Starch/poly(vinyl alcohol) heatsealable film: 2.

R. S. Lenk and R. E. Merrall
*School of Polymer Studies, Polytechnic of the South Bank, Borough Road, London, SE*1 *0AA, UK*

(*Received* 9 *April* 1980; *revised* 26 *March* 1981)

An earlier communication[1] described the preparation of plasticized cast heatsealable film based on modified starch and a suitable grade of poly(vinyl alcohol). In this paper we report the results of mechanical tests on films plasticized with humectant plasticizers. The first series deals with films plasticized by glycerol and the second with films plasticized by diethylene glycol ('Digol'). The final series gives the results of tensile tests on film plasticized with a standard amount of 50 parts of Digol per hundred parts of dry polymers, but with variable ratios of starch/PV alcohol.

EXPERIMENTAL

Materials

The starch used throughout this work was a hypochlorite converted corn starch as used in paper coating ('Flocote 64', Laing National) with an 'airdry' moisture content of 9–10%. The poly(viny alcohol) was an 88% ±1% hydrolysed product with 19.5 to 22.7% of residual acetate and a molecular weight of ~125 000 (BDH Chemicals).

Film preparation

The casting dope was prepared in the following manner: 20g each of airdry starch and PV alcohol were weighed into a 600 ml beaker and the mixed solids wetted out by the addition of 40 ml IMS. The beaker was fitted with a stirrer and placed in a larger beaker containing cold water, the latter serving as a water bath. 400 ml of distilled water and the required amount of humectant plasticizer were added and the water bath was gradually heated to 95°C with continuous stirring. The resulting dope was strained into a separating funnel through a fine wire gauze so as to remove any specks of gel that might still be present. The dope was then poured into PTFE lined flat rectangular baking trays. This ensured that the dope 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 further heating at this temperature for 16 h without ventilation. The resulting film could be readily stripped off and was allowed to regain its equilibrium moisture content at 50% r.h./20°C for 1 week.

A plot of the moisture content as a percentage of the film at equilibrium vs. the glycerol content expressed as parts per 100 of dry polymers can be seen as essentially linear. The second row in *Table 1* gives the interpolated values for the moisture contents of the equilibrated film for each plasticization level. All the remaining values in *Table 1* were calculated on the basis of these interpolated moisture contents.

On plotting the percentage of equilibrium moisture in the films as a function of the plasticizer content, the plasticiser content may be presented in two alternative ways, which differ from the plot just referred to above in that the curves are based on the glycerol content and on the total plasticizers (glycerol plus moisture) in the films at equilibrium respectively. Excellent curves were obtained. The curve for % equilibrium moisture vs. glycerol-only in the equilibrated films tends to a constant value at high plasticizer content. This is logical, since large amounts of humectant plasticizer attract increasing amounts of moisture until the other film constituents (i.e. the polymers) cease to play any significant role in the mechanism of moisture sorption and the overall moisture content becomes asymptotic to the value appertaining to the humectant by itself.

Tensile properties of equilibrated glycerol plasticized film

The tensile properties were determined on an Instron (Model CM) tensile testing machine at a strain rate of 0.5 mm s^{-1}, using parallel-sided specimens with a gauge length of 4 cm. The relative humidity and the temperature were as before, so that testing was carried out under the same conditions as those used for equilibrating the film.

Table 1 Composition of glycerol plasticized films (Series 1)

Parts glycerol per 100 parts of dry polymer	10	25	50	100	150
% moisture after equilibration (interpolated values)	6.0	9.5	16.5	31	45
% Starch (dry basis) % PV alcohol (dry basis)	42.7	36.2	27.8	17.25	11.0
% Glycerol in film at equilibrium	8.5	18.1	27.8	34.5	33.0
% Total plasticizers (glycerol plus water)	14.5	27.6	44.3	65.5	78.0

0032–3861/81/091279–04$02.00

Table 2 Tensile properties of equilibrated cast film as a function of the plasticizer content*

Parts glycerol per 100 parts of dry polymer	10	25	50	100	150
% Glycerol in film at equilibrium	8.5	18.1	27.8	34.5	33.0
% Total plasticizers (glycerol plus moisture) in equilibrated film	14.5	27.6	44.3	65.5	78.0
Initial modulus (N m^{-2} x 10^6)	280	98	15	4.3	1.8
Breaking strain (%)	26	30	108	165	215
Breaking stress (Ultimate tensile strength) (N m^{-2} x 10^6)	15	7	3.5	1.4	0.9

* Calculated from the interpolated moisture contents

Table 3 Composition of digol-plasticized films (Series 2)

Parts Digol per 100 parts of dry polymers		10	25	50	100	150
% Moisture after equilibration	As determined	7.6	13.1	22.6	37.0	38.9
	Interpolated value	8.8	13.5	21.4	37.0	38.9
% Starch (dry basis) % PV alcohol (dry basis)		*44.3	34.6	26.2	15.7	12.3
g Moisture attracted at equilibrium per 100 g of dry film		9.6	19.5	40.8	117.4	154.3
% Digol in film* at equilibrium		8.4	22.0	26.2	31.4	36.9
% Total plasticizers* (Digol plus moisture) at equilibrium		16.0	35.5	47.6	68.4	75.8

* Calculated from the interpolated moisture contents

SERIES 1—GLYCEROL PLASTICIZED FILMS

Preparation and composition

These films were prepared in strict accordance with the procedure already outlined. The moisture contents were determined after drying the cast film in an oven at 78° ~80°C for 24 h followed by equilibration at a relative humidity (r.h.) of 50±2% and at a temperature of 23° ±1°C for one week. The moisture content was determined by weight difference after drying the equilibrated film at 105°C for 24 h in an air oven with forced ventilation. The composition of the variously plasticized films is set out in *Table 1.*

They represent the mean of 5 determinations; standard deviation <20%; jaw breaks and obviously faulty results due to damage caused during the preparation of specimens were excluded. The results are given in *Table 2.*

The results of log modulus, % strain and ultimate tensile strength may be plotted out and presented in three different ways.

(i) vs. the glycerol content in the equilibrated film,

(ii) vs. parts glycerol per 100 parts of dry polymers,

(iii) vs. the total plasticizer content (glycerol plus moisture) in the equilibrated film.

If this is done, then both log modulus and % strain show remarkable linearity when they are plotted against the total plasticizer, while the other two curves bend in opposite directions. In the case of the ultimate tensile strength the curvatures are in the same directions, although the 'glycerol-only' curve in the equilibrated film is almost linear.

SERIES 2—DIGOL PLASTICIZED FILMS

Preparation and composition

The films in this series were prepared in the same manner as the glycerol-plasticized films and they were allowed to equilibrate under identical conditions of relative humidity and temperature. The plasticizer contents (diethylene glycol) were identical (on a weight for weight basis) with the levels of glycerol used in the *Series 1* films. The composition of the films is shown in *Table 3.*

As in the case of glycerol we find that at very high plasticizer contents (>100 parts Digol per 100 dry polymers) the equilibrium moisture contents tend towards a limiting value.

Tensile properties of equilibrated digol-plasticized film (Series II)

The tensile properties were again determined on an Instron tensile testing machine fitted with a CTM load cell which was calibrated at 2 kg full scale deflection. Parallel-sided specimens of gauge length 4 cm were tested at a constant strain rate of 0.5 mm s^{-1} under identical conditions of temperature and relative humidity as those under which the specimens were conditioned. The results given in *Table 4* were the means of at least 5 determinations and showed a standard deviation in the breaking stress of less than 20%, jaw breaks and obviously faulty results due to damage caused in the specimen preparation being excluded.

SERIES 3—EFFECT OF VARIATIONS IN STARCH/PV ALCOHOL RATIO

In this series we set an arbitary standard of plasticization (50 parts Digol per 100 parts of dry polymers) to investigate the effect upon the tensile behaviour of the resulting polymer film on altering the starch/PV alcohol ratio. Since, it is clearly of the greatest interest to establish to what extent the desirable properties are affected by increasing the amount of natural polymer, or conversely, whether an increase in the synthetic can be justified by results which more than compensate for increasing the petrochemical-based polymers fraction, in view of the fact that such resources are becoming scarcer and ever more

Table 4 Tensile properties of equilibrium cast film as a function of the plasticizer content for digol films

Parts Digol per 100 parts of dry polymers	10	25	50	100	150
% Digol in equilibrated film	8.4	22.0	26.2	31.4	36.9
% Total plasticizers (Digol plus moisture) in equilibrated film	16.0	35.5	47.6	68.4	75.8
Initial modulus (N m^{-2} x 10^6)	510	220	23.8	6.2	3.0
Breaking strain (%)	15.0	38.6	90	355	355
Breaking stress (ultimate tensile strength) (N m^{-2} x10^6)	8.5	3.9	3.0	2.0	1.35

Table 5 Tensile test results for starch/PV alcohol films plasticized with 50 parts digol per 100 parts dry polymers

Starch (parts per 100 total polymer)	30	40	50	60	68	80
Initial modulus (N m^{-2} x10^6)	15	33.5	23.8	32	44	32.5
Breaking strain (%)	355	151	90	226	223	114
Ultimate tensile strength (breaking stress) (N m^{-2} x10^6)	418	5.0	3.0	3.7	3.5	4.0

expensive. In short, Series 3 is concerned with optimizing the starch/PV alcohol ratio without actually considering the economics of materials selection except by implication.

The preparation of the case film was essentially similar to that described before. Six different mixtures were used in which the starch constituted 30, 40, 50, 60, 68 and 80 parts by weight of the 100 parts of total dry polymers, the balance being PV alcohol. It was observed that an increase in the starch fraction also produced an increasing tendency towards micelle formation, both during solubilization in water and, more especially, during the drying of the cast film in the oven at 80°C. We observed a distinct tendency for the starch to form the upper layer in the tray and produce a brittle layer which constituted a weakness after suitable equilibration (moisture regain) and which showed persistent brittleness when the tensile tests were carried out; this showed itself in fragmentation or delamination of the starch layer, leaving a highly elastic layer of plasticized PV alcohol which produced high strains before eventually breaking itself. The moisture content of the films was constant at around 22%.

The mechanical properties were determined under the same conditions as before; the results are shown in *Table 5*.

Plotting modulus, breaking stress and breaking strain vs. the percentage of the total dry polymers provided by the starch fraction revealed such a scatter of results that no unambiguous quantitative conclusions can be put forward. Nevertheless, the order of magnitude of the various parameters is the same in each case (modulus: about 10^7 N m^{-2}, breaking stress: $4 \pm 1 \times 10^6$ N m^{-2} and breaking strain: $250 \pm 150\%$).

DISCUSSION

The work reported above clearly indicates the need for assessing the results of the mechanical testing of starch/PV alcohol film plasticized with a humectant type plasticizer such as glycerol or diethylene glycol (Digol) on the basis of the complete plasticizer system (which includes the equilibrium moisture) rather than on the basis of the humectant plasticizer alone.

A comparison of the equilibrium moisture contents of Series 1 and 2 shows that the % moisture rises steadily with increasing plasticizer content in both cases. For any given plasticizer content the moisture content is similar in both series, but it is marginally higher in the Digol-plasticized series.

It can be seen that the raising of the level of plasticization causes a rapid decrease of the initial modulus and of the ultimate tensile strength, while the breaking strain increases correspondingly in both series. It is interesting to note that Digol-plasticized films have a significantly higher initial modulus than their glycerol-plasticized counterparts. The breaking strain is higher for glycerol-plasticized films than for the corresponding Digol films at low plasticizer contents (below 50 parts of humectant plasticizer per 100 parts of polymer) whilst the Digol series gives greater breaking strains than the glycerol series at higher plasticizer contents. The ultimate tensile strength of the glycerol-plasticized films is also higher than that of the corresponding Digol-plasticized films at low plasticizer levels.

In practice, it is possible to prepare a wide spectrum of film-forming materials ranging from stiff to rubbery—although the film becomes limp and clinging and is awkward to handle due to blocking at extreme levels of plasticization, which makes interleaving with other suitable films necessary. It is remarkable, however, that even at high levels of plasticization the film still possesses quite a high tensile strength, especially when we remember that the total polymer content represents perhaps only about 50% (and at the most extreme plasticization level as little as 22%) of the total mass, the balance being glycerol (or Digol) and water in roughly equal amounts.

It is more difficult to interpret the differences that exist at constant Digol plasticization with variable starch/PV alcohol ratios (series 3), but there are indications that more than one factor plays a role. Firstly, it is evident from the observations during solubilization, film formation, moisture regain and tensile testing that the compatibility of the two constituent polymers depends greatly on their relative concentrations, on the degree to which starch micelle formation occurs, on the domain size of the starch micelles and on the degree of separation into more or less discrete horizontal layers which occurs during film formation. All this greatly affects the behaviour and type of failure under tensile strain since we are essentially dealing with a laminate of discrete and possibly miltiple layers of two polymers. Good consistency of results and optimum compatibility appears to be obtained when the ratio of the two polymers is between 40:60 and 60:40 of starch/PV alcohol. When the starch fraction exceeds 60% the film tends to fragment on drying; indeed, the results for the 80% starch film were obtained on a number of fragments which were sufficiently large but which were brittle and weak until moisture regain had restored suppleness and flexibility. It is interesting to note that whilst the starch/PV alcohol ratio has a marked effect on the brittleness of the 'dry' film and also on the initial modulus of the equilibrated film its effect on the ultimate tensile strength is marginal. However, no thought of economising on petrochemical-based starting materials should lead one to imagine that starch levels much above 60% are realistic; a continuous production line (on an endless belt) for cast film of acceptable uniformity without embrittlement on drying prior to moisture regain would not be feasible—not, at least, at 50 parts (per hundred dry polymers) of plasticizer.

It is reasonable to regard the PV alcohol as the true film former and as the component which is actually being plasticized by the humectant plasticizer and by the water which it attracts. This provides the tough characteristics including rubberiness and high breaking strains at high plasticizer contents. The starch, however, would appear to act as a discontinuous filler which boosts the initial modulus and increases the tensile strength. The starch itself is not expected to be significantly toughened by the humectant plasticizer system.

If the starch micelles are small and well dispersed the behaviour (other than the stiffness) of the composite film will still essentially reflect the properties of PV alcohol—although the starch does contribute the additional and highly desirable properties of heat sealability and easy water solubility. Excessive amounts of starch seem to prevent the formation of a continuous phase of PV alcohol film. The intermediate stage may be pictured as a rather tenuous PV alcohol continuity with some accretions of starch in laminar deposits and in micellar aggregates. The latter will fail in a brittle manner and flake off during tensile testing leaving the basic continuous PV alcohol film structure to take the entire strain; which the PV alcohol film is quite capable of doing. This explains why the strain remains at least within the same order of magnitude when the starch content is between 40 and 80% and why the breaking strain is highest at 30% starch content. As regards the modulus, one would certainly expect an increase with increasing starch content and the trend in this direction is clearly seen. The ultimate tensile strengths would seem to be lowest in the middle range (50 ~ 60% starch fraction), but it must be borne in mind that the composite failure mechanism involves a mixture of toughness and brittleness which the plasticized PV alcohol and the starch contribute, in proportion to their volume fractions respectively. It clearly makes little sense to try and draw any fundamental inferences when two entirely different failure mechanisms contribute and interact during tests which are intended to present an overall picture of the tensile properties.

CONCLUSION

The formation of good continuous heatsealable and water soluble film using a ratio of between 40:60 and 60:40 of starch/PV alcohol suggests that it is unwise to attempt compositions outside of this range. It has been shown that both glycerol and Digol are suitable plasticizers for such films and may be incorporated in amounts varying from 10 to 150 parts per hundred dry polymers.

A series of experiments (series 3) was finally carried out in order to examine the effect of variations in the starch/PV alcohol ratio on film formation, on the mechanical properties and on the failure mechanism. Dry weight ratios ranging from 30:70 to 80:20 starch/PV alcohol at constant (50 parts per 100 dry polymers) Digol content were investigated. It is concluded that film formation and behavioural homogeneity (such as it is) is optimised in the middle range of the polymer component ratios (40:60 to 60:40) and that the initial modulus, the breaking strain and the breaking stress, while showing some trends with changing polymer ratios, remain of the same order of magnitude.

REFERENCE

1 Lenk, R. S. *Polymer* 1980, **21**, 371–373