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WORKING PARTY ON STRUCTURE AND PROPERTIES OF COMMERCIAL POLYMERS*

STRUCTURE AND PROPERTIES OF UNI- AND BIAXIALLY ORIENTED POLYPROPYLENE FILMS: PART 2— MECHANICAL AND OTHER END-USE PROPERTIES

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STRUCTURE AND PROPERTIES OF UNI- AND BIAXIALLY ORIENTED POLYPROPYLENE FILMS:
PART 2 — MECHANICAL AND OTHER END-USE PROPERTIES

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Abstract - Various properties of a series of uni- and biaxially oriented
polypropylene film have been determined in seven different laboratories
participating in a collaborative IUPAC Working Party programme. Small strain
(visco-) elastic properties, viz. Young's modulus, sonic modulus, dynamic
storage and loss compliances, were found to be mainly dependent on molecular
orientation in the non-crystalline phase and may be described, in a first
approximation, with the aid of a simple two-phase "lower bound" model.
The highly non-linear behaviour observed at larger strains, characterised by
yielding and/or ultimate rupture, was also found to be strongly dependent on
the initial state and degree of molecular orientation but it was, in general,
not possible to conclude definitely about respective contributions from
crystalline and non-crystalline phases. Characteristic differences in the
structure of uni- and biaxially oriented films, reported in Part 1, were also
revealed by technologically important properties such as impact resistance,
tear strength, thermal shrinkage, gas permeability, etc.

1.   INTRODUCTION

In Part 1 of the present report of the IUPAC Macromolecular Division's Working Party on
Structure and Properties of Commercial Polymers we have discussed results obtained in a
collaborative study on the structural characterisation of a series of uni- and biaxially
oriented polypropylene films (Ref. 1).   The films were prepared by Rhône Poulenc Films
Division by means of a continuous process using a commercial grade of isotactic
polypropylene, 'Napryl' 63200 (Naphtachimie), with a weight average molecular weight
of about 350,000 and a polydispersity $\overline{M}_w/\overline{M}_n = 4.8$.   Five uniaxially drawn films of
similar thickness ($160\mu m \pm 10\%$) and five biaxially drawn films of much smaller thickness
($21\mu m \pm 10\%$) were extensively investigated in six participating laboratories with the
aid of various experimental techniques in order to obtain quantitative data concerning
the following structural characteristics: volume and weight fractions of crystallinity,
molecular orientation in crystalline and non-crystalline phases (expressed in terms of
Hermans' orientation functions), long period spacings (determined by SAXS).   Agreement
between the results obtained in different laboratories was in general satisfactory.

Mechanical and other end-use properties determined on the same series of films will be
discussed in the following Part 2 which presents a survey of results obtained in
seven participating laboratories.   Each participant will be referred to by corresponding
numbers as follows:

1.   BASF, AG, Ludwigshafen am Rhein, F.R.G.

2.   ICI Plastics Division, Welwyn Garden City, U.K.

3.   SHELL Research B.V., Amsterdam, Netherlands

4.   SOLVAY et Cie, Brussels, Belgium

5.   T.N.O. Central Laboratory, Delft, Netherlands

6.   RHONE POULENC IND., Aubervilliers, France

7.   B.P. CHEMICALS, T.S.and A. (Plastics), Sully, U.K.

One of the main objectives of the programme was to investigate the relationship between
properties and structural order in oriented films, irrespective of the particular
processing conditions under which the films had been obtained.   For this reason, in our

discussion of properties we will avoid, as far as possible, any reference to the complex thermomechanical history to which the films had been submitted during manufacture and we will assume, a priori, that variations in the processing conditions liable to affect the properties of a film will necessarily induce a modification of its structure without changing the basic structure-properties relationships. The selected structural parameters, reported in Part 1, may prove to be insufficient, however, for a detailed description of structural modifications induced during processing and one should not expect, therefore, to be able generally to predict properties merely on the basis of a limited number of structural parameters. Nevertheless, it is worthwhile to investigate how a gradual change in those parameters affects a number of significant properties in order to conclude from the observed correlations, at least qualitatively, about the relative importance of the selected parameters and to find plausible explanations for any discrepancy or incompleteness.

An interesting question in the case of semi-crystalline polymers concerned the relative importance of molecular orientation effects in the crystalline and non-crystalline regions, respectively. The tabulated data reported in Part 1 show that in all films of the present programme molecular orientation in the non-crystalline phase is significantly lower than in the crystalline regions: in Fig. 1 we have plotted these data as f_{am} versus f_x for both uni- and biaxially drawn films. The degree of orientation is defined by the general expression:

$$f_p^{ij} = \frac{2}{3}(f_{ci} - f_{cj})_p \tag{1}$$

p refers to either the crystalline phase (p = x) or the non-crystalline phase (p = am); f_{ci} and f_{cj} are Hermans' orientation functions of the molecular c-axis with respect to the film coordinates i and j, respectively. As in Part 1, film coordinates will be indicated by capitals M (machine direction), T (transverse direction) and N (normal-to-the-film plane direction). In the case of uniaxial orientation with respect to the M-direction:

$$f_p^{MN} = f_p^{MT} = (f_{cM})_p$$
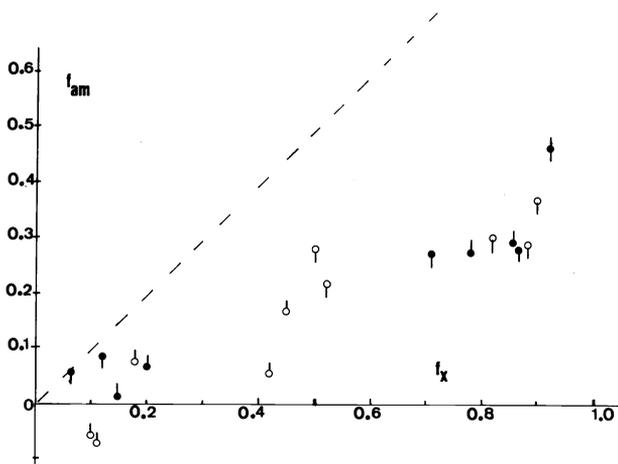
Fig. 1:   Non-crystalline versus crystalline orientation in uni- and biaxially drawn films:

        , f^{MN} ;   , f^{MT} (uniax)

        , f^{MN} ;   , f^{TN} (biax)

Although the data in Fig. 1 seem to indicate some degree of correlation between crystalline and non-crystalline orientation (in particular for the uniaxially drawn films) it is obvious that for a given degree of crystalline orientation f_{am}-values may still vary considerably in this series of films. As it will be shown in Part 3, variations in non-crystalline orientation are strongly dependent on the thermal history of the film. In the biaxially oriented films(obtained by sequential stretching) molecular orientation is always highest in the direction of second draw (T-direction), but the degree of imbalance is much higher in the non-crystalline than in the crystalline phase.   Films with nearly balanced crystalline orientation are, therefore, particularly useful for studies of angular variation of film properties since the importance of such variations may be

reasonably assumed to be related to the degree of unbalanced non-crystalline orientation in the film plane.

Many properties may depend on molecular orientation in both phases of the film and possibly be related to some average degree of orientation as proposed e.g. by Samuels (2): $f_{av} = v_x f_x + (1-v_x)f_{am}$, where v_x is the volume fraction of crystallinity (one example of such a property is the infrared dichroic ratio at 1256cm^{-1}, as shown in Part 1). However, for the series of films investigated here, the first term in the expression for f_{av} is much larger than the second one resulting in an approximately linear relationship between f_{av} and f_x (see Fig. 2), given by $f_{av} \simeq 0.8f_x$. Consequently, any observed empirical correlation between a property and f_{av} (or f_x) without reference to a specific quantitative theoretical model, cannot be invoked for concluding on the relative importance of molecular orientation effects in different phases. The same conclusion also applies to observed empirical correlations between properties and total birefringence: $\Delta n = v_x f_x \Delta^o_x + (1 - v_x)f_{am} \Delta^o_{am}$. Again the first term, representing the crystalline contribution, is by far the most important one in this series of films, leading to a strong correlation between Δn and f_x (or f_{av}). The approximate relationship between total birefringence and f_{av}: $\Delta n \simeq 0.034 f_{av}$ is depicted in Fig. 3.
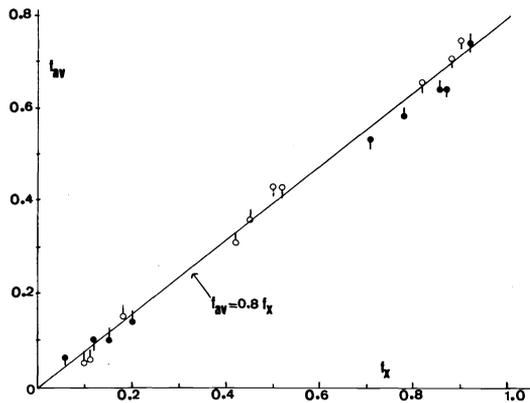
Fig. 2:   Average versus crystalline orientation.   Same meaning of symbols as in Fig. 1.

In the following chapters of this report we will encounter several examples of a strong correlation between a film property and observed total birefringence (or calculated f_{av}). It is obvious from the foregoing discussion that the mere existence of such correlations will only allow rather general, unspecific conclusions on the effect of molecular orientation. Additional information is in general, required for a more detailed description of orientation effects associated with structural order in a particular phase.
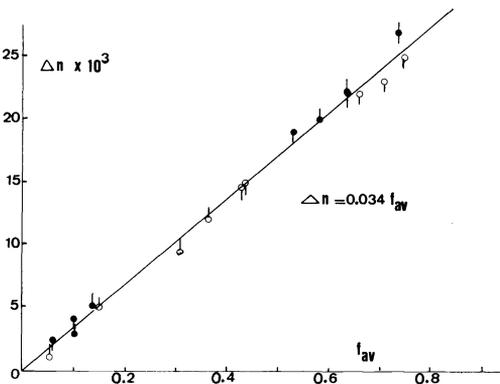
Fig. 3:   Total birefringence versus average molecular orientation.   Same meaning of symbols as in Figs 1 and 2.

2. SMALL STRAIN VISCOELASTIC PROPERTIES

At sufficiently small strains isotropic polymeric materials exhibit linear viscoelastic behaviour: tensile modulus e.g. will depend on temperature and strain rate (or frequency) but not on strain amplitude.   In oriented polymer films similar tensile behaviour at small strains is observed but modulus values will now also depend, in general, on the direction along which they are measured.   The tensile modulus of polypropylene, measured at room temperature, markedly depends on frequency (or time scale) as shown in Fig. 4 for the modulus of several uni- and biaxially drawn films.   The low frequency values were calculated from stress relaxation measurements by Participant 5, intermediate values represent the dynamic storage modulus at 110Hz, measured by Participant 4, with the aid of a "Rheovibron" instrument, whereas high frequency values were calculated from sonic velocity measurements at 10kHz by Participants 3 and 6 (pulse propagation meter manufactured by H.M. Morgan Co. Inc).   The effect of molecular orientation on the modulus at fixed frequency is evident from Fig. 4; frequency dependence, however, seems to be only slightly affected by the degree of molecular orientation (at least in the frequency range considered: $10^{-2} - 10^{4}$Hz).
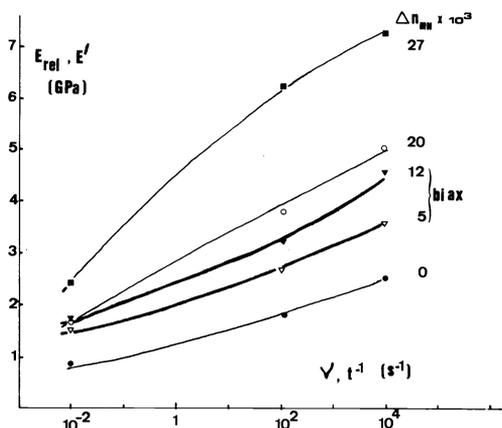
Fig. 4:   Frequency dependence at room temperature of tensile storage or relaxation modulus of uni- and biaxially drawn films.   Tensile stress parallel to M-direction.

Examples of the effect of temperature are given in Figs. 5 and 6 for uniaxially drawn films and in Fig. 7 for two biaxially oriented films.   Relaxation and dynamic storage moduli continuously decrease with increasing temperature; dynamic loss moduli pass through a maximum corresponding to the glass-rubber transition of isotactic polypropylene situated between 10° and 15°C at 110Hz and apparently independent of degree of molecular orientation.   In Fig. 7 dynamic mechanical data have been expressed in terms of storage and loss compliances defined as follows:

$$S' = E'/(E'^{2} + E''^{2}); \quad S'' = E''/(E'^{2} + E''^{2})$$

Since $E'' \ll E'$, the storage compliance S' is practically identical with the inverse of the storage modulus for these films; for the same reason the loss compliance S'' does not only depend on loss modulus but is also practically inversely propoertional to the square of the storage modulus.   As a consequence the temperature dependence of loss compliance is quite different from that of corresponding loss moduli (compare Figs 6 and 7). Anisotropy defined as the ratio between tensile moduli (or compliances) in the M- and T-directions, respectively, seems to be only slightly affected by temperature, at least in the case of biaxially oriented films.   A notable exception was observed for the relaxation and storage moduli measured in the T-direction of uniaxially drawn films: at relatively low temperatures these moduli decrease with increasing orientation (in the M-direction) but the opposite effect is observed at higher temperatures.   The temperature at which inversion takes place increases with frequency and seems to be related to the glass-rubber transition (Figs 5,6).   The resulting decrease in relative anisotropy with increasing temperature is not apparent from the loss modulus data for the same films. Similar observations on the dynamic mechanical behaviour of uniaxially oriented polypropylene films have been reported before (Refs 3,4) and seem to imply that basic deformation processes in an anisotropic film may gradually change as a result from increased segmental mobility in the non-crystalline regions above Tg, although it remains far from obvious why and how increased uniaxial orientation should lead to apparently
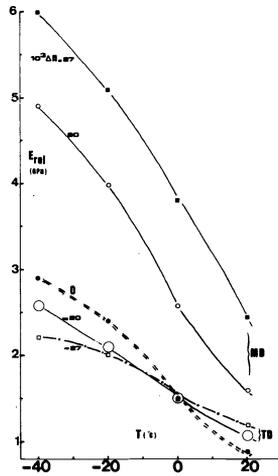
Fig. 5:   Relaxation modulus at 100 seconds and 1% elongation for isotropic and uniaxially drawn films, measured in M- and T-directions at different temperatures. (Participant 5).

enhanced stiffness in the T-direction.   The importance of the non-crystalline phase in determining mechanical behaviour of oriented semi-crystalline polymers is generally recognised and appears to be confirmed by the data presented here.
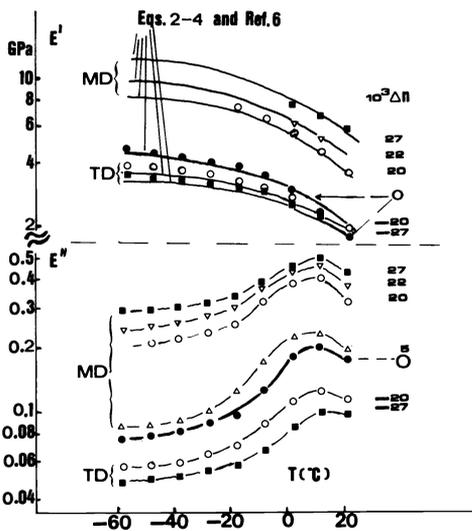
Fig.6
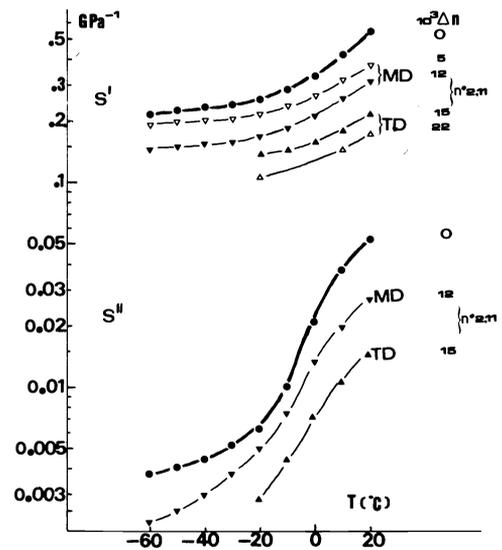
Fig.7

Fig.6:   Storage and loss moduli at 110Hz for uniaxially drawn films, measured by Participant 4.   Comparison with calculated values based on Eqs. (2 - 4) and Ref. 6.

Fig. 7:   Storage and loss compliances at 110Hz for biaxially drawn films as a function of temperature (Participant 4)

In the biaxially oriented film No. 2.11, e.g. both storage and loss compliances show pronounced anisotropic behaviour in the film plane (Fig. 7) which must be attributed to the relatively high degree of unbalanced non-crystalline orientation, the degree of imbalance in the crystalline phase being very small ($\sim$ 10% difference between f_x^{MN} and f_x^{TN}).

The predominant effect of non-crystalline orientation on viscoelastic behaviour at small strains may be described, in a first approximation, by means of a simple two-parameter model previously applied to sonic modulus measurements by Samuels (2) and to dynamic mechanical data by Seferis et al (5,6).   This model which may be deduced, under certain

simplifying conditions (Refs. 5 - 7), from a more general six-parameter model, leads to the following expressions for the compliances in the M- and T-directions of uniaxially oriented films:

$$S_{MD} = S^o_x v_x (1 - f^{MN}_x) + S^o_{am}(1 - v_x)(1 - f^{MN}_{am}) \qquad (2)$$

$$S_{TD} = S^o_x v_x (1 + \tfrac{1}{2}f^{MN}_x) + S^o_{am}(1 - v_x)(1 + \tfrac{1}{2}f^{MN}_{am}) \qquad (3)$$

S^o_x and S^o_{am} represent the intrinsic compliances of the randomly oriented (isotropic) crystalline and non-crystalline phases, respectively. For an unoriented film, Eqs. (2) and (3) reduce to:

$$S_{MD} = S_{TD} = S^o_x v_x + S^o_{am}(1 - v_x) \qquad (4)$$

Eq. (4) corresponds to the compliance of an isotropic two-phase material, calculated on the basis of the classical Reuss-averaging procedure (Ref. 8) assuming uniform stress distribution. With the aid of this model Samuels (2) has determined intrinsic sonic compliances for isotactic polypropylene films at room temperature and 10kHz frequency. Intrinsic dynamic storage and loss compliances in a broad range of temperatures, on the other hand, have been deduced from Rheovibron data by Seferis and co-workers for frequencies of 11Hz (Ref. 5) and 110Hz (Ref. 6) respectively. The tabulated intrinsic storage compliances in Ref. 6 (which between -60° and 20^oC vary from 0.152 to 0.176 GPa^{-1} for the crystalline phase and from 0.350 to 0.851 GPa^{-1} for the non-crystalline phase) have been substituted into Eqs. (2 - 4) in order to calculate S_{MD} and S_{TD} for the isotropic film (1.01) and three uniaxially drawn films (1.04 to 1.06) as a function of temperature. Fig. 6 shows fair agreement between calculated and measured values of the storage moduli but a similar comparison in the case of the loss moduli (not shown in Fig. 6) is less satisfactory. One of the reasons for disagreement may be associated with the various corrections required for extracting accurate and reproducible modulus values from the raw Rheovibron data (Refs. 9, 10); the importance of several proposed correction procedures for the treatment of data obtained on the present polypropylene films will be the object of further investigations.

Participants 3 and 6 measured sonic moduli at 10kHz and the results obtained on both uni- and biaxially drawn films were found to be in good agreement in most cases. Moreover, the 100 seconds relaxation moduli at -40^oC, determined by Participant 5, as well as the 110Hz storage moduli at 0^oC, measured by Participant 4, appeared to be very close in magnitude, in general, to the 10kHz sonic moduli at room temperature. All results obtained by these different methods in the case of uniaxially drawn films have been plotted in Fig. 8 versus the modulus values calculated from Eqs (2) and (3) by substitution of the measured orientation functions, tabulated in Ref. 1, and by adopting the values for intrinsic sonic compliances determined by Samuels (2): $S^o_x = 0.17$ and $S^o_{am} = 0.63$ GPa^{-1} (according to the tabulated data in Ref. 6 these values should represent intrinsic 110Hz storage compliances at a temperature slightly higher than 0^oC which is in fair agreement with the experimental data of Participant 4).
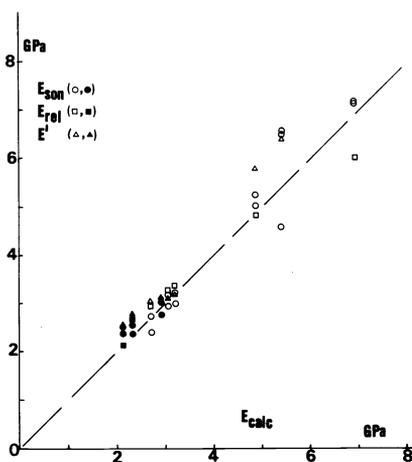
Fig. 8: Experimental relaxation, storage and sonic moduli of uniaxially drawn films versus calculated moduli, deduced from a two-parameter model. Data from Participants 3,4,5 and 6: open symbols: MD; closed symbols: TD.

The rather good agreement between calculated and measured moduli apparent from Fig. 8 is
still valid, approximately, at much higher degrees of uniaxial orientation as shown in Fig.9
in which we have included sonic modulus results by Participant 6 on uniaxially oriented
films obtained by drawing at different temperatures in a specially designed laboratory
tensile tester (see Ref. 1).   At the highest degrees of orientation attained, moduli
calculated from Eq. (2) are in general too high as one should expect for a two-parameter
model assuming infinite modulus (or zero compliance) for perfectly oriented phases (i.e.
for $f_x = f_{am} = 1$).   If this unrealistic assumption is abandoned a three-parameter model
will emerge (Ref. 7) which predicts that the moduli of highly oriented polypropylene films
will not only depend on the second moment of the orientation distribution functions (f_x, f_{am})
but also on the fourth moment (g_x, g_{am}).   Various evidence seems to indicate that a simple
relationship between the second and fourth moments generally holds for uniaxially oriented
polypropylene films and in that case tensile moduli of ultra-oriented films or fibers may
be predicted with good approximation from Eq. (2) after addition of a third term, inversely
proportional to the tensile modulus of perfectly oriented polypropylene.   The estimated
value of the latter, which should be identical with the tensile modulus along the c-direction
of the isotactic polypropylene crystal, is in the order of 40 GPa, in good agreement with
other theoretical and experimental estimates (Ref. 11).
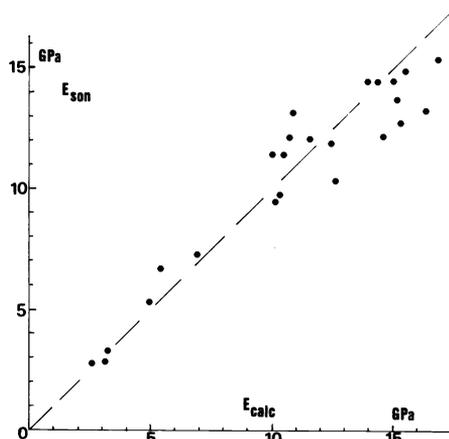
Fig. 9:   Sonic modulus of uniaxially drawn films (drawing temp. between 100° and 160°C)
versus calculated modulus based on two-parameter model (Eq. 2).   Data from Participant 6.

Equation (2) also allows a reasonable estimation of tensile moduli in both M- and T-
directions of biaxially oriented films by substitution of the appropriate orientation
functions, tabulated in Ref. 1, either: f_x^{MN} and f_{am}^{MN}, or f_x^{TN} and f_{am}^{TN} (Table 1, see next page)

The upper half of Table 1 refers to measurements in the M-direction, the lower half refers
to the T-direction. S_x and S_{am} represent the calculated crystalline and non-crystalline
contributions, respectively, to the tensile compliance in GPa^{-1};   it is obvious that the
latter are always significantly larger than the former illustrating the predominant effect
of non-crystalline orientation on the calculated modulus E_{calc}. E_{son} (3) and E_{son} (6) are
the sonic moduli at room temperature, measured by Participants 3 and 6 respectively,
E_{rel} (5) is the 100s relaxation modulus at -40°C from the data of Participant 5 and E' (4)
is the 110Hz storage modulus at 0°C determined by Participant 4.   All modulus values are
expressed in GPa - units.   The agreement between the various experimental modulus values
and the calculated ones is, in general, very satisfactory but it should be kept in mind
that the use of Eq. (2) in conjunction with the orientation functions defined by Eq. (1)
in order to calculate tensile compliances in the plane of a biaxially oriented film has not
yet found a rigorous theoretical justification (comparable to the treatment of birefringence
exposed in Ref. 1) and should be considered, for the moment, as purely empirical.

3. YIELD AND RUPTURE IN TENSION

At larger tensile strains the mechanical behaviour at room temperature becomes strongly
non-linear because of a gradual change in. film structure leading to phenomena like yielding
and, ultimately, failure.   Characteristic features of the stress-strain curve such as
yield stress and strain, rupture stress and elongation at break are in general strain rate
dependent.   Participant 1 investigated the strain rate dependence of yielding and rupture

TABLE 1:   Orientation and tensile moduli in biaxially drawn films

Film No.	v_x	f_x	f_{am}	S_x	S_{am}	E_{calc}	E_{son} [3]	E_{son} [6]	E_{rel} [5]	E' [4]
MD										
2.07	0.71	0.11	-0.075	0.107	0.196	3.3	3.7	3.3	3.4	2.3
2.08	0.71	0.10	-0.06	0.109	0.194	3.3	3.0	3.2	3.6	3.2
2.09	0.69	0.18	0.075	0.096	0.181	3.6	3.1	3.7	3.8	3.7
2.10	0.70	0.42	0.055	0.069	0.178	4.0	3.9	3.8	4.3	3.8
2.11	0.70	0.45	0.17	0.065	0.158	4.5	4.6	4.6	4.4	4.7
TD										
2.07	0.71	0.88	0.29	0.0145	0.130	6.9	6.5	6.7	5.8	6.1
2.08	0.71	0.90	0.37	0.012	0.115	7.8	6.1	6.6	6.2	6.7
2.09	0.69	0.82	0.30	0.021	0.137	6.3	6.6	5.6	6.5	-
2.10	0.70	0.52	0.22	0.057	0.147	4.9	4.8	5.4	5.5	6.1
2.11	0.70	0.50	0.28	0.060	0.136	5.1	5.2	5.8	5.8	6.3

in a range covering four decades; Fig. 10 shows the results concerning yielding in uniaxially drawn films.   With increasing orientation the transition from ductile to non-ductile behaviour (rupture without yielding) is displaced to lower strain rates; at a given degree of orientation yield stress slightly increases with strain rate but yield strain (measured in the M-direction) rapidly decreases with increasing rate of elongation.   In the T-direction both yield stress and strain are rather insensitive to strain rate and to degree of orientation.
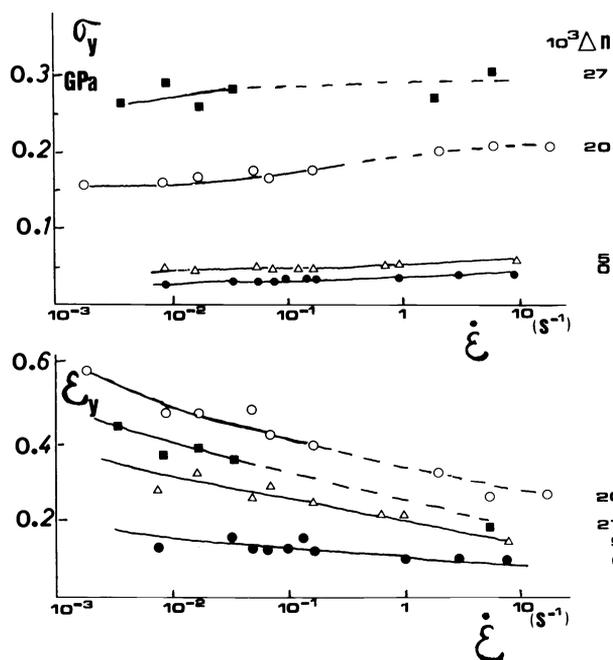
Fig. 10:   Yield stress and strain of uniaxially drawn films as a function of elongation rate;   discontinuous lines correspond to rupture without yielding.

Yield stress measured in the M-direction sharply increases with increasing degree of orientation in crystalline and non-crystalline phases for this series of films. As already explained in the introduction, the observed correlation between calculated orientation functions prevents any conclusion to be drawn on the relative importance of orientation effects in crystalline and non-crystalline regions, respectively, as it is quite evident from Fig. 11. The effect of molecular orientation on yield strain appears to be more complex: the latter first increases with initial orientation but then passes through a maximum for an estimated value of average orientation f_{av} equal to about 0.5 (see Fig. 12). If elongation rate is higher than $0.1s^{-1}$, the ductile-brittle transition occurs for f_{av}-values smaller than 0.5; the strain values plotted in Fig. 12 for higher degrees of orientation do no longer refer to yielding but to rupture.
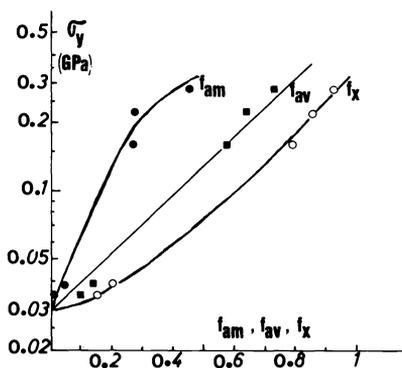
Fig.11
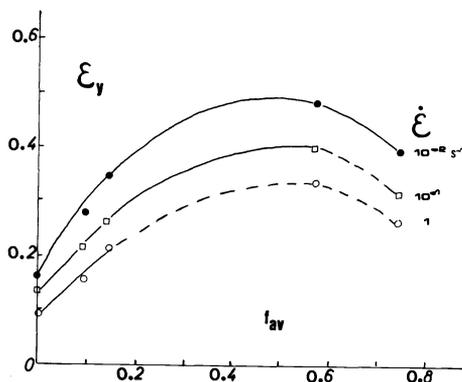
Fig.12

Fig. 11: Yield stress versus molecular orientation in uniaxially drawn films; elongation rate = $10^{-2}s^{-1}$ (Participant 1).

Fig. 12: Yield strain versus molecular orientation in uniaxially drawn films. (Participant 1).

The increase of both yield stress and yield strain illustrates the remarkable effect of initial molecular orientation on the onset of yielding in the M-direction and seems to indicate that the structural re-organisation associated with yielding becomes increasingly difficult to achieve in an oriented film and, eventually, impossible except at extremely low strain rates. In biaxially oriented films yielding is, in general, non-existent unless the degree of orientation in the direction of the applied tensile stress is very low ($f_{av} < 0.1$). It follows that only biaxial orientation is effective in complete suppression of yielding (even at low strain rates). On the contrary, uniaxially oriented polypropylene films will remain sensitive to yielding (at all strain rates) for relatively small stress and strain values in the transverse direction. The effect of strain rate on rupture is similar to its effect on yielding: rupture stress is rather insensitive to strain rate in both uni- and biaxially oriented films, but rupture strain decreases with increasing rate of elongation in particular at low degrees of uniaxial orientation (Figs 13 and 14). In the latter case a ductile-brittle transition for a strain rate of about $0.1s^{-1}$ is quite apparent but at higher degrees of orientation the transition seems to be absent or displaced to much lower strain rates ($\ll 10^{-3}s^{-1}$).

In biaxially oriented films rupture strain is practically independent of strain rate (except at very low degrees of orientation) and its value always remains higher than in uniaxially oriented films, the more so the higher strain rate (Figs 14 and 15). Rupture strain as a function of initial degree of orientation passes through a maximum (except at low strain rates) for $\Delta n \sim 0.005$ corresponding to an average orientation f_{av} of about 0.15. It follows that yield strain may increase and rupture strain simultaneously decrease with increasing degree of uniaxial orientation as long as f_{av} remains smaller than 0.5.

Rupture stress or tenacity (= rupture force/initial cross-section) is a rapidly increasing function of initial degree of orientation and correlates well with birefringence in both uni- and biaxially drawn films (Fig. 16). Intrinsic tensile strength, however, is better characterised by the "true rupture stress" equal to the tensile force divided by the cross-section at break:
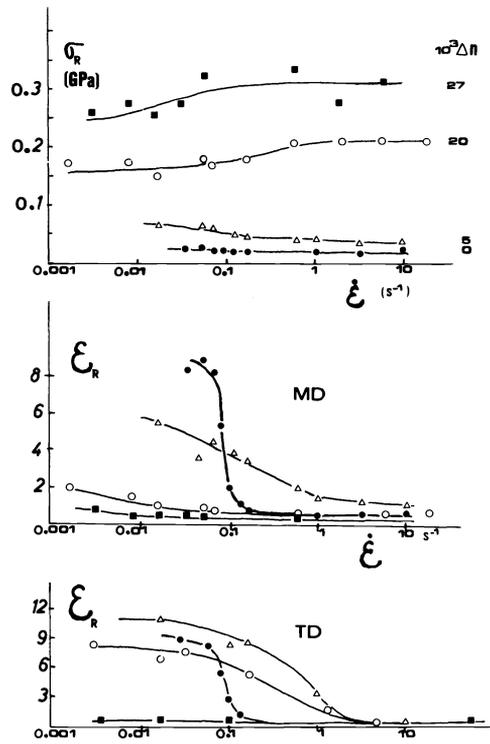
Fig. 13:   Rupture stress and strain of uniaxially drawn films as a function of elongation rate (Participant 1).
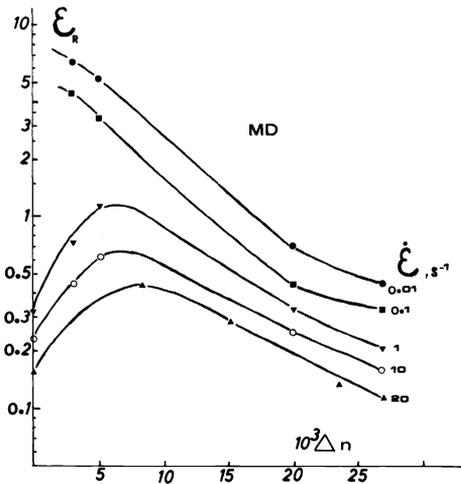
Fig.14
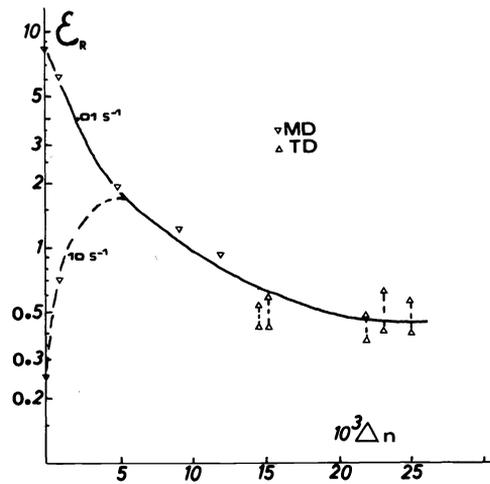
Fig.15

Fig. 14:   Rupture strain of uniaxially drawn films as a function of birefringence for different strain rates.   (Participant 1).

Fig. 15:   Rupture strain of biaxially oriented films as a function of birefringence in both M- and T-directions (Participant 1).

Intrinsic Tensile Strength $= F_R/A_R = F_R(1 + \varepsilon_R)/A_0 = \sigma_R(1 + \varepsilon_R)$

if F_R is the tensile force at break, A_R final and A_0 initial cross-sectional area; σ_R and ε_R are rupture stress and strain, respectively.
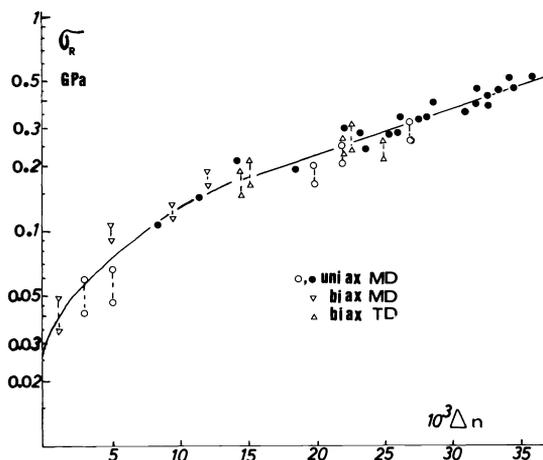
Fig. 16:   Rupture stress of uni- and biaxially oriented films as a function of birefringence (elongation rate from 10^{-3} to $20s^{-1}$).   Participants 1, 4 and 6.

True rupture stress as a function of birefringence for two different strain rates has been plotted for uniaxially drawn films in Fig. 17 and for biaxially oriented films in Fig. 18. At the lowest rate of elongation $(0.01s^{-1})$ initial degree of orientation has practically no influence on true rupture stress along the M-direction of uniaxially drawn films: tensile deformation at room temperature is apparently slow enough to allow structural re-organisation leading to a final state of uniaxial orientation independent of initial structural order, as first pointed out by Samuels (2).   This is still true, for low degrees of uniaxial orientation ($\Delta n \leqslant 0.005$),   if the applied tensile stress is parallel to the T-direction. At higher degrees of orientation, however, structural re-organisation   during the tensile test appears insufficient to compensate for the adverse effect of initial perpendicular orientation, and true rupture stress in the T-direction decreases until a final value, one order of magnitude lower than along the M-direction.   At high strain rate $(10s^{-1})$ the degree of structural order at failure will still strongly depend on the initial state of orientation, and hence true rupture stress in the M-direction rapidly increases as a function of initial uniaxial orientation.   True rupture stress in the T-direction, measured at high strain rate, remains at its low, isotropic value irrespective of the degree of uniaxial orientation.   As a final result, true rupture stress of highly oriented uniaxially drawn films becomes strongly anisotropic and independent of applied strain rate. The same conclusion applies to tenacity (Fig. 16) whose values differ only slightly from those of true rupture stress at high degrees of uniaxial orientation ($\varepsilon_R \ll 1$).

Since in biaxially oriented films both rupture stress and strain are rather insensitive to strain rate at room temperature, true rupture stress is also practically independent of strain rate except at very low degrees of orientation (Fig. 18).   The degree of orientation is also rather unimportant for true rupture stress (even at high strain rates) because the decrease in rupture strain nearly compensates for the increase in tenacity.   In film No. 2.11, characterised by a nearly balanced crystalline biaxial orientation, tenacity and rupture strain are still strongly direction dependent (ε_R is about twice as high in the M-direction compared to the T-direction) indicating that non-crystalline orientation exerts a significant influence on ultimate properties of oriented polypropylene films.

4. TENSILE RESILIENCE AND IMPACT RESISTANCE

Unidirectional tensile impact measurements by means of pendulum methods were performed by Participants 4 and 6 under similar but not identical conditions (in particular with respect to sample geometry).   Since the energy absorption measured in such tests essentially corresponds to the total amount of stored elastic energy at the moment of break, the results obtained should be proportional to the volume of deformed material (Ref. 12) and, hence, depend on the exact shape and dimensions of the specimen.   Usually the test results are expressed in terms of energy absorption per unit of cross-section and are, therefore, only comparable at identical sample geometry.   Results of Participants 4 and 6 referring to
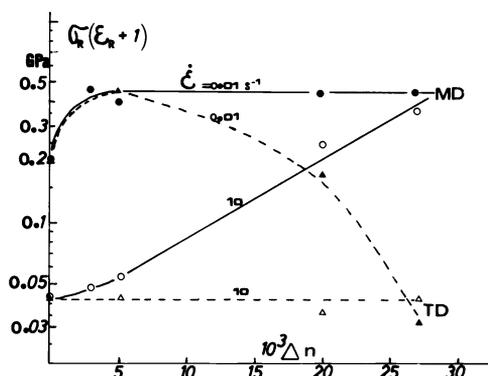
Fig.17
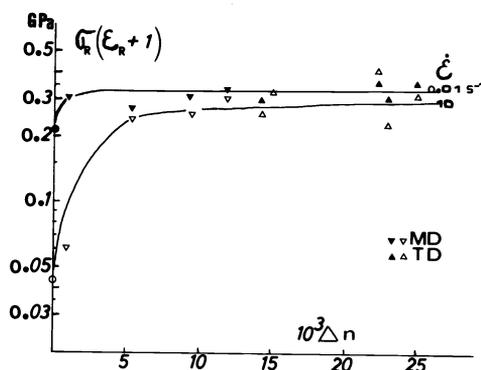
Fig.18

Fig. 17:   True rupture stress at two different elongation rates as a function of birefringence for uniaxially drawn films.

Fig. 18:   Same as Fig. 17 for biaxially oriented films.

uniaxially drawn films are shown in Fig. 19 and compared with tensile energy at break data calculated by Participant 1 by means of integration of recorded stress-strain curves at a strain rate of 10s^{-1} which is much lower than the strain rate experienced by the specimens in a tensile impact test (impact velocity ~ 3m/s).   In spite of the differences in specimen geometry and strain rate, reasonable agreement is observed between the results of the three laboratories: tensile resilience in the M-direction increases rapidly with uniaxial orientation but decreases in the T-direction.   In the film with highest degree of orientation tensile impact strength in the M-direction is about fifty times as high as in the T-direction.
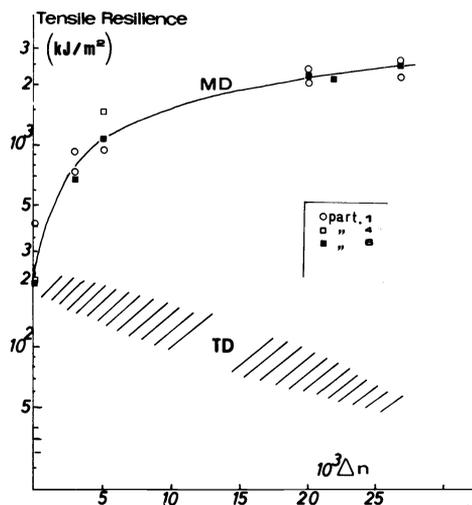
Fig.19
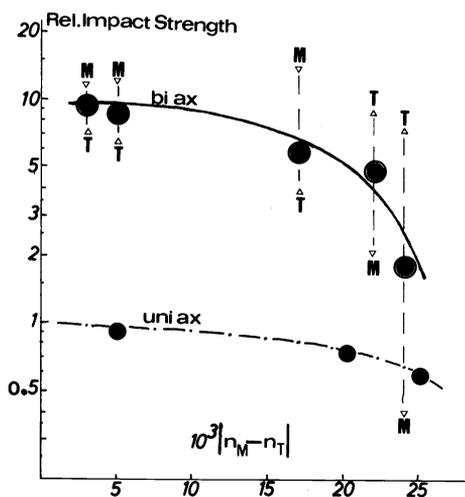
Fig.20

Fig. 19:   Tensile resilience of uniaxially drawn films as a function of birefringence; shaded area indicates experimental scatter of data measured in the T-direction. Participants 1, 4 and 6.

Fig. 20:   Multiaxial impact strength (relative values) of uni- and biaxially drawn films as a function of birefringence in the film plane   (Participant 7).   Triangles represent (relative) tensile resilience data, measured on biaxially drawn films in M- and T-directions (Participants 1, 4 and 6).

From a practical point of view one is often interested to know how a film withstands impact loading perpendicular to the film plane (in contrast with tensile impact along one direction in the film plane as described above). Such a loading will cause multiaxial straining in the plane around the point of impact and lead to fracture if the impact energy is sufficiently high. A pendulum instrument designed for measuring energy absorption under these conditions has been described by Williams and Ford (13) and was used by Participant 7 to investigate the present polypropylene films. Impact energy measured by means of this instrument is proportional, in a first approximation, to film thickness according to Ref. 13. Relative film impact strength per unit thickness (calculated with respect to the unoriented, isotropic film) has been plotted in Fig. 20 for both uni- and biaxially oriented films as a function of birefringence in the film plane ($n_M - n_T$ or $n_T - n_M$). It appears that in uniaxially drawn films, multiaxial impact strength slowly decreases with increasing orientation, because the reinforcing effect in the M-direction becomes insufficient to compensate for the weakening in other directions.

In the series of biaxially drawn films, multiaxial impact strength is always higher than in unoriented film, in particular for low degrees of imbalance (small Δn_{TM}) but impact strength decreases rapidly with increasing degree of imbalance (large Δn_{TM}). Similar observations have been reported for the impact strength of biaxially oriented polyethylene films (Ref. 14). The anisotropy in the film plane is clearly reflected by the tensile resilience values determined along M- and T-directions by Participants 1, 4 and 6. Average relative tensile resilience (relative with respect to unoriented film) data from the latter three laboratories, indicated by triangles in Fig. 20, appear to be either higher or lower than relative multiaxial impact strength for the same film, depending on the direction along which they are measured. It is noteworthy that in three films tensile resilience is highest in the direction of lower birefringence (M-direction), indicating that tensile resilience and rupture strain (measured at high strain rate) must be strongly correlated in biaxially oriented films as confirmed by the data in Fig. 21.
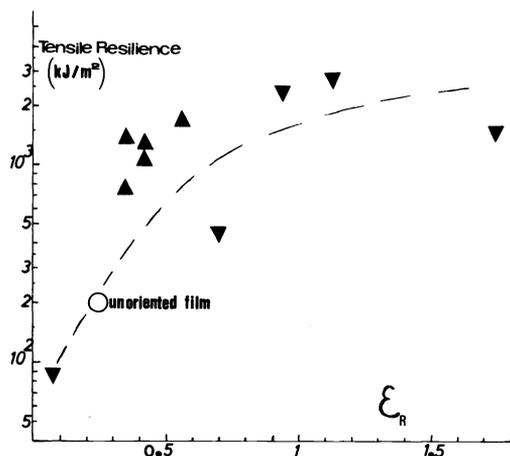
Fig. 21:   Tensile resilience in M- and T-directions of biaxially oriented films versus rupture strain (measured at $10s^{-1}$).

Such a simple correlation is not valid for uniaxially drawn films. The favourable effect of biaxial (opposed to uniaxial) orientation on multiaxial impact strength is obvious as well as its dependence on the degree of unbalanced orientation. In balanced (or nearly balanced) biaxially oriented films impact strength may still depend on absolute degree of molecular orientation in crystalline and/or non-crystalline phases. The data presented here do not yield information on this particular point but it is probable that improvement of impact strength will become relatively modest beyond a certain degree of orientation in analogy with the behaviour of true tensile strength shown in Fig. 18.

    5. TEAR STRENGTH

Initial tear resistance was measured by Participant 2 by means of tensile tests using the die "C" type of specimen as described in ASTM-D 1004 (or BS 2782, Method 308 A). The particular geometry of the specimen (see Fig. 22) produced a stress concentration at the tip of a $90°$ notch which initiates tearing for a given amount of specimen elongation. Only the maximum tensile load required for complete specimen rupture is noted irrespective of the mode, direction and rate of tear propagation and defined as maximum tear initiation force or initial tear resistance (I.T.R.). Tear propagation resistance (T.P.R.) was investigated by

Participant 3 according to ASTM-D 1 938 using the single tear "trousers" type of specimen (Fig. 22). In this test the tensile force required to propagate a tear (previously cut with a sharp razor blade) in the direction of the applied stress is measured at constant grip separation speed.

Both I.T.R. and T.P.R. are dependent upon specimen thickness but no simple correlation with thickness has been reported and comparison of data from specimens of dissimilar thickness is not recommended in general. For this reason absolute values for unoriented, uniaxially oriented and biaxially oriented films, respectively, should only be compared with circumspection. Nevertheless several conclusions concerning the effect of uni- and biaxial orientation on the tear strength of polypropylene films may be drawn from the experimental results obtained.

In the I.T.R. test the unoriented film exhibits ductility at $+23^{\circ}$C but it is brittle at -40°C. If uniaxially oriented specimens are submitted to traction in the M-direction their tensile behaviour becomes ductile at -40°C. I.T.R. values for MD-stressed uniaxially drawn films increase with increasing molecular orientation as shown in Fig. 22, where I.T.R. measured at $+23^{\circ}$ and -40°C is plotted as a function of Δn_{MN}. Although tearing starts perpendicular to MD, propagation occurs in the direction parallel to MD. In the T.P.R. test on the same uniaxially drawn films it was also found impossible to make the tear propagate in a direction perpendicular to MD. If the long axis of the I.T.R. specimens is at an angle of 90° or 45° with respect to MD, ductility progressively disappears with increasing molecular orientation, even at 23°C, and I.T.R-values in this case are practically independent of molecular orientation. Tear propagation again occurs along MD and T.P.R-values decrease rapidly with increasing molecular orientation.

Summarising the above results it may be concluded that <u>uniaxial orientation</u> increases I.T.R. only if tearing is initiated perpendicular to MD. Tear propagation always occurs along MD and will be easier the higher the degree of molecular orientation; T.P.R-values are at least an order of magnitude lower than I.T.R.
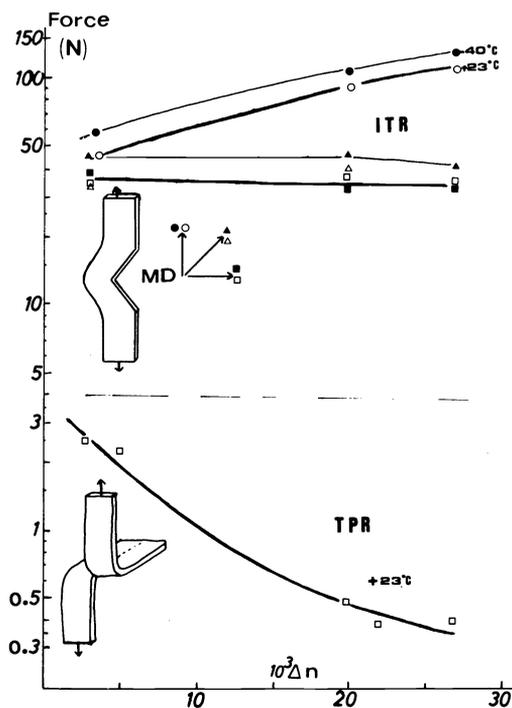
Fig. 22:   Initial Tear Resistance and Tear Propagation Resistance of uniaxially drawn films versus birefringence along the direction of tear propagation (MD). Participants 2 and 3.

Failure in biaxially drawn films submitted to the I.T.R. test was, in general, ductile at both $+23^{\circ}$C and -40°C, irrespective of tear initiation and propagation directions. In the nearly balanced film 2.11, I.T.R-values measured in three directions (MD, TD and at 45°) were practically identical and equal to about 4 N at 23°C and about 7.5 N at -40°C. These

values may be compared with I.T.R. $\sim$ 35 N (23°C) and $\sim$ 50 N (-40°C) for about 8 times
thicker unoriented films (estimated by extrapolation of the curves in Fig. 22). Although
it is impossible to separate the effects of thickness reduction and biaxial orientation it
is noteworthy that the relative decrease in I.T.R. is much smaller than the reduction in
T.P.R. The T.P.R-value for film 2.11 measured in two directions(MD and TD), is only
0.035 N at 23°C whereas the extrapolated value for an 8 times thicker unoriented film would
be at least equal to 3 N, i.e. about two orders of magnitude greater (see Fig. 22). It
seems reasonable to attribute the observed differences to the greater molecular orientation
sensitivity of tear propagation compared with tear initiation. This difference in
sensitivity which is obvious for uniaxially drawn films is also evident from the results
for biaxially drawn films (Fig. 23) in particular for relatively low degrees of orientation
in the direction of tear propagation. Beyond a minimum degree of orientation (corresponding
to $\Delta n \sim 0.005$ or $f_{av} \sim 0.15$) tear propagation resistance decreases much slower with further
increase of molecular orientation, along the tear direction (either MD or TD).
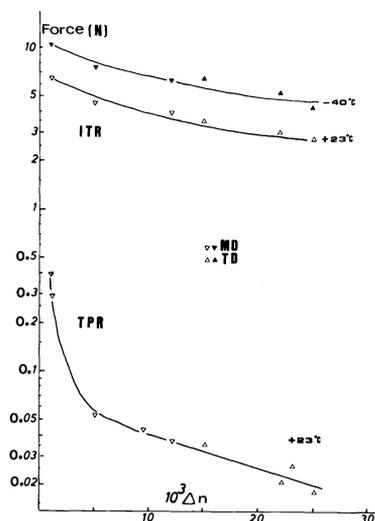
Fig. 23: Initial Tear Resistance and Tear Propagation Resistance of biaxially oriented
films versus birefringence along the direction of tear propagation (either MD or TD).
Participants 2 and 3.

Initial Tear Resistance, measured by stressing in either MD or TD, also seems to depend
mainly on the degree of orientation with respect to the direction of tear propagation. The
latter direction coincides with the tear initiation direction. The situation is different
when tearing is initiated at an angle of 45°: in this case measured I.T.R-values were
found to be closer to the higher values (corresponding to tear initiation in the direction
of minimum orientation) than to the lower values obtained with tear initiation along the
direction of maximum orientation. Tear propagation, however, always occurred along the
direction of maximum orientation (TD) in this case.

Generalising these observations one might conclude that tear initiation resistance in an
unbalanced biaxially oriented film is approximately the same in all directions but one:
the direction of maximum molecular orientation, associated with lower I.T.R. (this contrasts
with the tear initiation behaviour of uniaxially oriented films which is also characterised
by one singular direction, corresponding however to a higher I.T.R. in this case). Both
I.T.R. and T.P.R. decrease with increasing orientation with respect to the direction of tear
propagation, either MD or TD depending on the direction in which tearing is initiated.
Tear propagation is more sensitive to molecular orientation than tear initiation. Finally,
the results obtained on the nearly balanced film 2.11, in particular, lead to the conclusion
that tear strength may be correlated, in a first approximation, with average orientation f_{av}
although it is not possible to define exactly the respective contributions of the
crystalline and non-crystalline phases.

6. THERMAL SHRINKAGE, DIMENSIONAL INSTABILITY AND SHRINKAGE STRESS

An important part of the internal tensile strains induced during uni- or biaxial stretching
may be recovered by thermal annealing in the absence of external constraints. Dissipation
of stored potential energy under these conditions will be accompanied by dimensional changes
(shrinkage) which are very rapid above 100°C in the case of oriented polypropylene films.

(Refs 15 - 17).   Shrinkage measurements at temperatures between $110°$ and $160°C$, carried out
by Participant 1 by means of a glycerol bath, confirmed rapid attainment of equilibrium
(within some tens of seconds in most cases) for both uni- and biaxially oriented films.
Participants 2 and 4 performed shrinkage measurements by means of oven heating; in the
latter case equilibrium attainment may be slower because of reduced heat transfer which
might explain some discrepancies between results obtained by Participants 1 and 4, in
particular for uniaxially drawn films.   For the very thin, biaxially drawn films, the
results of all participants were in fair agreement, independent of the mode of heating.

If total tensile strain λ_o induced by uniaxial elongation were recoverable, shrinkage ratio
SR defined as the fractional decrease in length would attain a maximum value:

$$(SR)_{max} = \left[(l_i - l_f)/l_i\right]_{max} = (\lambda_o - 1)/\lambda_o,$$

if l_i is the length before and l_f the length after shrinkage.

Results obtained with uniaxially drawn films (Fig. 24) show a rapid increase of shrinkage
with annealing temperature, but even at $160°C$ measured shrinkage ratios remain substantially
lower than the maximum values corresponding to completely recoverable strain.   The effect
of temperature is clearly demonstrated by the curves in Fig. 25 representing relative
shrinkage ratios: $(l_i - l_f)/(l_i - l_o) = (\lambda_o - \lambda_f)/(\lambda_o - 1)$, i.e. the absolute amount of
length contraction during shrinkage $(l_i - l_f)$ divided by the length increase $(l_i - l_o)$ due
to stretching (Refs 15, 18).
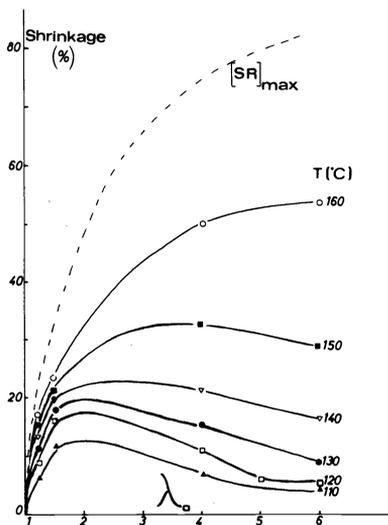
Fig.24
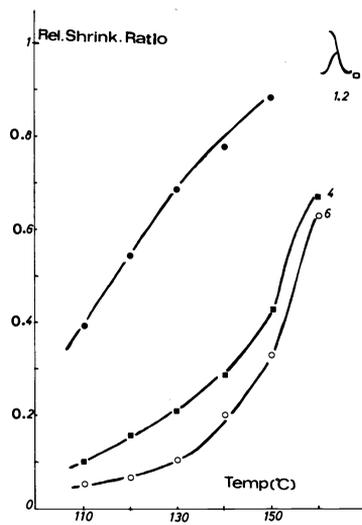
Fig.25

Fig. 24: Shrinkage ratio at different temperatures for uniaxially drawn films versus
nominal draw ratio. Participants 1, 2 and 4.

Fig. 25: Relative shrinkage ratio of uniaxially drawn films as a function of annealing
temperature.

Relative shrinkage ratio approaches its maximum value (= 1) only for the film of lowest
draw ratio (λ_o = 1.2) but the shape of the curves for higher oriented films ($\lambda_o \geqslant 4$)
suggests that shrinkage may proceed still further at higher annealing temperatures and that
a major part of the total induced tensile strain will be eventually recovered at the melting
temperature in agreement with previous observations reported in the literature (Refs 15 - 17).

Dimensional instability at a given temperature, a property of practical interest, is
completely determined by the absolute shrinkage ratio; it is noteworthy that the latter, in
a rather broad range of temperatures, passes through a maximum if plotted as a function of
initial, nominal draw ratio (Fig. 24).   Similar plots are obtained if any measure for the
degree of molecular orientation (Δn, f_x, f_{am}, f_{av}) is substituted for draw ratio λ_o.
Maximum shrinkage corresponds to draw ratios associated with non-uniform elongation of
polypropylene (Ref. 19) characterised by local cross-section reduction ("Necking").   Beyond
the necking region, i.e. for λ_o-values larger than 4 in this series of films, dimensional
instability decreases with increasing degree of orientation up to temperatures of at least
$150°C$.   The enhanced stability may be attributed to the formation of an oriented

microfibrillar structure in substitution of the initial spherulitic structure, characteristic of isotropic or weakly oriented polypropylene films. At still higher temperatures a major part of the oriented crystalline phase will melt out rapidly and shrinkage ratios will be completely determined by the amount of recoverable strain in the oriented non-crystalline phase which behaves as a rubber elastic network.

Both absolute and relative shrinkage ratios for biaxially oriented films are considerably lower than in uniaxially drawn films (Figs. 26 and 27). In the highly unbalanced films shrinkage is lowest along the direction of higher orientation (TD) up to relatively high temperatures (Fig. 26); in the nearly balanced films, however, shrinkage is higher along the direction of highest non-crystalline orientation (TD) for all temperatures above 120°C (Fig. 27).
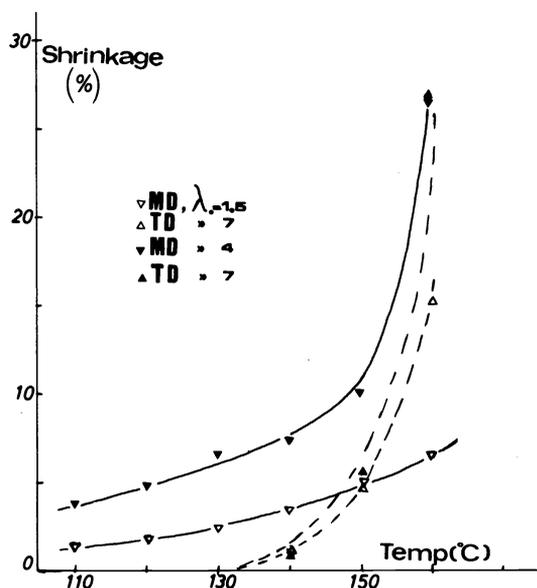
Fig.26
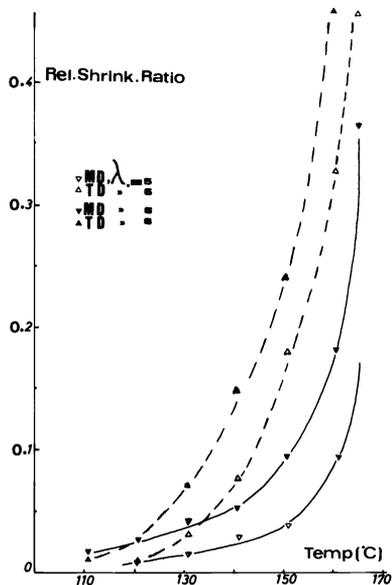
Fig.27

Fig. 26: Shrinkage ratio of unbalanced biaxially drawn films (along MD and TD) versus annealing temperature. Participants 1 and 4.

Fig. 27: Relative shrinkage ratio of nearly balanced biaxially drawn films (along MD and TD) versus temperature. Participants 1 and 4.

Assuming that thermal shrinkage in uni- and biaxially drawn films is primarily caused by gradual disorientation of a strained molecular network due to partial melting of more or less voluminous crystalline network junctions, the maximum amount of shrinkage attainable at high temperature would be mainly dependent on the degree of non-crystalline orientation, as previously shown by Samuels (16). However, the amount of shrinkage attainable at a given temperature below the ultimate thermodynamic melting temperature of isotactic polypropylene strongly depends on the processing history of the film, in particular on draw and post-draw anneal temperatures. Although structural parameters such as crystallinity and average degree of molecular orientation in crystalline and non-crystalline regions may be affected, to various extents, by the thermomechanical history of the film, mere knowledge of these parameters seems to be insufficient, in general, to predict dimensional instability as a function of temperature. The effect of thermal history may be understood by assuming that crystalline network junctions will melt out at a temperature close to the one at which they have been formed during processing. Experimental evidence in favour of this point of view has been recently provided by Tunnicliffe et al (17) who have shown a strong correlation between relative shrinkage ratio and fraction of crystalline material melting out at the same temperature. The latter quantity was calculated from the endothermic melting peak area determined by differential scanning calorimetry (DSC).

A simple 1:1 correlation was found for three samples of uniaxially drawn polypropylene films (nominal draw ratio = 7), but for two other samples with different thermomechanical histories, the observed relationships were different although still indicating a positive correlation between shrinkage and partial melting of crystalline material. We have applied a similar analysis to the data obtained in the present programme by calculating fractional melting peak areas for several temperatures between 110° and 160°C from DSC-traces

obtained by Participant 3 at a scan rate of 20°C/min.   The existence of a positive
correlation between shrinkage and fractional melting peak area is obvious from the results
plotted in Fig. 28, but a unique relationship for uniaxially drawn films seems only to exist
for samples with draw ratio ≥ 4, characterised by a microfibrillar crystalline structure.
In weakly oriented films in which the spherulitic morphology has not yet been completely
destroyed, release of internal strain required apparently a very limited amount of melting
only (Fig. 28, curves for λ_o = 1.2 and 1.5).
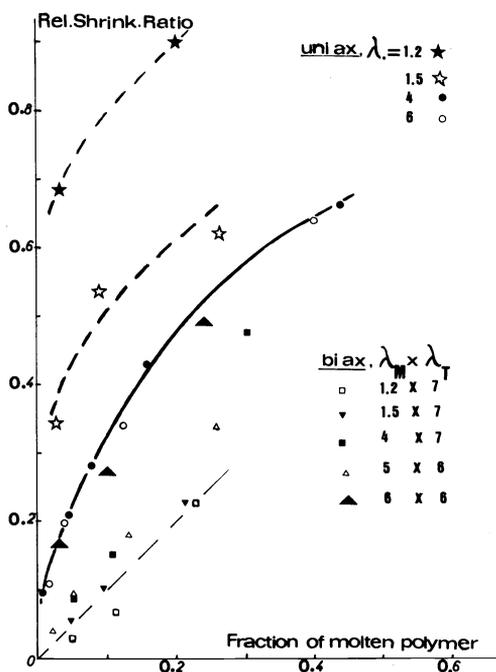
Fig. 28: Relative shrinkage ratio (Participant 1) versus fractional melting peak area
(Participant 3) between 110° and 160°C, for uni- and biaxially drawn films.

Fig. 28 also shows the results obtained with biaxially drawn films; relative shrinkage ratio
in this case has been defined as the relative reduction in surface area upon shrinkage:

$$(\text{Rel. SR})_{biax} = \left[(\lambda_M \lambda_T)_i - (\lambda_M \lambda_T)_f \right] \Big/ \left[(\lambda_M \lambda_T)_i - 1 \right]$$

For the nearly balanced film with nominal draw ratios 6 x 6, results are in good agreement
with the experimental curve for uniaxially drawn films with microfibrillar crystalline
structure.   The results obtained for the other biaxially drawn films, however, obey a
different relationship which for small shrinkage ratios approximates a 1:1 correlation.   In
spite of the quantitative differences with respect to the results reported in Ref. 17, the
data displayed in Fig. 28 seem to confirm that the predominant effect of thermomechanical
history on shrinkage and dimensional instability may be explained in terms of thermal
instability of crystalline domains in a more or less extended temperature range below the
thermodynamic equilibrium melting temperature.   The broadness of this range is assumed to
be closely related to the temperatures at which the crystallites have been formed and/or
annealed.   Samuels (16) has already shown that the build-up of internal strain in the
amorphous network during stretching as well as its gradual release during subsequent
shrinkage may be quantitatively described in terms of non-crystalline orientation functions.
A complete model which also accounts for the stabilising effect of the crystalline phase and
the relationship between partial melting and release of internal strain, is however, still
lacking.

If an oriented polymer film is heated while restrained from shrinkage, an external tensile
force has to be applied in order to maintain its length constant.   The observed retractive
or shrinkage force passes through a maximum as a function of temperature, due to the
simultaneous build-up and relaxation of internal tensile stress in the oriented amorphous
network.   Maximum shrinkage stress in both uni- and biaxially oriented films has been
measured by Participants 1, 4 and 6 on small specimens cut from a piece of film of limited
surface area (~0.25m²).   Results obtained under these conditions were in general, in
good agreement but mean values determined in quite different parts of the same film

sometimes diverged significantly. Apparently, shrinkage stress is quite sensitive to local
variations in orientation (and/or other structural parameters) which may be more difficult
to detect by birefringence measurements since no important fluctuations from one part of a
film to another have been observed in the latter kind of measurements. The importance of
the divergence between minimum and maximum values can be judged from Fig. 29 which
represents a plot of the non-crystalline contribution to birefringence, given by:
$\Delta n - v_x f_x \Delta_x^o$ (see Ref. 1), versus shrinkage stress reduced to unit cross-section of non-
crystalline phase. We have also indicated in Fig. 29 the most frequently observed values
in at least two different laboratories. If the maximum shrinkage stress is identical with
the internal stress in the deformed amorphous network, its value should be directly
proportional to the non-crystalline birefringence and the ratio between the two variables
plotted in Fig. 29 should be equal to the stress-optical coefficient of polypropylene at
the stretch temperature. Wales (20) has determined the stress-optical coefficient of
molten polypropylene by means of flow birefringence measurements and found a value of
9.10^{-10} m^2/N at 210^oC. This value has been used to draw the straight line indicated in
Fig. 29.
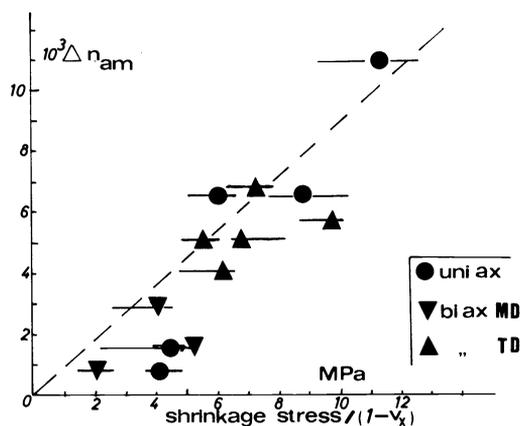
Fig. 29:   Non-crystalline birefringence in uni- and biaxially drawn films versus
shrinkage stress in amorphous phase.   Comparison with stress-optical law for molten
polypropylene.(Ref. 20).   Experimental data from Participants 1, 4 and 6.

The scatter in the experimental data makes it difficult to ascertain the effective existence
of a linear relationship but it is obvious that the experimental results are not in
contradiction with the stress-optical law observed by Wales. The temperatures at which
maximum shrinkage stress was observed, are not the same for uni- and biaxially drawn films;
in the latter case, moreover, they are much higher in the T- than in the M-direction.
These temperature values are obviously related to the processing history of the films and
to the thermal stability of the crystalline phase in accordance with the results of free
shrinkage measurements discussed above. Maximum shrinkage stress, on the contrary, seems
to be mainly determined by non-crystalline orientation and only indirectly affected by
thermomechanical history during processing. (Ref. 19).

7. GAS PERMEABILITY

Gas permeability with respect to carbon dioxide and nitrogen was determined for some films
by Participant 5 by means of a method described in Ref. 21. Participant 1 measured the
permeability of most films with respect to CO_2, N_2 and O_2 by means of another experimental
device (Ref. 22).   The results obtained by Participant 5 were systematically 20-25% lower
than those measured by Participant 1 which cannot be explained by a lack of reproducibility,
the standard deviation of the numerical data being less than 10% in both laboratories. The
ratio P_{CO_2}/P_{N_2} was found to vary between 16 and 20 in both laboratories. According to
Participant 1 the ratio P_{CO_2}/P_{O_2} was practically the same for all films, irrespective of
state and degree of orientation, and equal to 3.4 ± 0.3. The permeability to oxygen
measured at 23^oC for four uniaxially drawn films is plotted as a function of the non-
crystalline orientation (f_{am}) in Fig. 30.   Assuming gas permeation through the crystalline
phase to be negligible it might be expected that permeability will be mainly determined by
the volume fraction and degree of orientation of the non-crystalline phase.   Volume
fraction of amorphous phase in the uniaxially drawn films varies only little (between
0.35 and 0.40) and it is reasonable, therefore, to attribute the significant decrease in

permeability shown in Fig. 30 to the increasing degree of molecular orientation, associated with the formation of a microfibrillar morphology. The shape of the curve suggests that further increase of f_{am} beyond a value of about 0.3 - 0.4 will no longer affect permeability to any important extent.
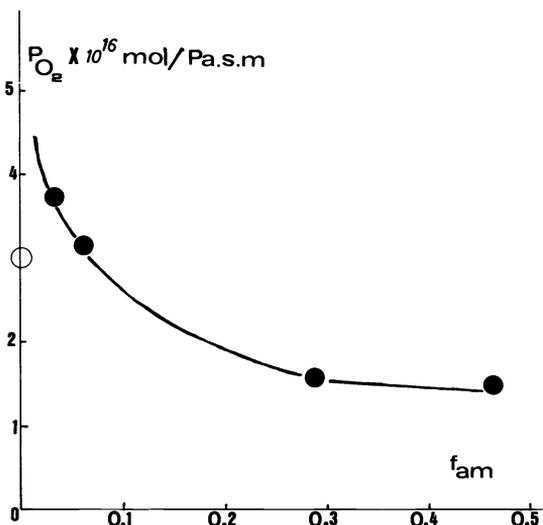
Fig. 30: Oxygen permeability of uniaxially drawn films as a function of non-crystalline orientation. Data from Participant 1.

We have also indicated in Fig. 30 a permeability value determined by Participant 1 on a much thicker isotropic film; this value is significantly lower than the one which might be extrapolated from the curve for uniaxially drawn films. It is also lower than the value reported by Stannett (23) for polypropylene films of similar density ($907 kg/m^3$). Stannett's value for P_{O_2}, equal to $7.10^{-16} mol/Pa.s.m.$ would be in better agreement with the data plotted in Fig. 30 and would tend to indicate that uniaxial orientation might reduce permeability down to about 20% of the initial value for isotropic polypropylene. In the series of biaxially drawn films permeability values were of the same order of magnitude as in uniaxially drawn films: according to measurements by Participant 1, P_{O_2} varied between 2 and $3.10^{-16} mol/Pa.s.m.$, without any apparent correlation with degree of orientation. For the nearly balanced film No. 2.11, Participant 5 measured P_{N_2} and P_{CO_2}-values as low as in the uniaxially drawn film with highest degree of orientation (Film 1.06); the P_{O_2}-values for the same films measured by Participant 1, however, showed a 45% higher permeability for the biaxially drawn film in spite of its higher density. Since gas permeability must be strongly related to segmental mobility in the non-crystalline phase a somewhat higher value for biaxially (compared to uniaxially) oriented films is not unexpected.

8. PHOTO-OXIDATION AND UV-STABILITY

A detailed study of the rate of oxygen absorption as a function of light intensity, oxygen pressure and temperature was carried out by Participant 5. In this report we will only summarise some of its principal results. UV-stability characterised by the induction time needed to reach a steady-state oxygen absorption at 70°C was found to be of comparable magnitude for isotropic and biaxially oriented films. For uniaxially drawn films UV-stability was found to be significantly higher but its value was only slightly dependent on degree of orientation. If we assume that the induction time will be shorter the higher the segmental mobility of the molecular chains in the amorphous regions, in accordance with the findings of Rapoport et al (24), we may expect an inverse relationship between UV-stability and gas permeability. The plot shown in Fig. 31 seems to confirm, indeed, the existence of such a correlation between induction time, on the one hand, and oxygen permeability (measured by Participant 1) on the other.

The steady-state rate of oxygen absorption which increases with light intensity and oxygen pressure was found to be higher for the uniaxially drawn films than for the isotropic one and still higher for the biaxially drawn films. These differences are probably not related to structural variations but only caused by the large differences in thickness between the isotropic, uniaxially-and biaxially oriented films respectively.
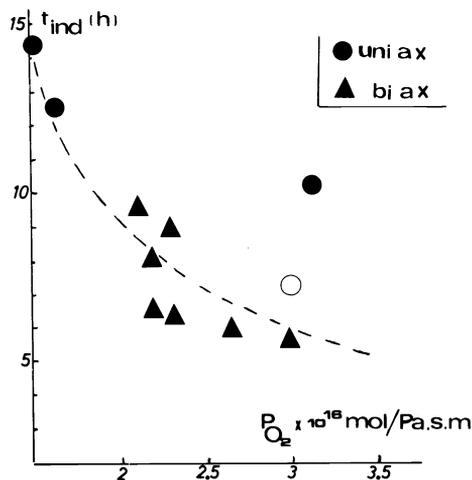
Fig. 31:   Induction time (UV-stability) at 70°C (1 atm O_2-pressure, light intensity = 885 W/m²) for uni- and biaxially drawn films (Participant 5) plotted versus O_2-permeability measured by Participant 1.

9.   OPTICAL PROPERTIES

Participant 4 carried out transmission and haze measurements according to ASTM D 1003 and obtained the following results (Table 2).

TABLE 2:   Optical properties of uni- and biaxially drawn films.

Film No.	Draw Ratio	Thickness (micrometres)	Density (kg/m³)	Transmission (%)	Haze (%)
1.01	1 x 1	716	902	84	68
1.02	1.2 x 1	152	907	90	19
1.03	1.5 x 1	151	903.5	91	17
1.04	4 x 1	181	903.5	91	7.7
1.05	5 x 1	173	905	90	11
1.06	6 x 1	169	903	91	5.4
2.07	1.2 x 7	21	912	91	7.3
2.08	1.5 x 7	25	912	93	3.1
2.09	4 x 7	19	910	92	0.3
2.10	5 x 6	20	911	90	18
2.11	6 x 6	22	911	92	6.2

Transmission values varied only slightly and were found to be comparable for both uni- and biaxially drawn films, notwithstanding the differences in thickness.   Reduction in haze as a result from either uni- or biaxial drawing is quite significant, but it is also obvious from the data in Table 2 that haze values are not exclusively determined by the state and degree of molecular orientation.   Crystallinity (density) and possibly thickness may also have an effect on the amount of haze but the limited number of data presented here do not permit any accurate estimation of the influence of these variables.

10. CONCLUSION

Although the results of this collaborative study fully confirm the important effect of structural order on many mechanical and other properties of technological interest, it is not yet possible to express, in the framework of a general theory, all properties in terms of a limited number of structural parameters characteristic of the state and degree of molecular orientation in semi-crystalline polymer films. In the case of uni- and biaxially oriented polypropylene films, investigated here, many properties appear to depend strongly on the volume fraction and degree of orientation of non-crystalline regions. Small strain viscoelastic behaviour, in particular, seems to be mainly determined by structural order in the non-crystalline phase and may be quantitatively described with the aid of a simple two-parameter model not only for uniaxially oriented films as first shown by Samuels (2) but also in the case of biaxially oriented films if use is made of the biaxial orientation functions defined in Part 1 of this report (Ref. 1). Further theoretical and experimental analysis (in particular with regard to angular variation of properties in the plane of biaxially oriented films) is needed, however, in order to reach definite conclusions.

Taking account of the importance of structural order and segmental mobility in the non-crystalline phase, for many properties of practical interest, a more detailed information than those provided by Hermans' orientation functions would certainly be useful. In this respect, the investigations of Zachmann and co-workers (25) combining X-ray diffraction, birefringence and NMR measurements, are of particular interest.

Ultimate properties such as impact resistance and tear strength of biaxially oriented polypropylene films have been shown to depend markedly on the degree of unbalanced molecular orientation. The latter is closely related to the manufacturing conditions of film processing but the characterisation procedures developed in Part 1 allow a quantitative description of the degree of imbalance in both crystalline and non-crystalline phases without any knowledge of the thermomechanical history of the films. Thermal shrinkage and dimensional instability are also strongly influenced by film processing conditions but can not be predicted on the basis of "global" structural parameters (such as determined in Part 1) only. DSC measurements reveal important variations in thermal stability of the crystalline phase (probably due to variations in crystallite size and structural defects) which can only be accounted for by means of a more refined structural analysis. The relationship between thermomechanical history and molecular orientation will be further discussed in Part 3.

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