggregates cannot behave as inorganic porogen such as $CaCO_3$ to create microvoids during film stretching.

Figure 6 compares a sectional profile for Sample No. 6 before (a) and after (b) the film was stretched to 500%. In the unstretched film, no porosity was present and TPXS resembles native starch particles, albeit much smaller, due to a cross-link affect.[16] After stretching, large, cavernous voids surround the TPXS particles. A similar result (not shown for sake of brevity), but with slightly smaller TPXS domains, was obtained for Sample No. 5.

Clearly the cross-linked starch demonstrated the porogenic ability to create air passages across the film, similar to those that result when $CaCO_3$ is used to produce stretched breathable films. In comparison, particle sizes and shapes are regular and round whereas $CaCO_3$ particle sizes and shapes are irregular. A plausible explanation is related to possible higher modulus of the cross-linked starch, which resists deforming under the tension of the film stretch.

Figure 7 compares a sectional profile for Sample No. 2 before (a) and after (b) the film was stretched to 500%. Unlike the TPXS of Samples No. 5 and 6, the cross-linked starch from Ingredion™, which was converted to TPXS here, was not a spherical particle. Rather, these TPXS domains were angular with shape similar to many $CaCO_3$. After stretching, good film debonding and porosity due to the presence of the cross-linked starch was visible. This film, while similar in structure to the other cross-linked starches, lacked the level of breathability that could be developed.

The SEM data for the stretched films of all 70/30 blends of the copolyester and TPXS are very similar in structure regardless the fact that they are produced by different chemistry and from different manufacturers. Thus, the majority of increased breathability appears attributable to the pores that form around the porogens, which is consistent with the literature around stretched-breathable films.[9,10,25,29,30] That said, the cross-linked starch produced by phosphorus trichloride oxide treatment had angular structure and did not develop as high of levels of breathability as the spherical TPXS porogens. As has been found for $CaCO_3$, TPXS particle size and shape appear to play a role in micropore development. Alternatively, it is commonly believed that the level of film debonding as proportionally related to a percentage of the film that can be extended or stretched.[29,30] Perhaps, interfacial adhesion to the copolyester matrix differed between the two types of cross-linked starches.
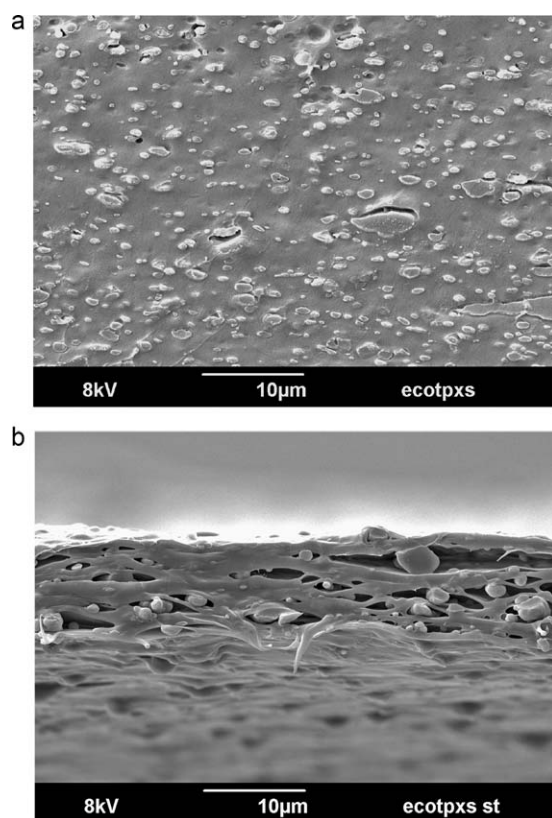

Figure 7. Structure of Ecoflex®/TPXS-B (70/30) film. Scanning electron micrographs of cross-sections through the thickness of the film (**a**) before stretching and (**b**) after stretching to 500%.

CONCLUSIONS

In summary, biodegradable and breathable films comprising a biodegradable copolyester and cross-linked starches as natural polymer porogens were developed. Two types of the cross-linked starch made by two different processes were investigated to show the uniqueness of research findings. Filler size, shape, and resistance to a shear force during the film stretch appear to be important factors for breathability development. The film processing is readily scalable onto commercial equipment available in polymer industry and film properties are within a satisfactory range for many applications.

ACKNOWLEDGMENTS

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