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AN INVESTIGATION INTO THE FORMATION OF PLASTICIZER CHANNELS IN PLASTICIZED POLYMER FILMS

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ABSTRACT

The effects of plasticizer, polyethylene glycol (PEG-600), on the sucrose permeability, void volume and morphology of cellulose acetate free films were investigated. The sucrose permeability of cellulose acetate free films was found to decrease with increasing PEG-600 to a minimum and increase dramatically when they were plasticized by over 30% (w/w) PEG-600. The decrease in sucrose permeability of cellulose acetate free films with increasing plasticizer at low plasticizer concentrations could be interpreted by the antiplasticization effect, and the dramatic increase of sucrose permeability of cellulose acetate free films at high plasticizer level could be explained by the formation of plasticizer channels. The void volume of cellulose acetate free films were calculated by determining the water content in the films, and the effect of PEG-600 on the morphology of cellulose acetate free films was studied by using the scanning electron microscopy (SEM). Both the void volume and SEM studies supported the assumption that the plasticizer channels would be formed in the polymer films which contain high concentration of plasticizer.

INTRODUCTION

A plasticizer can be defined in terms of the desired properties of a given polymer-plasticizer system. In pharmaceutical controlled release film coatings, plasticizers or low-molecular-weight diluents, are added to polymers to modify their physical properties and to improve their film forming characteristics (1-3). Plasticization , in general, refers to a change in the thermal and mechanical properties of a given polymer which involves: (a) lowering of rigidity at low temperature; (b) lowering of transition temperature, at which substantial deformations can be effected with not too large forces; (c) increase of the elongation of polymers. These changes in the mechanical properties also affect the permeabilities of polymer films (4-5). The effects of the plasticizers on the water permeation and mechanical properties of cellulose acetate were investigated by Guo (6). He found the water permeability of cellulose acetate decreased with increasing plasticizer to a minimum and then increased with higher concentration of plasticizer. Low plasticizer concentrations cause a decrease of water permeability by antiplasticization.

Plasticizers differ in their ability to modify the properties of a polymer. The plasticizing efficiency of the dialkyl phthalates and the polyethylene glycols on ethylcellulose and hydroxypropyl methylcellulose films, for example, have been measured by Rowe et al (7) and Sakellariou et al (8). The plasticizing efficiency of the four phthalates was found to be diethyl > dimethyl > dibutyl > dioctyl. The plasticizing efficiency of the polyethylene glycols decreased with increasing molecular weight, with the high molecular weight solid members exhibiting phase separation. The effects of plasticizers on the water vapor transmission of cellulose acetate phthalate were studied by Lachman and Drubulis (9). They found that the water vapor transmission of cellulose acetate phthalate plasticized by dimethyl phthalate, or Citroflex-2, first decreased with increasing plasticizer and then increased with higher concentrations of plasticizer. They suggested that at low plasticizer concentration, the plasticizer filled the interstices of the polymer and caused a decrease in water vapor transmission of cellulose acetate phthalate.

Further addition of the plasticizer had only a dilution effect on the polymer film, and the water vapor transmission increased.

The thermodynamic aspects of the disappearance of antiplasticization in slightly plasticized polymer films at high temperature were studied by Guo and coworkers (10). They found that when the temperature was raised above the glass transition of the polymer films, the polymer films contained enough energy to overcome the interaction between the polymer and plasticizer molecules and the antiplasticization effect disappeared. The disappearance of antiplasticization was also proved by the decrease of relaxation activation energy of polymer films at high temperature. The effects of physical aging and antiplasticization on the water transport properties of glassy cellulose acetate film-coated tablets were investigated by Guo (11). He found that a pronouncedly additive effects of physical aging and antiplasticization on the water permeability of cellulose acetate film-coated tablets when they were affected by longer physical aging time and lower plasticizer concentration. A theoretical study suggested that the free volume in the glassy polymer should consist of at least two independent parts, one on which is affected by annealing and the other by antiplasticization.

MATERIALS AND METHODS

The polymer solutions were prepared by dissolving cellulose acetate, 4% w/v, (398-10, FMC Corp., Lot # SA 740, Mw_w = 177000, Mw_n = 58500, 39% acetyla) and polyethylene glycol (Lot # 28F-0031, Approx. Mol. Wt. 600) in 4:1 v/v acetone/methylene chloride mixture. The plasticizer levels, in the dry plasticized cellulose acetate films, were prepared from 0 to 40 % w/w. Two milliliters polymer solution was poured into an aluminum evaporating pan and covered with an inverted funnel to prevent solvent removal by convection. After drying, the free films were lifted off the pan and cut into 2.0 cm diameter circular pieces. The film samples were stored in a desiccator for a minimum of one week. The effect PEG-600 on the morphology of cellulose acetate free films was studied by using scanning electron microscopy (SEM).

The sucrose permeability tests of cellulose acetate free films were performed in a standard diffusion cell system at 25°C. The system included a MGW Lauda M3 water circulator (Messgerate-Werk Lauda, Lauda-Konigsofen, West Germany) and 3 mL Side-by-Side diffusion cells (Crown Glass Co., Vineland, NJ). Before each permeability experiment was performed, the thickness of the film was measured. Two 3 mm silastic gaskets were placed on each side of the circular film and placed between each half of diffusion cell. The cells were then clamped to prevent leakage. In the donor side of the system, a saturated sucrose solution in the presence of excess sucrose was placed, while distilled water was added to the receiver side. In order to reduce boundary layer effects, stirring bars were added into both cells. The water in the receiver side was monitored at 200nm using a Masterflex Pump Drive (Cole Parmer Inst., IL) in conjunction with a Lambda 3B UV/VIS Spectrophotometer (Perkin Elmer Instruments, Norwalk, CT). The sucrose permeability of cellulose acetate films can be calculated from

$$P \bullet S \bullet \Delta C = \frac{dM}{dt} \qquad (1)$$

where P is the sucrose permeability coefficient, S is the surface area of the film that contacts with solution, ΔC is the concentration difference of sucrose between the two diffusion cells, and dM/dt is the weight change of sucrose with respect to the time in the receiver cell.

The comparison of theoretical and experimental PEG-600 levels in the cellulose acetate films, and the void volume of cellulose acetate free films were proceeded and calculated by the following steps:

(1) obtain the weight of polymer film sample (W_o).

(2) drop the film sample into a vial which are filled with deioned water for over night.

(3) take the film sample out from the vial, wipe them with Kimwipes, and measure the weight of the sample (W_w) immediately.

(4) place the sample into an oven at 45°C, periodically weigh the sample until to the constant wights (W_d).

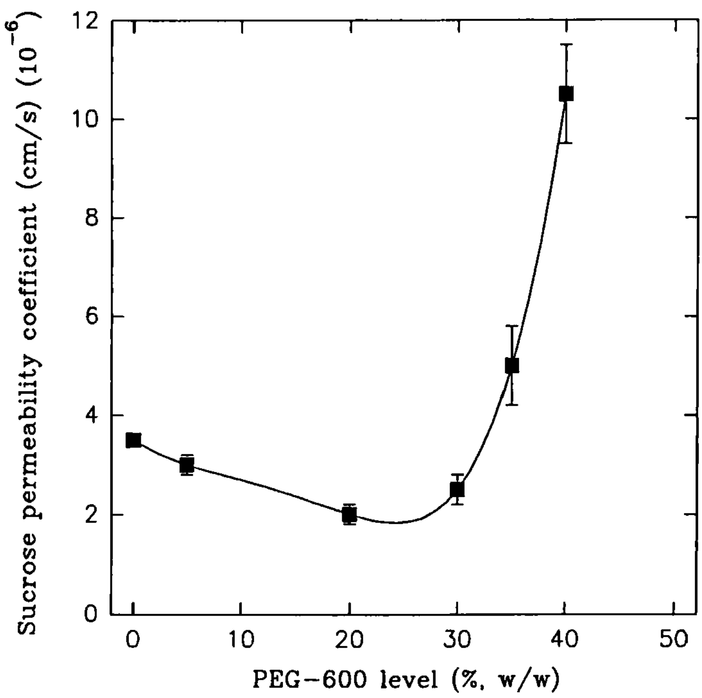


FIGURE 1

The effect of PEG-600 on the sucrose permeability of cellulose acetate free films.

(5) measure the experimental plasticizer ratio (%, w/w) by $(W_o - W_d)/W_o$.

(6) measure the plasticizer volume (V_p) by $(W_o - W_d)/1.128$. (the density of PEG-600 = 1.128 g/cm^3)

(7) measure the total volume of water (V_W) in the dry film by $(W_w - W_d)/1$. (the density of water = 1 g/cm^3)

(8) get the void volume of polymer per unit weight of polymer by $(V_w - V_p)/W_d$.

RESULTS AND DISCUSSION

The effect of PEG-600 on the sucrose permeability of cellulose acetate free films is presented in FIGURE 1. The sucrose permeability of cellulose

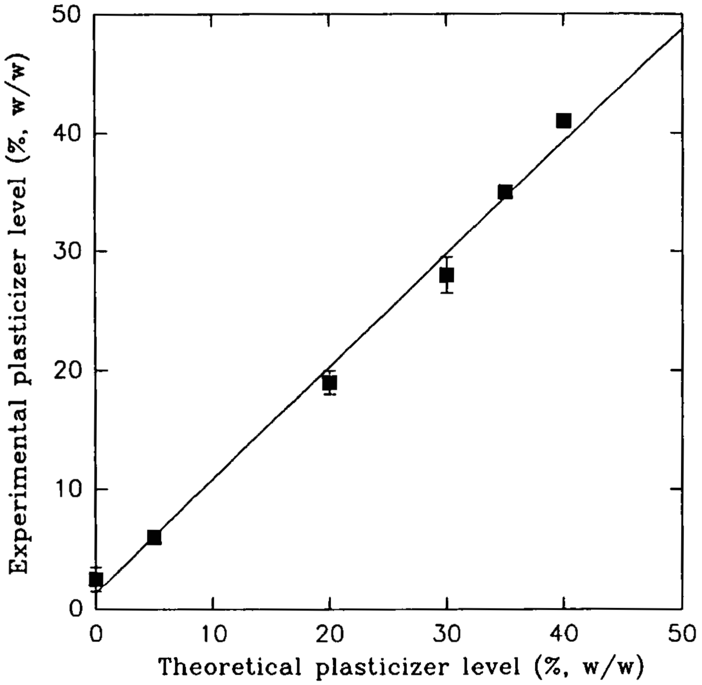


FIGURE 2

The comparison of theoretical and experimental PEG-600 levels in the cellulose acetate free films.

acetate free films was found to decrease with increasing PEG-600 to a minimum and increase dramatically when they were plasticized by over 30% (w/w) PEG-600. The decrease in sucrose permeability of cellulose acetate free films with increasing plasticizer at low plasticizer concentrations could be interpreted by the antiplasticization effect. Antiplasticization arises from an interaction between the polymer and the plasticizer molecules and decreases the molecular mobility of the polymer and plasticizer. This effect was confirmed by mechanical measurements of polymer free films at the same experimental temperature (6). The dramatic increase of sucrose permeability of cellulose acetate free films at high plasticizer level could be explained by the formation of plasticizer channels.

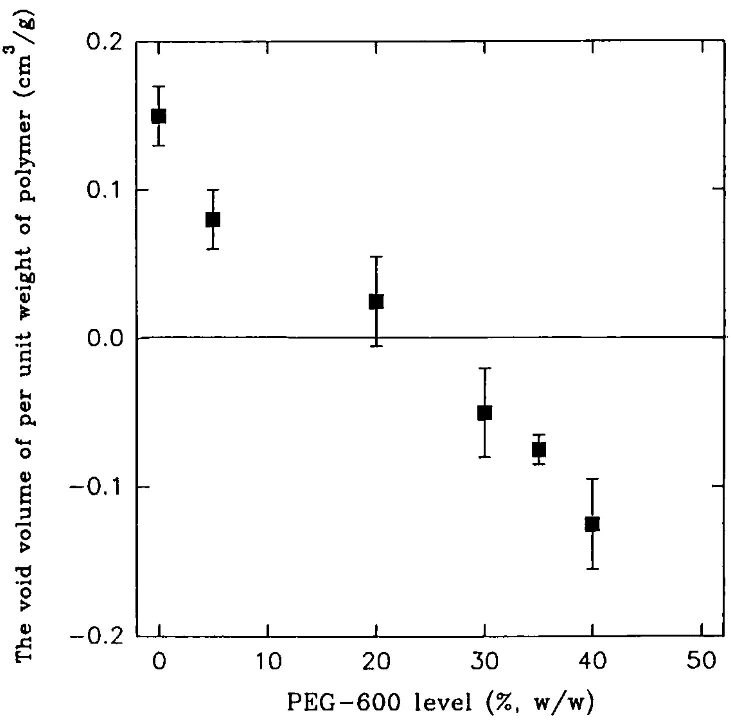
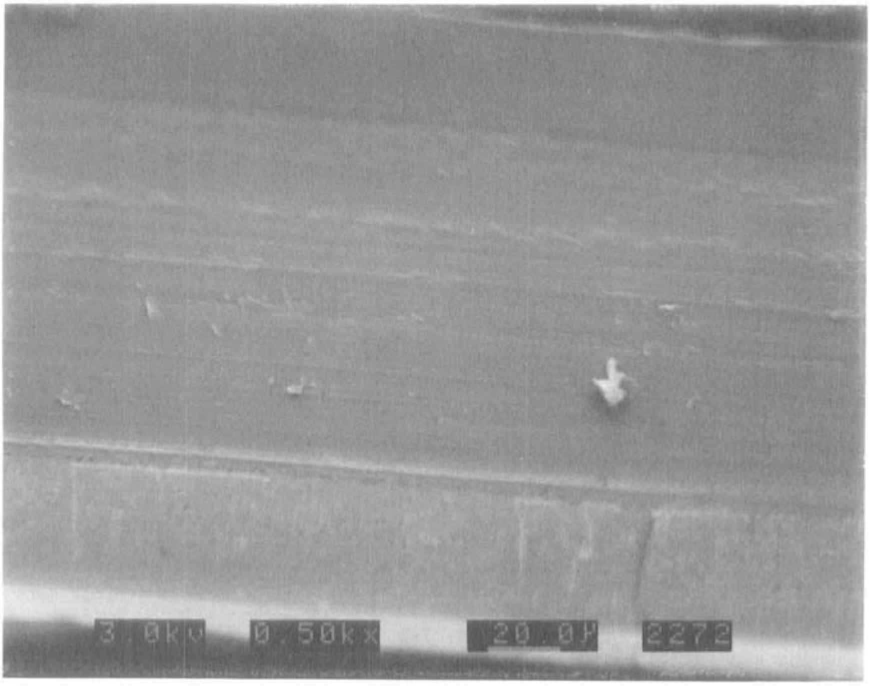


FIGURE 3

The effect of PEG-600 on the void volume of cellulose acetate free films.

The comparison of experimental and theoretical PEG-600 levels in the cellulose acetate films is illustrated in FIGURE 2. It was found that the experimental plasticizer level is very consistent with the theoretical plasticizer level. Therefore, the PEG-600 contents in all the experiment are reliable.

The effect of PEG-600 on the void volume of cellulose acetate films is shown in Figure 3. The void volume per unit weight of polymer was found to decrease with the plasticizer level to negative value when the plasticizer level is above 25% w/w. When the polymer system contended low concentration of plasticizer, the void volume was gradually occupied by the plasticizer molecules and would decrease with the plasticizer level continuously. However, after the plasticizer level was above 25%, the void volume had been



(4a)

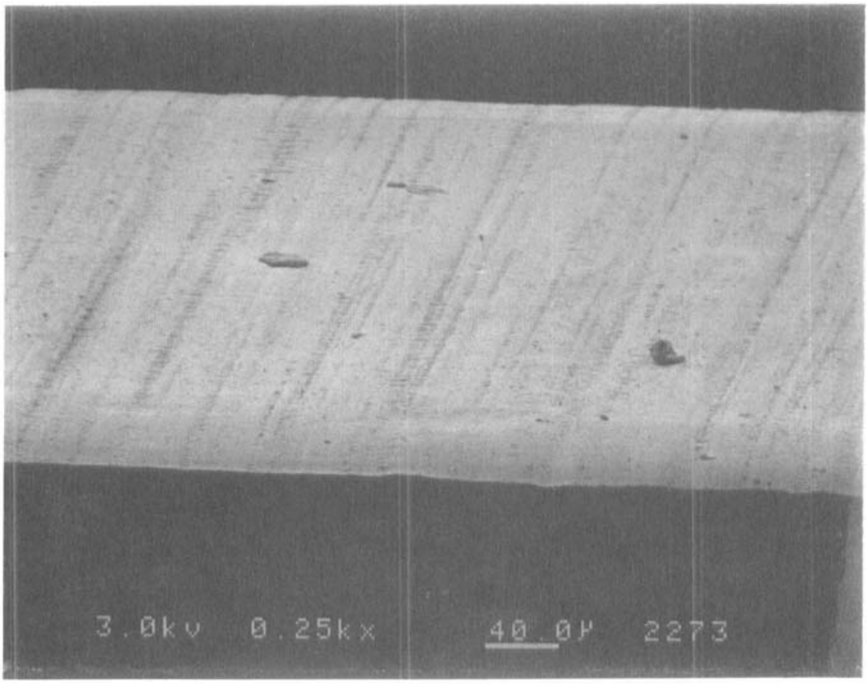
FIGURE 4

The cross-section scanning electron micrographs of (a) unplasticized, (b) 10% and (c) 40% plasticized cellulose acetate free films.

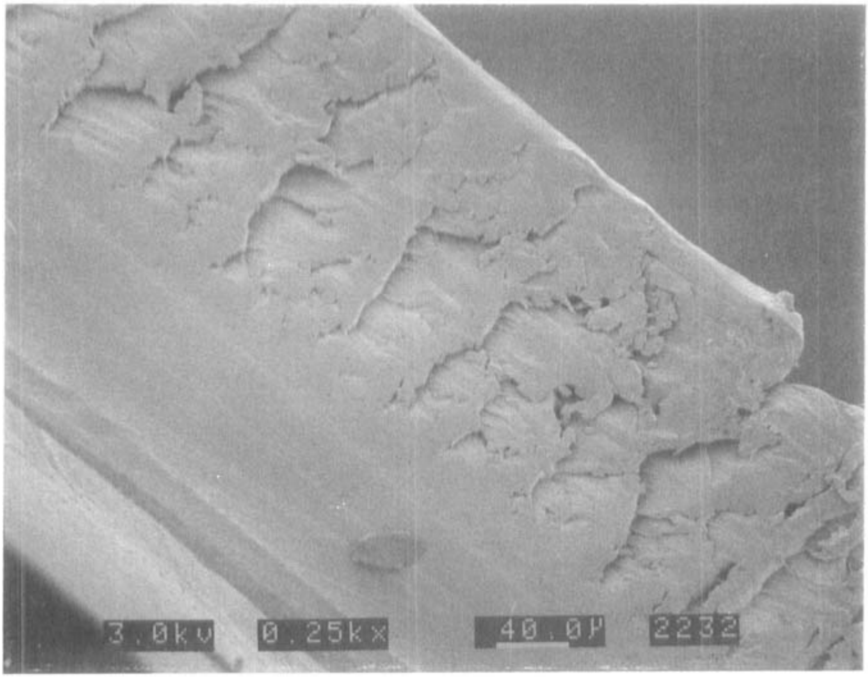
totally occupied by the plasticizer molecules, the further increase of plasticizer would not change the void volume any more, and the negative value results of void volume were due to the comparison with the volume increase of plasticizer channel aggregation.

The scanning electron micrographs of unplasticized, 10% and 40% plasticized cellulose acetate free films are shown in FIGURES 4a-4c. The morphology of cellulose acetate free films were significantly changed with the increasing of plasticizer levels. The plasticizer was found to aggregate together in the polymer film which was plasticized by 40% PEG-600.

Summarily, it can be concluded that after the polymer films are plasticized to a certain extent, the plasticizer will no longer disperse in the

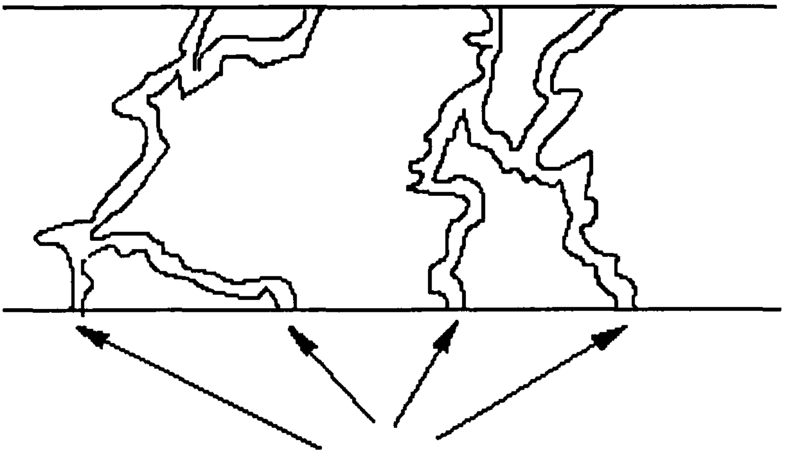


(4b)



(4c)

FIGURE 4 Continued.



Plasticizer Channels

FIGURE 5

The schematic illustration of the plasticizer channels in the polymer films.

polymer films homogeneously, but will form a continuous phase and many plasticizer channels would be found. The diagram which illustrates plasticizer channels in the polymer film is presented in FIGURE 5. The existence of plasticizer channels will increase with the plasticizer level.

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