Novel Desiccants Based on Designed Polymeric Blends

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ABSTRACT: We describe a novel concept for the preparation of desiccants based on polymeric blends. A hydrophilic channeling agent (e.g., PEG) is blended with a hydrophobic polymer (e.g., polypropylene) to produce interconnecting hydrophilic channels within the hydrophobic polymer. To make the system desiccating, a water-absorbing material is blended into the polymeric matrix to become distributed within the hydrophilic portion. The resultant blend may be molded and cast into plug-type inserts and liners for closed containers, or formed into films, sheets, beads, or pellets; its uses include pharmaceutical and industrial applications. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 317–327, 2001

Key words: desiccant; channeling agent; molecular sieves; polymers; sleeves

INTRODUCTION

There are many commercial products that require storage or shipping in a controlled humidity environment. One important example is in the shipment and storage of solid pharmaceuticals whose efficacy is compromised by moisture. The initial packaging of the pharmaceutical typically occurs within a controlled environment in a factory where the product is sealed in a moisture-free container. The container is selected to have low permeability to moisture. Therefore, the pharmaceutical will normally be protected from moisture until it reaches the end user. However, once received by the customer, the container will be opened repeatedly for continued access to the drug. Upon each opening, moisture-bearing air

will be introduced into the container and subsequently sealed with the product after closure. Unless this moisture is somehow removed from the headspace of the container, it may be absorbed by the drug, resulting in deterioration. For this reason, it is common practice to include desiccating units in the same package as the drug.[1–3]

Other applications, for example, in the electronics industry, also may require low moisture for optimal performance. A desiccating agent is usually included within the housing to remove excess moisture during the initial packaging stage, and to prevent subsequent moisture seepage into the container. Because of the delicate nature of the electronic components, it is important that the desiccant be free of desiccant dust fines ("dusting") to prevent contamination and performance degradation. Therefore, shielding the working components from actual contact with the desiccating material within the containers is critical.

In general, there are three primary types of desiccating agents that are used.[1] The first includes chemical compounds that form solid hydrates. One example is anhydrous salts that absorb moisture to form stable salt hydrates. In this reaction, a stable compound is formed, holding the moisture captive. The second type of desiccant compounds reacts with moisture to form new compounds. The reaction is generally irreversible at low temperature, and requires a significant amount of energy to regenerate desiccant properties. The third type of desiccant removes moisture via physical absorption accomplished via "wicking" of moisture through fine "capillary" structures in the desiccant particles. The pore size and density determine the absorption properties of the desiccant. Examples include molecular sieves, silica gels, clays (e.g., montmorillimite clay),[2,3] and starches. This class of desiccants is preferred for many applications because they are both inert and water insoluble. The molecular sieve pore sizes that are suitable for application range between some 3 to 15 Å, and that for silica gel beads is about 24 Å.[1]

The present article introduces a novel desiccant system based on polymeric blends containing desiccants. The system is made of a hydrophobic polymer, a hydrophilic channeling agent, and an appropriate desiccant. Our goal is to describe the fabrication process and morphology of this dust-free desiccant, and to elucidate its mechanism of action. The system is characterized by means of optical and scanning election microscopy and thermal and mechanical analysis, as well as in terms of swelling and water absorption properties.

MATERIALS AND METHODS

Film/Desiccant Preparation

The blend in the present work includes a desiccant such as molecular sieves, polypropylene (PP) as the base polymer, and a polyglycol as a hydrophilic channeling agent. The fractions of the various components range from 30–80% PP (w/w) [e.g., PP homopolymer available from Exxon (3505), having a melt flow of 400] and 5–20% (w/w) of the polyglycol [e.g., poly(ethylene propylene glycol) available from Dow (15–200). The components are first dry mixed in a Henschel mixer, and then fed to a compounder. A Leistritz twin screw extruder or a Werner Pfleider mixer can be used to achieve a good melt mix at about

140–170°C. The melt can then be either extruded to form a film or converted into pellets using dry air cooling on a vibrating conveyer. The formed pellets containing channels can then be either injection-molded into beads, or coinjected with PP as the inside layer of a container.

Several films were prepared for the current work, as described below (all percentages henceforth are w/w).

Film #1, PP93/PEG7

93% of PP (Polypropylene) [Exxon Chemicals, trade name Escorenet 8) PP 3505G] and 7% of poly(ethylene glycol) (PEG) (Dow Chemical, trade name E-4500) were mixed to produce a uniform blend. The blend was then fed through a Leistritz twin-screw extruder at temperatures in the 16 zones ranging between about 145 and 165°C, at a feed rate of about 40 lb/h, at a screw speed of about 460 rpm, and a six-inch die. The extruded composition was then fed through a three-roll hot press at temperatures ranging between about 85 and 92°C to produce a film of some 4 mm in thickness.

Film #2, PP68/PEG12/MS20

68% of PP, 12% of PEG, and 20% of molecular sieve, 4A (Elf Atochem, trade name Siliporite molecular sieve, 4 Å) were sufficiently mixed to produce a uniform blend. The blend was then extruded using conditions similar to those used with film 1 to produce a film of about 4 mm thick.

Film #3, PP35/PEG12/MS53

34.9% of PP, 12.0% of PEG, 52.8% of molecular sieve, 4 Å, and 0.3% of a gray colorant were sufficiently mixed to produce a uniform blend. The blend was then extruded using conditions similar to those used with film 1 to produce a film of about 4 mm thick.

Film #4, PP100

100% of PP. The blend was extruded using conditions similar to those used with film 1 to produce a film of about 4 mm thick.

Film #5, PP88/PEG12

88% of PP and 12% of PEG were sufficiently mixed to produce a uniform blend. The blend was then extruded using conditions similar to those used with film 1 to produce a film of about 4 mm thick.

Film #6, PP68/PEG12/MS20

68% of PP, 12% of PEG, and 20% of molecular sieve, 4 Å were sufficiently mixed to produce a uniform blend. The blend was then extruded using conditions similar to those used with film 1 to produce a film of about 4 mm thick.

Film #7, PP50/MS50

50% of PP and 50% of molecular sieve, 4 Å were sufficiently mixed to produce a uniform blend. The blend was then extruded using conditions similar to those used with film 1 to produce a film of about 4 mm thick.

For absorption measurements, a new series of polymeric films and molecular sieves were manufactured. They are listed below.

Film CS9 (sleeve) was made of the following components: 60% of molecular sieves (Elf Atochem) Siliporite, 30% of PP FT120WVIIX (Aristec), and 10% of PEG E-4500 (Dow). All components were extruded into pellets at temperature zones varying from 80 to 145°C, utilizing a constant pressure on the extruder. These pellets were then injection molded into sleeves to determine the difference in channel formation in injection molding vs. extrusion.

Film CS9L was extruded into a 15-mm film at temperature zones varying from 145 to 165°C, utilizing a low extrusion pressure (20 bar).

Film CS9H was extruded into a 15-mm film at temperature zones from 145 to 165°C, utilizing a high extrusion pressure (2500 bar).

Film CS10 (sleeve) was made of the following components: 40% of Silica Gel, 50% of PP FT120WVIIX (Aristec), and 10% of PEG E-4500 (Dow) was extruded into pellets at temperature zones varying from 70 to 155°C, utilizing a constant pressure on the extrude. These pellets were then injection molded into sleeves to determine the difference in channel formation in injection molding vs. extrusion.

Film CS10L was extruded into a 15-mm film at temperature zones varying from 145 to 165°C, utilizing a low extrusion pressure (20 bar).

Film CS10H was extruded into a 15-mm film at temperature zones varying from 145 to 165°C, utilizing a high extrusion pressure (2500 bar).

Film CS11 (sleeve) was made of the following components: 60% of molecular sieve, 10A (Elf Atochem) Siliporite, 30% of PP FT120WVIIX (Aristec), and 10% of PEG E-4500 (Dow). This material was extruded into pellets at temperature zones varying from 80 to 145°C, utilizing a constant pressure on the extruder. These pellets were then injection molded into sleeves to determine the difference in channel formation in injection molding vs. extrusion.

Film CS12 (sleeve) was made of the following components: 60% of molecular sieve, 4 Å (Elf Atochem) Siliporite, 30% of PP FT120WVIIX (Aristec), and 10% of PEG 12-200 (Dow). This material was extruded into pellets at temperature zones varying from 80 to 145°C, utilizing a constant pressure on the extruder. These pellets were then injection molded into sleeves to determine the difference in channel formation in injection molding vs. extrusion.

Film CS12L was extruded into a 15-mm film at temperature zones varying from 145 to 165°C, utilizing a high extrusion pressure (2500 bar).

Film CS13 (sleeve) was made of the following components: 40% of Silica Gel, 50% of PP FT120WVIIX (Aristec), and 10% of PEG 15-200 (Dow). This material was extruded into pellets at temperature zones varying from 70 to 155°C, utilizing a constant pressure on the extruder. These pellets were then injection molded into sleeves to determine the difference in channel formation in injection vs. extrusion.

Film CS13L was extruded into a 15-mm film at temperature zones varying from 145 to 165°C, utilizing a low extrusion pressure (20 bar).

Film CS13H was extruded into a 15-mm film at temperature zones varying from 145 to 165°C, utilizing a high extrusion pressure (2500 bar).

Film CS15 (sleeve) was made of the following components: 60% of molecular sieve, 10 Å (Elf Atochem) Siliporite, 30% of PP FT120WVIIX (Aristec), and 10% of PEG 15-200 (Dow). This material was extruded into pellets at temperature zones varying from 80 to 145°C, utilizing a constant pressure on the extruder. These pellets were then molded into sleeves to determine the difference in channel formation in injection molding vs. extrusion.

Film CS15L was extruded into a 15-mm film at temperature zones varying from 145 to 165°C, utilizing a low extrusion pressure (20 bar).

Film CS15H was extruded into a 15-mm film at temperature zones varying from 145 to 165°C, utilizing a high extrusion pressure (2500 bar).

Swelling and Weight Loss Experiments

Circular disks (1.1 cm in diameter) were cut out from each polymeric sample, and initial dry weight of each was recorded. Samples were subsequently incubated in 2.0 mL of distilled water

and left shaking at room temperature. At 1, 2, 3, and 34 days, the disks were removed, the surface was blotted dry, and the sample was weighed to determine the extent of swelling. At each time point, the distilled water was replaced to provide for sink conditions. At the end of the study, the samples were frozen, lyophilized to remove the water, and the sample was weighed to determine mass loss. Percent swelling is defined as [the wet weight at a time point (t_x) − initial dry weight (t_{zero})]/initial dry weight $(t_{zero}) \times 100$. "Dry" indicates the final sample weight following the 34-day (t_{34}) incubation in water and lyophilization.

Thermal Analysis Using Differential Scanning Calorimetry (DSC)

The processed film samples were analyzed using a Perkin-Elmer DSC7 equipped with a TAC 7DX thermal controller according to manufacturer's protocols. Samples were heated from −50 to 250°C at a rate of 10 or 15°C/min, then cooled at the same rate, and then heated once again to 250°C at the same rate. For each film, the melting point (°C) and enthalpy (ΔH, J/g) for the first heating ramp (1°) and the second heating ramp (2°) were calculated using Perkin-Elmer's Pyris software (Version 2.01).

Morphological Analysis by Scanning Electron Microscopy (SEM)

The structural properties of the films were imaged using a Hitachi S-2700 SE microscope operating at 8-kV accelerating voltage to minimize irradiation damage. Each film sample was visualized in three perspectives: (1) the surface, (2) the fractured cross-section (0°), and (3) the fractured cross-section at a 90° angle with respect to orientation #2. Preincubation film samples were directly sputter-coated with a 5–10-nm layer of gold-palladium with a Polaron Instruments Sputter Coater E5100. Postincubation samples were incubated at room temperature for 24 h in 10 mL of 70% (w/v) ethanol with agitation. The ethanol was discarded, and the samples were air dried overnight, followed by freezing and lyophilization overnight to remove any residual moisture and sputter coating.

Mechanical Testing

Polymers were studied using an Instron Model 4442 instrument equipped with a 500N static load cell. Using a template, polymer films were cut into rectangles 25.4 mm wide and 95 mm long with variable thicknesses of 0.19 to 0.46 mm. The films were contoured into a "dogbone" shape in the center (where the width was 15 mm) to ensure that breakage occurred at the center and not near the grips. The films were mounted between 1-inch wide, 500N Max load, screw-action grips. The grip and gauge lengths were set to 46 and 38 mm, and the crosshead speed was 50.8 mm/min. The following parameters were calculated at peak and at break: load, displacement, strain (linear change per unit length), percent strain, stress (load divided by cross-sectional area), energy (area under the stress–strain curve at break or peak) and Young's modulus (slope of the stress vs. strain curve in the linear region). Results were analyzed with Series IX software (Version 8.06).

Water Absorption Properties

Film samples fabricated with processing conditions as described before (CS9–CS15) were evaluated for moisture absorption using the following test method: (a) one environmental chamber was preset for 72°F and 10% relative humidity ("Rh"), and another was preset for 72°F and 20% Rh; (b) the dish was weighed and the weight recorded; (c) the scale was tarred to remove the weight of the dish from the balance; (d) the film was added to the weighed dish; (e) the material was weighed and the weight recorded; (f) the dish with the sample was placed in the environmental chamber; (g) the sample was left in the chamber for the desired time; (h) after the desired time was reached, the dish with the sample was removed, reweighed, and the weight recorded; and (i) the percent moisture gained per gram of molecular sieves was calculated by (total weight gain of sample)/(weight of molecular sieve in sample) $\times 100$.

RESULTS AND DISCUSSION

A monolithic system in which a hydrophilic agent formed interconnecting channels throughout a hydrophobic polymer, is presented in Figure 1. This is a schematic cartoon depicting the morphology of a three-phase system consisting of the hydrophobic polymer, hydrophilic agent, and water-absorbing material. Suitable channeling agents can presumably include any hydrophilic material (e.g., PEG), which following heating above melting point during mixing can subsequently phase separate from the hydrophobic polymer during cooling.
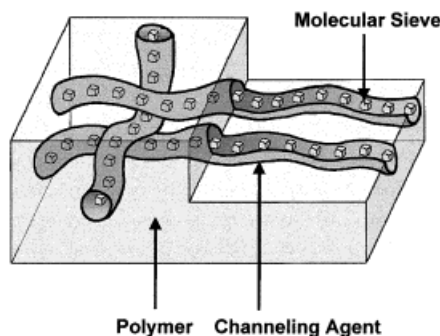
Figure 1 Schematic representing the monolithic composition made of a three-phase systems.

For this study, the films were prepared by first mixing the three components in a dry form. Then, while extruding as described in the Experimental section, the mixture was heated to 145–165°C. At this temperature, both PP and PEG polymers are in a molten state, yet due to the preferential affinity between the desiccant and the channeling agent being greater than between the polymer and the desiccant, the desiccant preferentially partitions into the hydrophilic agent phase. The hydrophobic polymer and the channeling agent are not miscible with each other, even at high temperatures. This immiscibility is critical in creating the interconnecting channels within the hydrophobic polymer. The first evidence for the existence of two phases when PP is mixed with PEG, followed by melting and cooling, is shown in Figure 2. Under crosspolarized light, both the crystalline structure of PP and the spherulitic structure of PEG are clearly visible, indicating that phase separation has occurred after cooling.

Mechanical Strength

Table I lists various parameters pertaining to the mechanical properties of polymeric blends. They indicate that addition of molecular sieves (MS) to PP resulted in a decreased load at peak, displacement, and Young's modulus. The addition of PEG reduced the amount of load to peak, but the displacement, percent stress at peak, and Young's modulus increased. These parameters improved in the film containing PP, MS, and PEG in a 68 : 20 : 12 ratio, while they decreased as the amount of PP was lowered, as demonstrated with the film PP35 : MS53 : PEG54.

Swelling Experiments

To further evaluate the morphology of the polymeric compositions, samples were hydrated in water and studied for the degree of swelling as well as weight loss after complete drying. Film 1 was composed of 93% of PP and 7% of PEG, film 2 contained a blend of 68% of PP, 12% PEG and 20% of MS; and film 3 contained 35% of PP, 12% of PEG and 52% of MS.

Figure 3 shows that film #1 did not swell or lose weight over the course of 34 days, suggesting that the channeling agent was completely entrapped in the hydrophobic polymer and inaccessible to the outside water. Film #2 gained approximately 3% of its initial weight swelling and lost approximately 9% of its initial weight at the end of the 34 days of incubation presumambly due to the leakage of the channeling agent. Likewise, film #3 gained approximately 6% and lost approximately 8% of its initial weight at the end of the 34-day incubation period. The swelling and loss of the water-soluble channeling agent exhibited by films #2 and #3 suggest the existence of interconnecting channels from the surface throughout the interior of the films. In these experiments, we could observe weight loss only if there were interconnecting channels through the sample.

Thermal Analysis

The purpose of the following experiments was to demonstrate that PP-PEG blends formed two separate phases. Table II and Figure 4 show the melting point (°C) and enthalpy (ΔH, J/g) for the first heating ramp (1°) and the second heating ramp (2°). Because the samples are only heated to 250°C, the molecular sieve in film samples #2 and
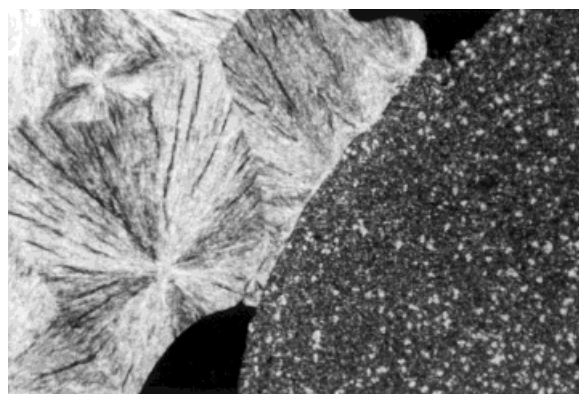

Figure 2 Optical microscope photograpgh of the interface between PP and PEG blends that were melted at 180°C and cooled to room temperature. The picture depicts the large spherulite of the PEG and the smaller spherule of the PP, indicating formation of a phase-separated system.

Table I

|	Load at Peak kgf (SD)	Stress at Peak kgf/mm²	Displacement at Peak mm	Strain at Peak %	Load at Break kgf	Stress at Break kgf/mm²	Displacement at Break mm	Strain at Break %	Young's Modulus kgf/mm²
100% PP	6.343 ± 2.677	1.665 ± .703	0.885 ± 0.472	1.908 ± 1.018	6.343 ± 2.677	1.665 ± 0.703	0.886 ± 0.472	1.908 ± 1.018	120.980 ± 14.764
50% PP 50% MS	10.391 ± 2.560	0.715 ± 0.203	0.440 ± 0.047	0.949 ± 0.101	10.391 ± 2.560	0.715 ± 0.203	0.440 ± 0.047	0.949 ± 0.101	71.055 ± 17.214
88% PP 12% PEG	3.738 ± 0.503	0.775 ± 0.104	1.066 ± 0.510	2.298 ± 1.099	3.708 ± 0.568	0.768 ± 0.118	1.092 ± 0.508	2.354 ± 1.095	66.750 ± 18.540
68% PP 20% MS 12% PEG	6.686 ± 9.181	1.670 ± 2.259	3.560 ± 1.160	7.676 ± 2.501	6.786 ± 9.181	1.670 ± 2.259	3.560 ± 1.160	7.676 ± 2.501	134.230 ± 38.024
35% PP 53% MS 12% PEG	6.734 ± 2.447	0.759 ± 0.222	0.820 ± 0.046	1.768 ± 0.099	6.734 ± 2.447	0.759 ± 0.222	0.820 ± 0.046	1.769 ± 0.099	54.597 ± 14.478
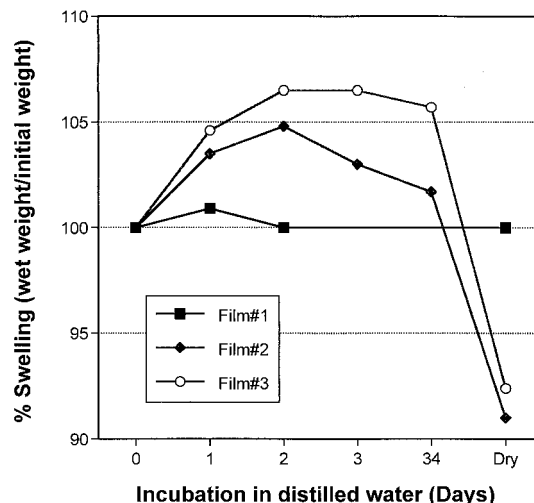
Figure 3 Swelling and weight loss analysis of three film samples: Film #1 (PP93%PEG7%) Film #2 (PP68% PEG12%MS20%), Film #3 (PP35%PEG12%MS53%).

#3 do not melt, and no melting point data was recorded.

The 100% PEG sample exhibited a single melting point at 63°C, while film #4 (100% PP) had a melting point at 157°C. Film #5 displayed both peaks at 58°C (PEG) and 157°C (PP), indicating that the two are phase separate. Note that if the two were mixed and formed a solution, then the peaks would not correspond to the original melt temperatures of the pure polymers, but would be shifted. Film #6 exhibits only the distinct PP peak at 160°C. The molecular sieves did not melt in this temperature range nor did they affect the melting temperature of pure PP. Film #7 again showed two distinct peaks: one for PEG at 57°C and one for PP at 157°C, indicating that in the three-component mixture all three phases were separated.

Film samples #2 and #3 were part of the swelling and weight loss analysis presented above. Two distinct peaks were evident: for PEG at 59°C and for PP at 158°C, indicating that in the three-component mixture all components were phase separated before incubation in water. When the polymer film was incubated in water for 34 days at room temperature (film #2: postincubation) and tested by DSC, the positions of the peaks remained the same, indicating that the components were still phase separated. However, the area of the PEG peak (indicated by ΔH) was greatly reduced. This result shows that PEG had been extracted during the prolonged water incubation. This observation also provides further confirmation for the weight loss data in Figure 3,

Table II

Sample	PEG Peak °C	PEG ΔH J/g	PP Peak °C	J/g
100% PEG	1° 63.8	190.4	None	None
100% PP (Film #4)	1° None	None	162.7	78.5
	2° None	None	157.2	96.1
PP88/PEG12 (Film #5)	1° 57.7	22.2	161.7	80.5
	2° 58.0	20.4	157.4	79.7
PP50/MS50 (Film #7)	1° None	None	159.4	42.3
	2° None	None	160.0	42.8
PP68/PEG12/MS20 Film #6	1° 56.4	19.4	162.2	70.0
	2° 57.2	17.1	156.8	58.0
PP68/PEG12/MS20 Film #2 (preincubation)	1° 58.5	20.8	163.0	60.6
	2° 58.8	16.0	157.7	53.7
Film #2 (postincubation)	1° 55.8	0.38	163.0	86.2
	2° 57.5	0.46	158.5	67.9
PP35/PEG12/MS52 Film #3 (preincubation)	1° 59.3	18.8	162.5	40.3
	2° 56.5	10.1	158.2	24.9
Film #3 (postincubation)	1° 55.5	0.14	160.5	46.9
	2° None	None	156.0	26.0

and demonstrates that the PEG component was largely extracted by means of interconnecting channels within the bulk PP matrix. Film sample
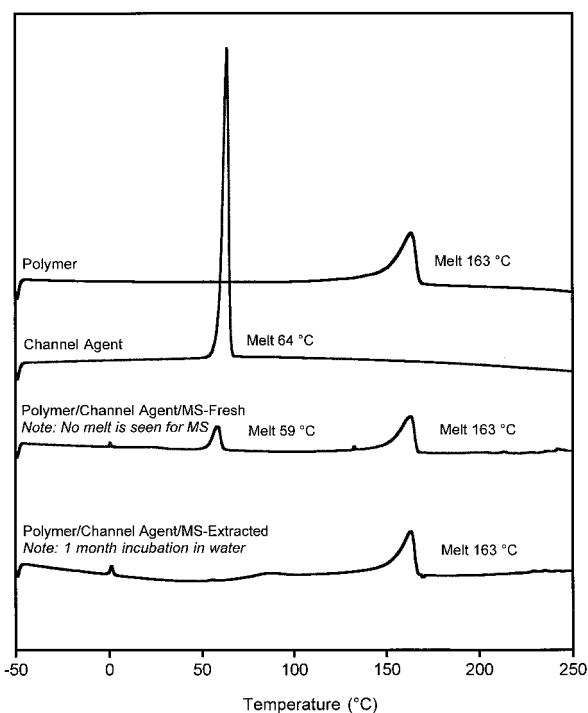

Figure 4 DSC curves of a several samples as indicated on the figure.

#3 showed the same behavior as #2. The thermal peak corresponding to PEG was not detectable (film #3: postincubation), demonstrating nearly complete extraction of PEG during incubation in water. This confirmed the weight loss depicted in Figure 3 in which the same film lost approximately 8% of its initial weight. All these data support the assumption that the PEG is forming interconnecting channels within the polymer.

In addition, the glass transition (T_g) analysis from the DSC data also demonstrate that the hydrophobic polymer and the hydrophilic channeling agent exist in separate phases. Pure PP exhibits a T_g of -6°C, while pure PEG exhibits a T_g at -30°C. DSC data for film #5 exhibited two distinct T_gs, which correspond to the respective polymers (-6°C for PP and -30°C for PEG), pointing to the phase-separated state.

Morphological Analysis

Figures 5 is a scanning electron photomicrographs of film sample #4 (100% PP), and indicates that the hydrophobic polymer has a typical dense, homogenous morphology with no substantial porosity (data not shown) and shows plate-like domains of the polymer revealed during brittle fracture of the film.

Figure 6(a)–(d) shows scanning electron photomicrographs of film sample #5 (made of 88% of
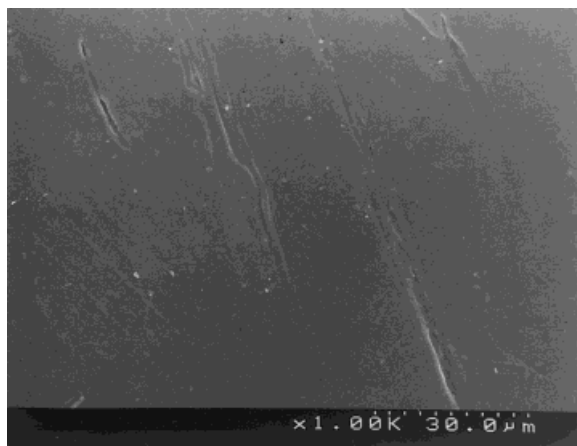
Figure 5 Scanning electron photomicrographs of a film sample of Film #4 (100% PP).

a heterogeneous morphology with dense fibrillar matrix interspersed with domains of PEG-derived lamellar structures. The outer surface, shown in Figure 6(a), is dense, and displays no porosity. The cross-sectional view [Fig. 6(b)–(d)] shows fibrillar domains of PP coated with lamellar strands of PEG. Figure 6(c) is a cross-sectional view of film #5 fractured at a perpendicular angle, which shows the fibrillar PP matrix interspersed with solid, amorphous cylinders of PEG.

Figure 7(a)–(b) shows scanning electron photomicrographs of film sample #6 (50% of PP and 50% of MS); thus, a typically homogeneous dense matrix and discrete molecular sieves, which can only occasionally be seen and are deeply embedded in the polymer despite this high loading. The outline of the molecular sieves (1–10 microns) can be seen embedded beneath the surface of the polymer. The cross-sectional view [Fig. 7(b)] shows plate-like domains of the polymer and a grainy appearance due to a high loading of molecular sieves.
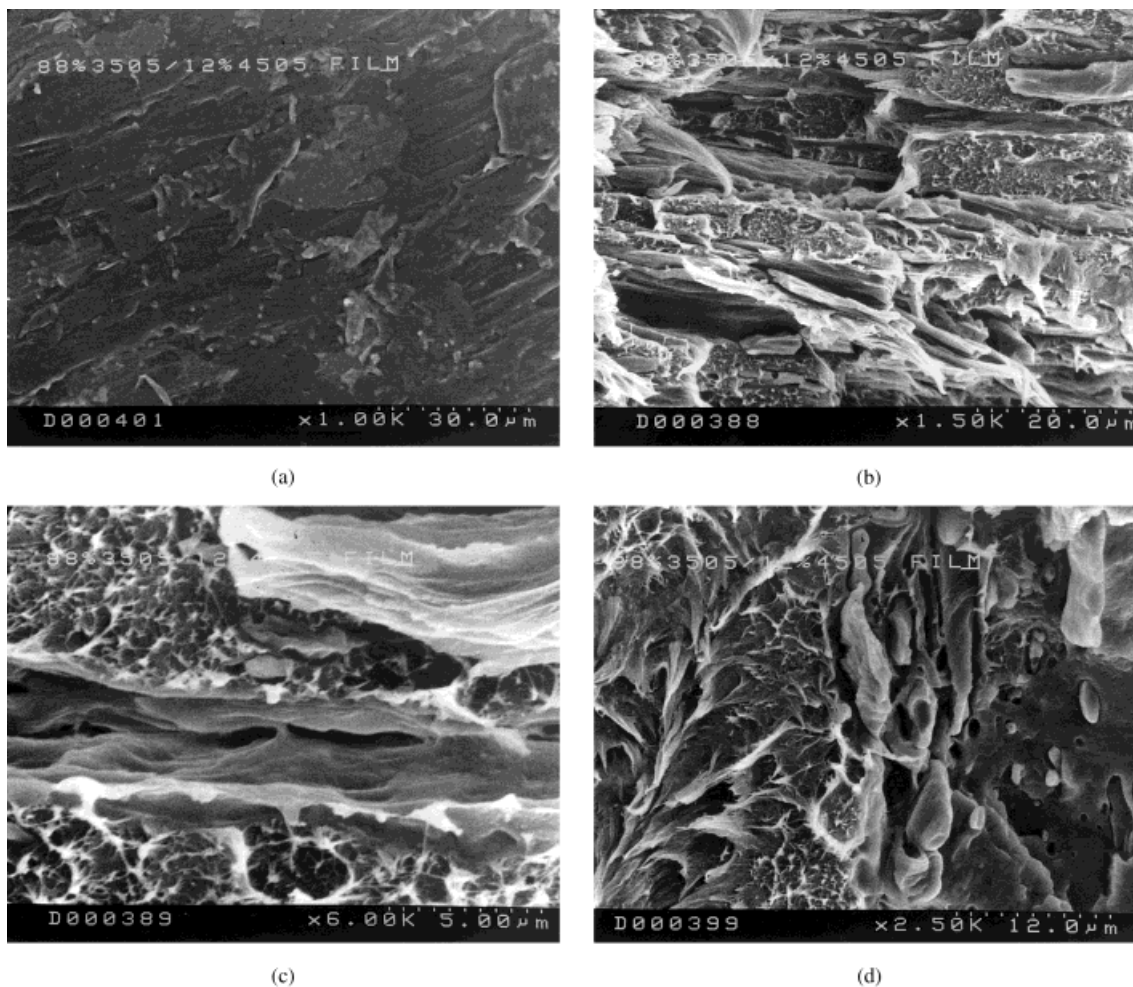
PP and 12% of PEG PP), which illustrate that a two-phase system consisting essentially of the hydrophobic polymer and the hydrophilic agent has

(a)

(b)

(c)

(d)

Figure 6 (a)–(d) Scanning electron photomicrographs of a film sample of Film #5 (PP88/PEG12).
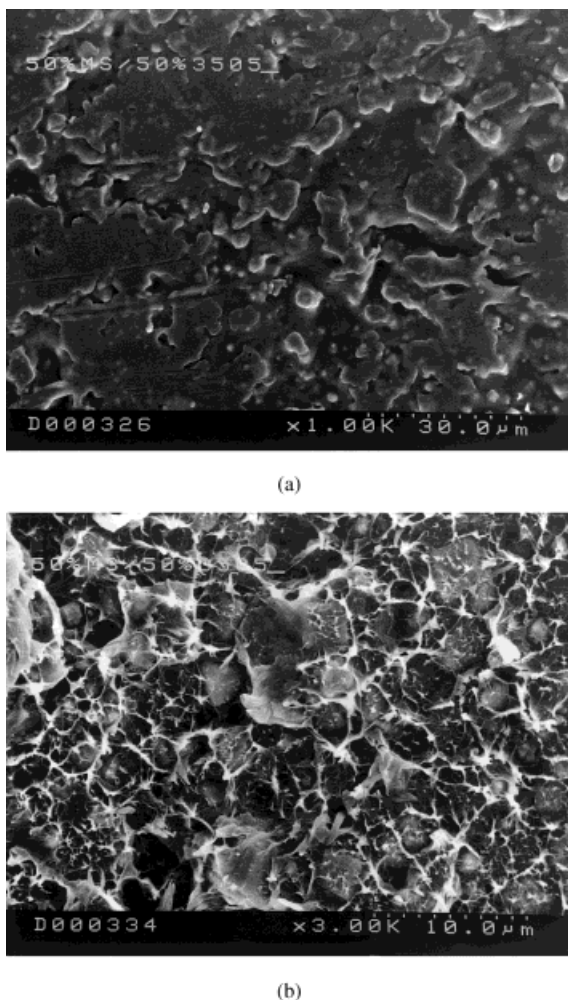
(a)

(b)

Figure 7 (a)–(d) Scanning electron photomicrographs of a film sample of Film #6 (PP50%MS50%).

Figure 8(a)–(d) shows scanning electron photomicrographs of film sample #3 (53% of molecular sieves, 35% of PP and 12% of PEG). They show a three-phase system with a typical channel morphology. Figure 8(a) shows the outer surface at a magnification of 500 times that is covered with long channels, measuring 5–30 microns in length, and filled with numerous discrete molecular sieve particles. A cross-sectional view [Fig. 8(b)], at a magnification of 350 times, reveals a clear channel morphology with long channels running in the fracture orientation. Figure 8(c) is a cross-sectional view in the perpendicular orientation at a magnification of 350 times, and appears to show holes. Figure 8(d) is the same as Figure 8(b) but at a higher magnification, and it shows channels containing discrete molecular sieves, as well as agglomerates of many sieves embedded in the PEG phase. Consequently, based on what we see in Figure 8(b), it is likely that

the holes seen in Figure 8(b) and 8(c) are locations where the molecular sieve fell out during fracture preparation for SEM.

In conclusion, the SEM results further support the formation of interconnecting channels. Because the process begins at a temperature at which the hydrophilic agent is in a molten form while the water-insoluble polymer is in a solid form, we believe that the third component (molecular sieve) is interacting with the liquid hydrophilic agent. Consequently, we assume that the interconnecting channels are formed because the hydrophilic agent flows easily and fills the gaps between the solid polymer and the molecular sieve components. As the process continues and the temperature increases, the hydrophobic polymer melts, and hence, the composition becomes more uniform.

Absorption Properties

Figures 9–12 depict absorption rates of different film formulations. Several points should be taken into account while evaluating these figures; these include the rate of absorption and the maximum capacity of each sample. Figure 9 compares the absorption rate of CS9L to CS9H, which were formed with molecular sieves and PEG4500. The only difference between those films is the pressure that was applied during manufacturing. The graph indicates that the water absorption rate of the film processed at a low pressure is lower than that of the one prepared at a high pressure, although both reach the same capacity of 100 h. The same figure indicates that for CSL and CSH film, made with silica gel and PEG4500, both the rate of absorption and the maximum capacity was much lower than for the same films made with molecular sieves (e.g., sample 9H and 9L). Yet, for the silica gel it seems that a higher pressure (CS10H) resulted in a lower absorption rate and a lower capacity than the film manufactured with lower pressure (CS10L). This shows that the method of fabrication could alter the water absorption rate, as well as the capacity. However, we will demonstrate that the ability to change the type of channeling agent and desiccant still affords much flexibility in terms of manipulating both characteristics. Figure 10 compares the formulations made with PEG 200 (low molecular weight). Interestingly, samples made with either molecular sieve (CS12L) or silica gel (CS13L) display much higher absorption rates, as well as water absorption capacity, than the samples prepared with a higher molecular weight PEG (Fig.
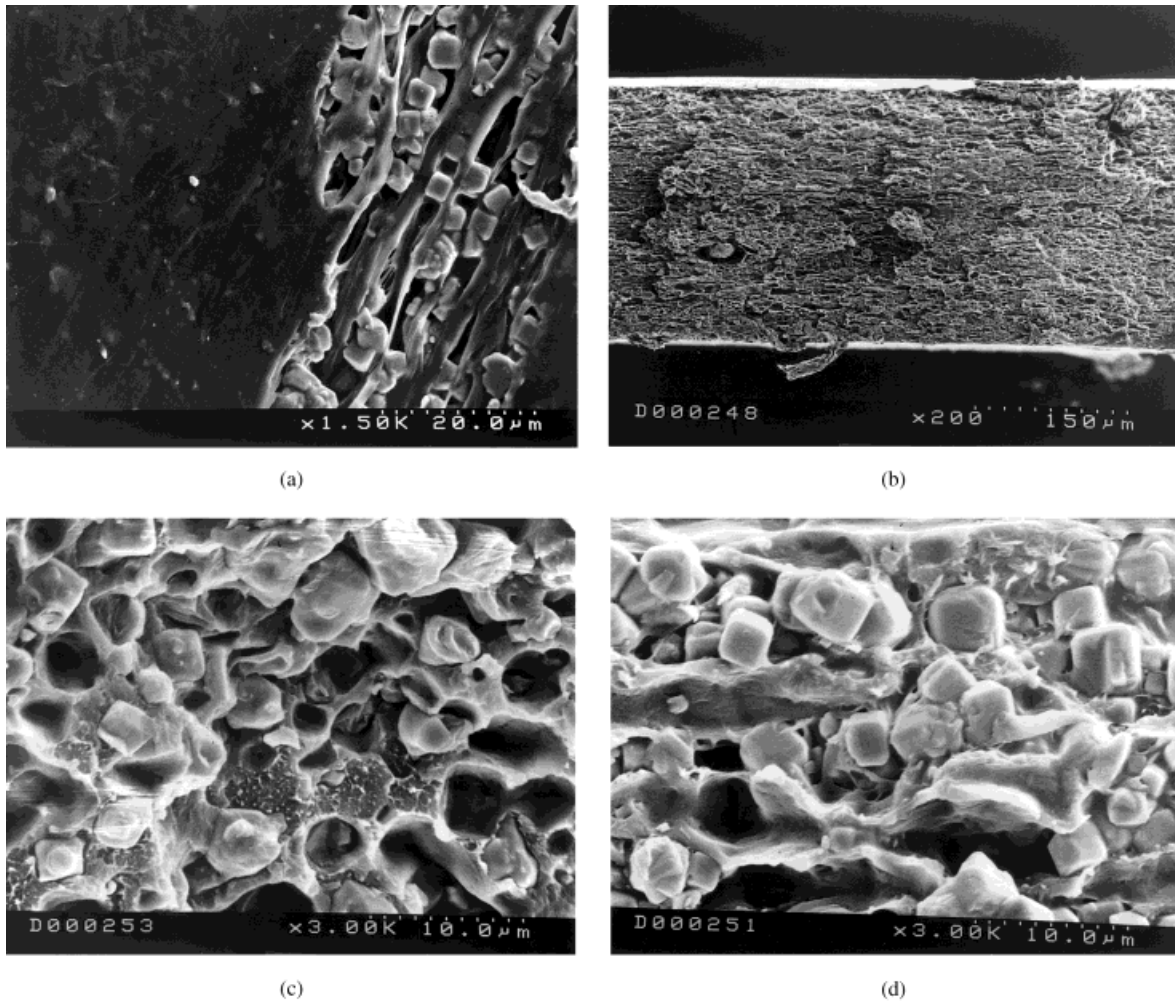
(a)

(b)

(c)

(d)

Figure 8 (a)–(d) Scanning electron photomicrographs of a film sample of Film #3 (PP35/PEG12/MS53).

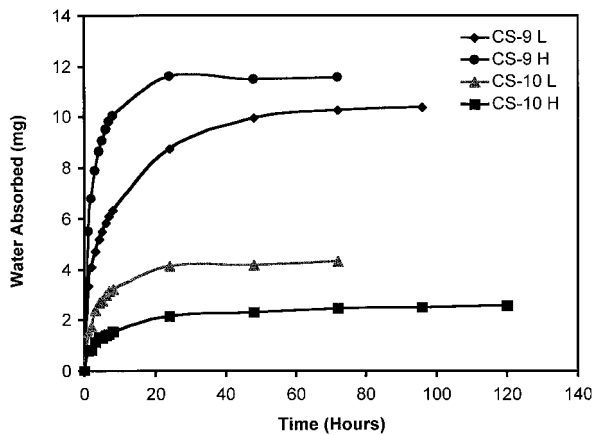9). The effect of pressure on fabrication with PEG200 indicates that the higher the pressure, the higher is the water absorption rate and capacity. Figure 11 compares several formulations of sleeves manufactured by extrusion. The results show that by combining with correct channeling agent, either PEG4500 or PEG200, leads to a high
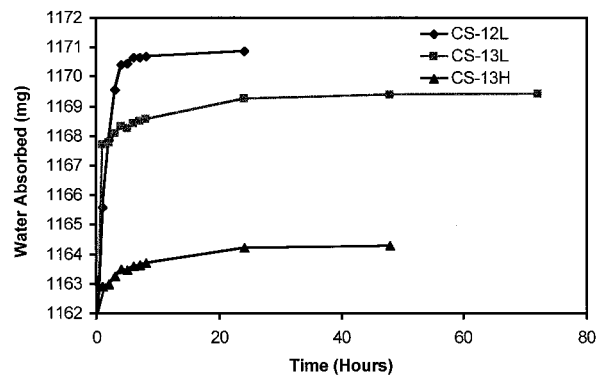

Figure 9 Absorption rate and capacity curves for films made with MS and silica gels.

Figure 10 Absorption rate and capacity curves for films made with MS and silica gels.

water absorption rate and capacity. This film will be used as an insert inside medical devices. Frequent opening and closing of sealed devices requires both the high rate of water absorption and the high absorption capacity. Both are optimized with these examples.

Figure 12 compares specificity of two types of sleeves made with two different desiccants: silica and molecular sieve. At least with the low molecular weight PEG, it is clear that the latter performs much better.

CONCLUSIONS

Our work describes a desiccant fabricated on the basis of polymeric blends containing interconnecting channels. These interconnecting channels allow external moisture to migrate into the exterior to where the water-absorbing material is located. These channels are filled with a hydrophilic agent (the channeling agent) that controls the transmission rate into the polymeric structure. The blends form a three-phase monolithic composition that could be prepared as a rigid solid polymer while also exposing the water-absorbing material to the environment.

The desiccating agents were selected to possess an affinity to the channeling agent. Consequently, during cooling, when the interconnecting channels are formed in the hydrophobic polymer matrix, the desiccating agent is believed to partition into the hydrophilic domains.

We have found that the higher the desiccant concentration in the mixture, the greater the absorption capacity of the final composition. How-
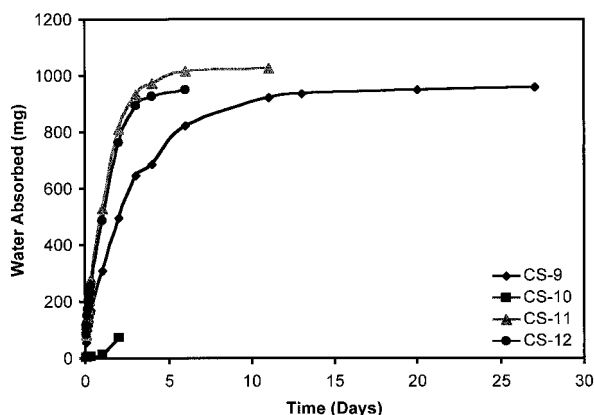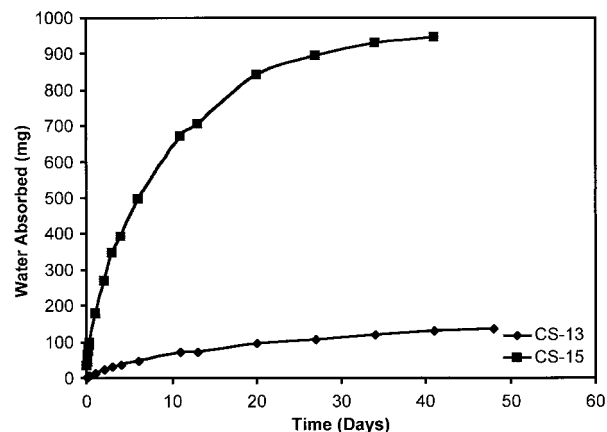
Figure 12 Absorption rate and capacity curves for sleeves made with MS and silica gels.

ever, this higher desiccant concentration also makes the blend more brittle and more difficult to thermally form, extrude, or injection mold. For that reason, a maximum desiccant load is probably some 60 to 70% (w/w) with respect to the channeling agent, or from 10 to 60% (w/w) with respect to the hydrophobic polymer.

The latter presumably may be any thermoplastic material, although our study has concentrated mostly on PP and polyethylene. These polymers are well suited to the task because of their low cost, ease of fabrication via extrusion and film rolling, and excellent mechanical properties. Even in cases where the film is brittle, the package may be molded so that while its interior portion includes the desiccant, the exterior portion is formed from the pure polymer or a composition with a lower desiccant loading level. For example, a package having an interior "sleeve" portion composed of the polymer–desiccant–channeling agent blend and an exterior portion composed of the pure polymer typically will not only be more durable, but will also act as a moisture barrier that resists the transmission of moisture from the exterior into the interior of the package.

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Figure 11 Absorption rate and capacity curves for sleeves made with MS and silica gels.