soluble in aromatic and aliphatic solvents and in nitromethane, but are soluble in ether, dioxane and tetrahydrofuran.

The synthesis described above, although illustrated for the case of vinyl pyridine, is completely general and may be used for the addition of any vinyl monomer onto a siloxane backbone.

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An unsupported water soluble and heat sealable film from predominantly non-fossil raw materials

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The development of a polymeric film product with desirable properties, largely manufactured from renewable raw materials, will be viewed with considerable interest.

Poly(vinyl alcohol) film[1], and films based on combinations of poly(vinyl alcohol) with serum albumin[2] and poly(vinyl alcohol) with low molecular weight poly(ethylene glycol)[3] have been reported.

During the period of rapid development of man-made polymers based on cheap petrochemical raw materials, the potential use of materials incorporating natural products such as starch has been largely passed over, although starches which had been enzyme- or hypochlorite-converted have found extensive use as so-called film-forming starches, employed as pigment binders for paper coating. Such materials have not so far found widespread application as ingredients for unsupported film. For some years, I have been aware that modified starches and poly(vinyl alcohol) can be cosolubilized in water to provide a casting dope for film[4]. The system also makes it possible to impart a degree of water resistance by inclusion of liquid urea–formaldehyde resins which can further condense during the dehydration stage of the subsequent film casting procedure. More important still, the mechanical properties are decisively affected by the inclusion of up to 150 pph of polymers of suitable humectant plasticizers such as water-soluble mono- or oligomeric diols e.g. ethylene glycol, diethylene glycol (Digol) or glycerol. These not only have a plasticizing effect in their own right, but also ensure that the film, after drying, attracts quantities of moisture from the atmosphere which relate to the amount of humectant plasticizer included in the formulation.

The film products thus obtained are brittle in the anhydrous form (i.e. when freshly cast in the manner to be described when the plasticizer content is low). However, even with low plasticizer content, the film becomes tough after attracting its quota of equilibrium moisture. With high plasticizer content, the film shows distinctly elastomeric features, becomes increasingly pliable and clinging and yet maintains surprisingly high strength and elongation at break. Furthermore, all cast film so obtained readily heat-seals to itself, bonds paper to paper and adheres tenaciously to a variety of substrates including glass and certain polymers.

The actual proportions of poly(vinyl alcohol) and starch are not highly critical, within limits. For the present work a ratio of 50:50 by wt (including the equilibrium moisture present in air-dry converted starch – about 10%) was used and a small constant amount of urea and formaldehyde was added to form urea–formaldehyde resin *in situ*. After addition of humectant plasticizer, preparation of the film and storage at constant humidity and temperature, the moisture content was determined.

Materials

The starch was a hypochlorite-converted corn starch for paper coating (Flocote 64, Laing National) with an 'airdry' moisture content of 9–10%. The poly(vinyl alcohol) was an 88 ± 1% hydrolysed product with 19.5–22.7% of residual acetate and $MW \sim 125\,000$ (BDH Chemicals).

Film preparation

The casting dope was prepared in the following manner: 20 g each of airdry starch and poly(vinyl alcohol) powders were weighed into a 600 ml beaker fitted with a stirrer. 2 g urea were added and the mixed solids were wetted out by the addition of 40 ml IMS. This prevented lump formation during the subsequent solubilization. The beaker was then placed in a larger beaker filled with cold water, 10 ml formalin solution (40% w/v), 400 ml water and the pre-determined

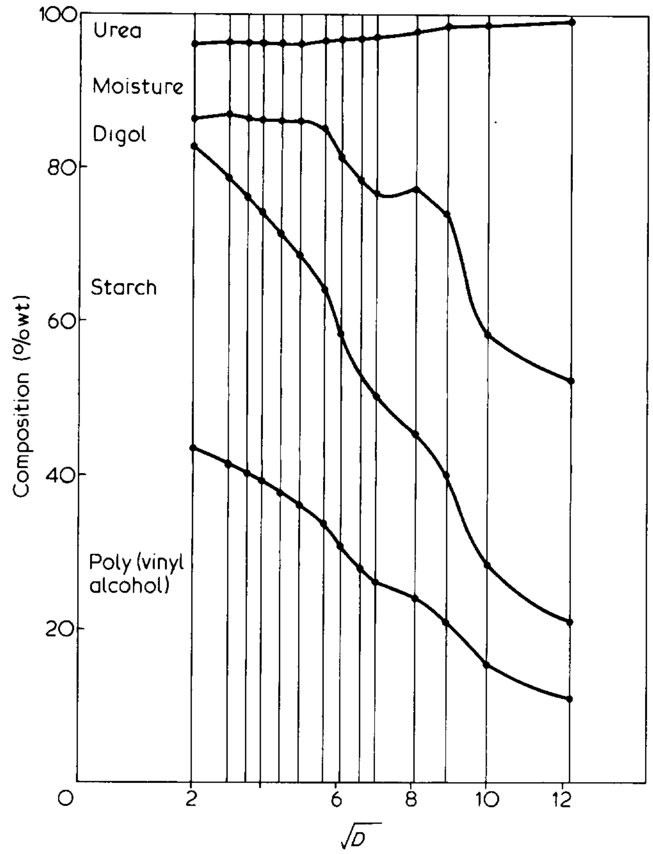

Figure 1 Composition of equilibrated film *versus* $\sqrt{D}$ (root of pph Digol/combined air dry polymers). Starch contains 10% water. R.h., 50 ± 2%; temperature, 23°C

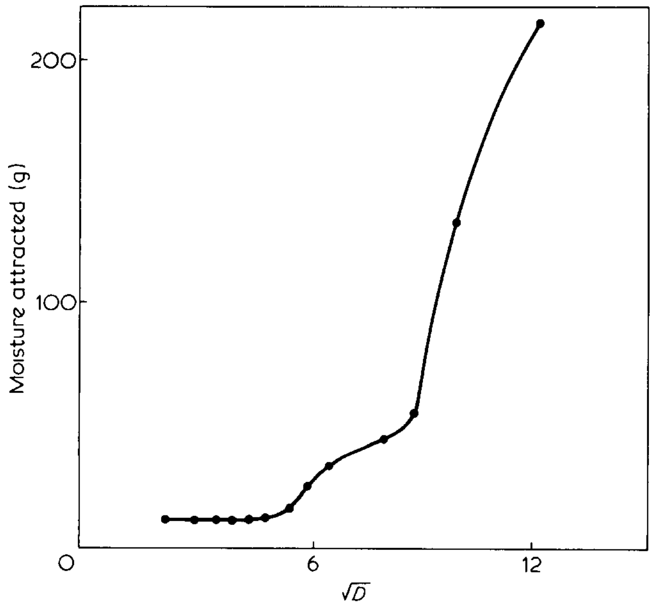

Figure 2 Moisture attracted (regained) during equilibration (g) per 100 g (air dry) polymers *versus* $\sqrt{D}$ (pph Digol/air dry polymers, allowing for *c.* 10% moisture in air dry starch)

quantity of humectant plasticizer were added, and the water bath was gradually heated from room temperature to 95°C with continuous stirring. The resulting dope was strained into a separating funnel through fine wire gauze so as to remove any small specks of gel that might still be present. The dope was then cast into PTFE-lined flat rectangular baking trays. This ensured that it was essentially free from air bubbles. The trays were placed in an oven at 78°C with forced ventilation for 4 h and this was followed by continued heating at the same temperature without forced ventilation for a further 16 h. The resulting film could be readily stripped off and was allowed to regain its equilibrium moisture content at 50% r.h./23°C for 1 week.

Moisture contents were then determined by weight difference after drying the equilibrated film at 105°C for 24 h.

Results

The moisture content and detailed overall composition of film, to which 5–150 pph airdry plasticizer had been added during the preparation of the casting dope, were determined. The results are given in *Figures 1–3*. All film was strong, heat sealable and gave a strong bond when used as a heat-activated laminating layer between two plies of paper and between a number of other materials. The mechanical and bonding characteristics will be reported in the near future.

Conclusions

The inspection of the composition of film plasticized to varying degrees using Digol showed that it is possible to prepare film containing as little as 10% each of starch and poly(vinyl alcohol), the balance being water and liquid plasticizer. Not only is this in itself remarkable, but the film (although somewhat clinging when extremely plasticized) still has good mechanical properties.

The development of a water soluble film of this type suggests a number of possible applications, notably (i) repulpable

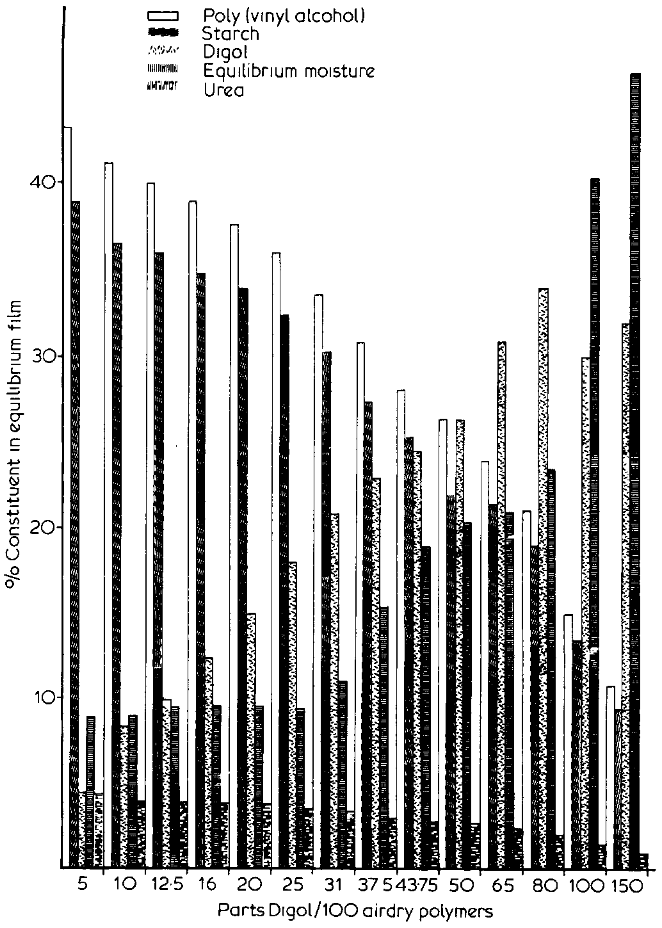

Figure 3 Overall composition of films at equilibrium

splicing film in paper manufacture; (ii) heat sealed dosage sachets for objectionable powdery processing additives such as carbon black, intense dyes and hazardous chemicals which are to be introduced into aqueous or partially aqueous media e.g. duplicating inks, emulsion paints, pharmaceuticals etc. The possibility of using comminuted dry film for moulding purposes is being investigated currently.

The most significant feature of this investigation, however, is the use of starch. In the present formulation, it comprises half of the constituent polymers, is cheaply available from renewable (i.e. non-fossil) sources and opens up exciting new perspectives in materials technology.

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Effect of chain composition of PET on small-angle X-ray scattering

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Introduction

The results reported here are part of an investigation into the effect of chain composition on structure, unit cell dimensions and melting behaviour of poly(ethylene terephthalate) (PET). PET is a copolyester generally containing a variable amount (at least 1–5 mol %) diethylene glycol (DEG)[1], the quantity of which affects the structure and properties of the polymer. Here, the influence of DEG content on the small-angle X-ray scattering (SAXS) of PET is examined.

Experimental

Commercial PET (BASF, W. Germany) with different amounts (up to 15 mol %) of DEG was melted and spun in air. The bristles were drawn about 5 times and isothermally annealed (with fixed ends) in vacuum for 6 h at various temperatures between 80° and 250°C. SAXS measurements were carried out with a Kratky camera (slit collimation) using Ni-filtered CuKα radiation and a scintillation counter. Equal amounts of samples were used. The volume crystallinity, w_c, was calculated from density measurements[2].

Results and Discussion

Curves for bristles with different amounts of DEG are shown in *Figure 1*. During these measurements the fibre axis was oriented perpendicular to the slit direction of the X-ray camera. A strong increase of the overall intensity with increase of DEG content was observed. In addition, the position of the maximum was shifted to smaller values, indicating an increase in the long spacing L with increase of amount of DEG in the chain molecules (*Figure 2*).

This scattering behaviour is surprising since the volume fraction (*Table 1*) of the crystalline phase w_c falls by at least three times with increase of DEG content almost independently of the annealing temperature (*Table 1*). Moreover, the situation most often observed is that scattering power increases with crystalline fraction[3]. The unit cell parameters, however, do not depend on the comonomer (DEG) content in the PET molecules[4]. Hence, we concluded that the chains or chain segments containing a higher amount of

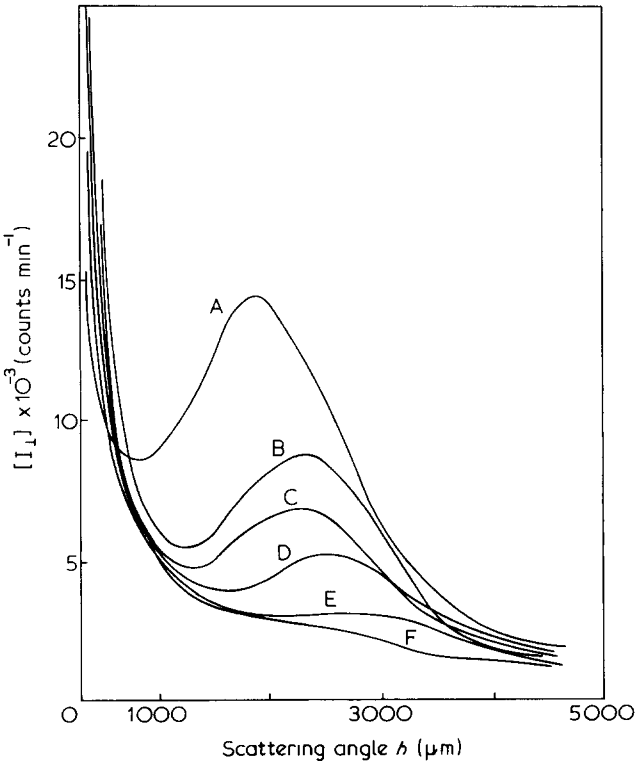

Figure 1 SAXS curves $I_\perp(\theta)$ of drawn PET with different DEG contents annealed at T_a = 240°C for 6 h. DEG content (mol %): A, 14.90; B, 5.80; C, 4.27; D, 1.83; E, 3.09; F, 3.60. $h = 2.2 \times 10^5 \tan 2\theta$