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Characterisation of the structure of filled polymer film coatings using ion beam etching

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Summary

The structures of hydroxypropyl methylcellulose films containing a number of pigments and fillers have been examined using ion beam etching. Whereas the large talc particles tended to lie flat in the plane of the coating, the small talc particles were more randomly orientated. Red iron oxide and yellow iron oxide formed aggregates, but did not affect the orientation of the large talc particles in mixed films. No orientation or breakage of the acicular yellow iron oxide particles occurred in the formulations studied.

Introduction

Solid additives in the form of pigments, opacifiers and fillers are often added to tablet film coatings for the purposes of either improving identification and appearance by the use of colours (Rowe, 1983) or preventing the degradation of light-sensitive drugs by the use of opacifiers (Rowe, 1984a; 1985a) or decreasing the incidence of film coating defects such as cracking and edge splitting by the use of talc and other fillers (Rowe, 1982; 1984b). An understanding of the microstructure of such films and the influence of morphology on the observed macroscopical features, e.g., opacity and absence of defects, is essential in the optimisation of the formulation and process conditions. However, classical methods available to probe such structures, e.g. light microscopy, are inadequate, often, at best, yielding indirect information. A more modern technique shown by Roberts (1973) to be applicable to pigmented polymer films is that of ion beam etching of the samples prior to examination by scanning electron microscopy. In this technique the sample is etched by bombardment with high-energy argon ions or atoms in a vacuum. The relatively soft polymer is vapourised leaving the hard pigment particles in relief. Thus information about the particles in situ can be obtained by viewing the etched sample using scanning electron microscopy (Sawyer and Grubb, 1987). This technique has been used to characterise the structure of some formulations of hydroxypropyl methylcellulose containing a number of pigments and fillers commonly used in tablet film coating.

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Materials and Methods

The solid additives red iron oxide, yellow iron oxide and talc (two samples each with different mean particle sizes) were obtained from D.F. Anstead Ltd. (Billericay, Essex, U.K.) and used as received. Dispersions in a 5% w/w aqueous methanol solution of hydroxypropyl methylcellulose (Pharmacoat 606, Shin-Etsu Chemical Co., Tokyo, Japan) were prepared using a small laboratory ball mill and films were prepared by casting onto a siliconised glass substrate bounded by a nylon ring 10 cm in diameter. The films were dried overnight on a level surface in a hot air oven at 60 °C.

A 3-mm disk of film was placed in the sample holder of an iron beam thinning instrument (Ion-Tech Ltd., Teddington, U.K.) and rotated between two ion guns which bombarded both surfaces of the sample with argon atoms (atoms are preferred to ions when the surface is non-conducting). All samples were etched for 20 min at 5 kV, 2 mA at an angle of 15 ° to the surfaces before being sputter-coated with gold and examined using scanning electron microscopy. The top surface (i.e. that formed in contact with air) was examined in each case.

Results and Discussion

Fig. 1 shows a scanning electron photomicrograph of a film containing 5% v/v talc (mean size 20 μm) before and after etching. It can be seen that before etching the film appears smooth, consistent with its high measured gloss (51.2 measured at a 60 ° angle; Rowe, 1985b; Gibson et al., 1988) with no evidence of filler on the surface. However, after etching the large flakes of talc and their alignment parallel to the plane of the coating can be clearly seen.

Fig. 2 shows scanning electron photomicrographs of etched films containing 25% v/v of talc of two mean particle sizes. It can be seen that whereas the large talc particles all lie flat in the plane of the film, the smaller talc particles are much more randomly distributed, but here again, they do tend to lie in the plane of the film. It is interesting to note that the effect seen with the large talc particles is consistent with them causing a large decrease in the rate of water vapour transmission as seen by Parker et al. (1974) for films containing talc of a similar size. However, the structure as shown by the small talc particles would be consistent with little or no decrease in water vapour transmission as seen by Okamafe and York (1984).

The alignment of asymmetric filler particles in films is of prime importance to the formulator. Fig. 3 shows a scanning electron photomicrograph of a film containing 5% v/v of yellow iron oxide (a pigment with acicular shaped particles, approximately 2 μm long; Pilpel, 1969). It can be seen that the particles have aggregated and are in no way aligned in an orderly fashion like matches in a match-box. It is interesting to note that the

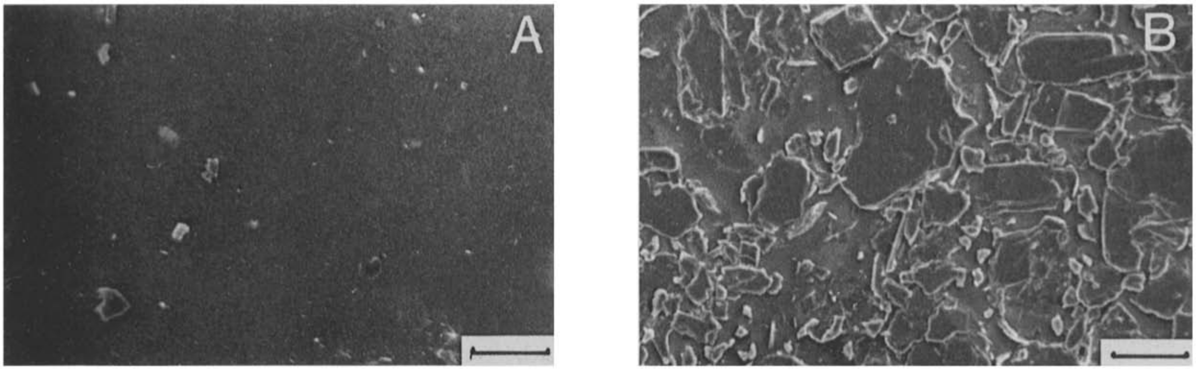

Fig. 1. Scanning electron photomicrographs of a film containing 5% v/v talc (mean size 20 μm) before (A) and after (B) etching. Bars = 30 μm.

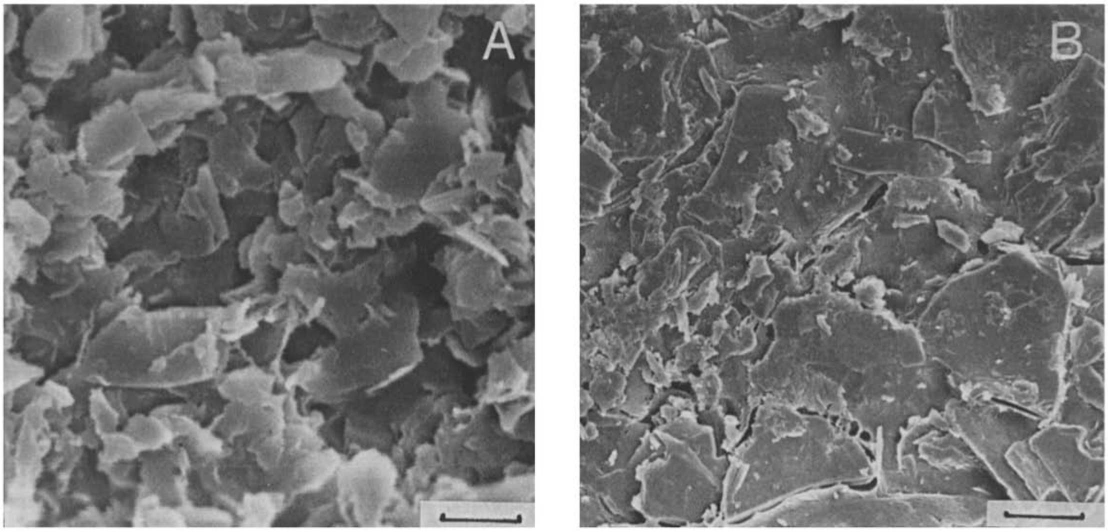

Fig. 2. Scanning electron photomicrographs of etched films containing 25% v/v talc of mean size 5 μm (A) and 20 μm (B). Bars = 2 μm (A) and 50 μm (B).

needles have not been destroyed by the ball-milling process used to prepare the suspension prior to film casting.

Often film formulations contain a mixture of a coloured pigment, e.g. an iron oxide, and talc to decrease the incidence of the defect known as edge splitting (Rowe, 1984b). A scanning electron photomicrograph of a film containing 5% v/v talc (mean size 20 μm) with and without 5% v/v red iron oxide is shown in Fig. 4. It can be seen that while the red iron oxide (mean size 0.2 μm) forms large aggregates up to several μm in diameter, it does not effect the alignment of the large talc flakes. A similar effect can be seen with the yellow iron oxide on comparing the photomicrographs in Fig. 5 with those in Figs. 1 and 3. While the yellow iron oxide aggregates do not affect the alignment of the talc flakes, the talc does not affect the aggregation of the acicular yellow iron oxide.

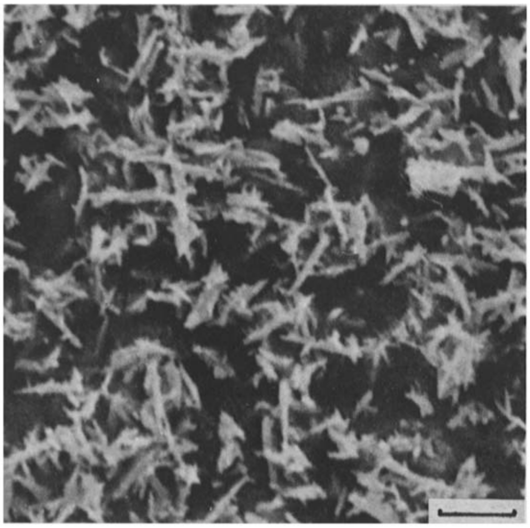

Fig. 3. Scanning electron photomicrograph of an etched film containing 5% v/v yellow iron oxide. Bar = 2 μm.

In conclusion, it can be seen that the technique of ion beam etching provides a relatively simple and rapid method for probing the structure of filled polymer films. Although in all the experiments reported etching was for a fixed time, it is possible, by varying the time the sample is exposed to the ion beam, to vary the depths at which the polymer is etched. In this way it is possible to probe the structure of the film as a function of depth from air/film interface (Donaldson et al., 1986). It is also possible to replicate the etched surface and examine the replica in the transmission electron microscope and thus obtain an image

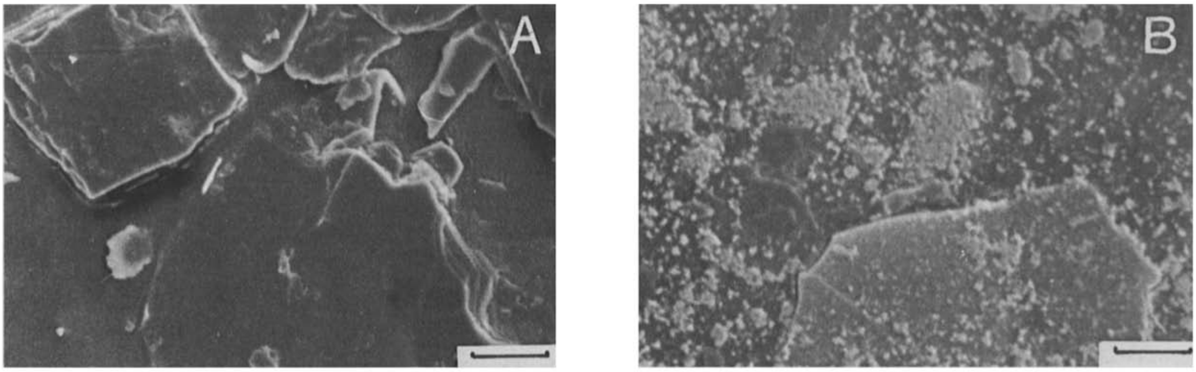

Fig. 4. Scanning electron photomicrographs of etched films containing 5% v/v talc (mean size 20 μm) alone (A) and with added 5% v/v red iron oxide (B). Bars = 10 μm.

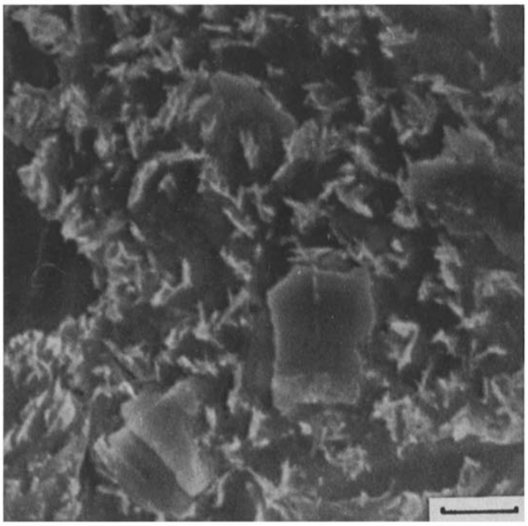

Fig. 5. Scanning electron photomicrograph of an etched film containing 5% v/v talc (mean size 20 μm) and 5% v/v yellow iron oxide. Bar = 3.5 μm.

suitable for computer analysis (Donaldson et al., 1986).

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