

Mechanical properties of semicrystalline polymer-polypropylene

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Abstract. The elastic properties of polypropylene have been investigated in terms of a phenomenological model, which is a modified form of the Takayanagi's two-phase model. In the present model both the change of crystallinity and orientation of the crystalline chains have been taken into account. The orientation effect at the drawn state has been considered in a simplified manner. It has been shown that a partially aligned crystalline phase may be considered as a superposition of a perfectly aligned crystalline region in an elastically isotropic randomly oriented crystalline phase. The predicted values of elastic modulus agree with experimental values.

Keywords. Semicrystalline polymer; mechanical properties; two-phase model; polypropylene.

1. Introduction

The existing models dealing with mechanical properties of partially crystalline polymers are phenomenological and the model elements do not correspond to the fine structure at the molecular level. Of the different models the one-phase (Ward 1962) and the two-phase models (Takayanagi *et al* 1966) have been widely used. The different models and the structure of polymers are reviewed in detail by Hadley and Ward (1975 a, b).

The Young's modulus along the draw direction (E_0) and perpendicular to the draw direction (E_{90}) and shear modulus (G) for polypropylene (PP) have been measured at various temperatures and upto very high draw ratio by different workers (Chan *et al* 1978; Hadley *et al* 1969; Leung *et al* 1980).

The Ward's model (Ward 1962) considers the partially crystalline polymer to be a one-phase material and takes no account of the way in which the two phases are inter-linked, neglecting the role of crystallinity to a first approximation. It further assumes that the mechanical anisotropy is directly related to the degree of molecular orientation (Ward 1962; see page 286 of Hadley and Ward 1975b). But it is experimentally established (Alexander 1969) that a partially crystalline polymer consists of more than one phase and so far as the mechanical properties are concerned both the volume fraction of crystalline phase and the orientation of molecular chains (Ward 1962) are important. The Ward's model has been applied to interpret the elastic moduli of PP (Hadley *et al* 1969; Chan *et al* 1978) but the range of values predicted is usually too large to be meaningful for comparison with experimental values. Even the experimental values fall outside this range for most of the draw ratios. One can understand

this difficulty in view of the observation by Hadley and Ward (1975a, p. 1173) that the Ward model is not applicable to PP in particular.

The Takayanagi's model tries to interpret the elastic moduli of the polymer in terms of those of its constituents (Takayanagi *et al* 1966; Takayanagi and Kajiyama 1973; Prevorsek 1971). But this model is intended for highly drawn polymers and does not deal with the gradual growth of anisotropy from the undrawn state. Recently Biswas and Basu (1980) proposed a model for the mechanical properties of partially crystalline polymers and applied it to interpret E_0 and E_{90} values of PP at room temperature and at -83°C . In what follows we present the detailed features of the proposed model.

2. Modified two-phase model

In the proposed two-phase model the change in the volume fraction of crystalline phase (henceforth called crystallinity) and molecular orientation have been incorporated in the light of structural information available (for review see Hadley and Ward 1975 a,b). From x-ray studies (Alexander 1969; Deopura *et al* 1977) it is evident that at the undrawn state a partially crystalline polymer consists of two phases—crystalline and amorphous. Of these the amorphous phase is isotropic. So the experimental fact that a polymer is elastically isotropic at the undrawn state demands the crystalline phase to be isotropic as well. This state may be considered as a combination of randomly-oriented crystalline particles in an amorphous matrix. At this stage it has only one Young's modulus (E) given by

$$\frac{1}{E} = \frac{\chi_0}{E_P} + \frac{1 - \chi_0}{E_A} \quad (1)$$

where χ_0 is the crystallinity at the undrawn state and E_P is the Young's modulus of the randomly oriented fully crystalline material which can be calculated by using equation (5.14) of Ward (1962) and E_A is the Young's modulus of the amorphous phase.

Next we consider the polymer at the drawn state. The x-ray patterns (Alexander 1969) of the drawn specimens reveal the presence of preferred orientation in the direction of the drawing. Recent studies (Dasgupta *et al* 1979) on stretched PVC films indicate that the major contribution to the observed orientation on uniaxial stretching originates from the crystalline region of the polymer.

In the Ward model the elastic constants of the ensemble of partially oriented units have been expressed in terms of the elastic constants of the units. A similar procedure cannot be applied in a two-phase system, where the situation is complex. It has not been possible to construct a quantitative two-phase model incorporating the orientation effect. We consider the orientation effect in a partially oriented crystalline region of the polymer in a somewhat simplified manner. It can be shown that so far as the effective elastic behaviour is concerned, the partially oriented crystalline phase of the polymer may be the combination of a portion composed of aligned chains and the remaining portion composed of crystallites arranged at random (see Appendix for justification).

In the Takayanagi's model the expressions for E_0 and E_{90} are deduced on the assumption that a portion of the crystalline phase (of volume concentration $(1-a)$ $(1-b)$ of figure 1) is at constant stress with the amorphous phase and that this combination is at constant strain with the remaining portion of the crystalline phase (for expressions of E_0 and E_{90} see Takayanagi *et al* 1966). Here we also assume that the crystalline chains having chain axis within a small angle with the draw direction have a different stress-strain relation than the other partially-oriented chains. If X be the crystallinity at any arbitrary draw ratio n ($n > 1$), p the fraction of the crystalline phase supposed to be composed of perfectly-aligned chains, then the volume concentration of the amorphous phase and the two fractions of the crystalline phase will be as shown in figure 2. Now so far as the value of p , the fraction of the crystalline portion consisting of perfectly aligned chains, is concerned it is obvious that it will be some function of the draw ratio (n) with $p=0$ for $n=1$ *i.e.* for the isotropic undrawn state. Unfortunately, direct experimental information is not

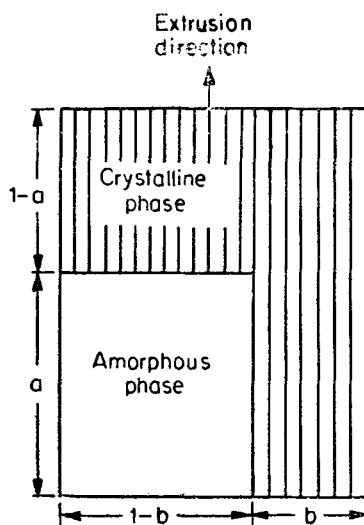


Figure 1. Schematic diagram of crystalline and amorphous phase in Takayanagi's model (Takayanagi *et al* 1966).

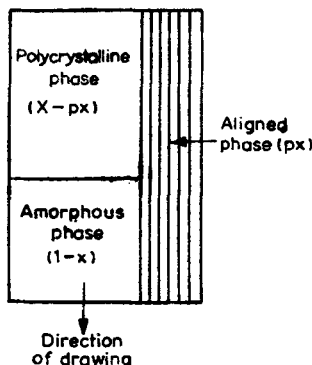


Figure 2. Schematic diagram of the two fractions of crystalline phase and the amorphous phase envisaged in the present model.

available at present. As an alternative we suggest a two-parameter empirical relation obtained by trial and error,

$$p = A [1 - \exp - (n - 1)^2/\beta]. \quad (2)$$

In the Appendix we discuss a justification of the above empirical formula.

In the light of the above discussions the expressions for the E_0 , E_{90} and G may be derived in the same manner as in the Takayanagi's model and are given below:

$$E_0 = p \chi E_{\parallel}^{(c)} + (1 - p \chi) E', \quad (3)$$

$$E_{90} = p \chi E_{\perp}^{(c)} + (1 - p \chi) E', \quad (4)$$

where
$$\frac{1}{E'} = \left(\frac{\chi - p \chi}{E_P} + \frac{1 - \chi}{E_A} \right) \cdot \frac{1}{1 - p \chi}, \quad (5)$$

and
$$G = p \chi G^{(c)} + (1 - p \chi) G', \quad (6)$$

where
$$\frac{1}{G'} = \left(\frac{\chi - p \chi}{G_P} + \frac{1 - \chi}{G_A} \right) \cdot \frac{1}{1 - p \chi}, \quad (7)$$

where $G^{(c)} = C_{44}^{(c)}$ and G_A and G_P are the shear modulus for the amorphous and polycrystalline phase respectively. The value of the shear modulus G at the undrawn state follows from equation (1) and is given by

$$\frac{1}{G} = \frac{\chi_0}{G_P} + \frac{1 - \chi_0}{G_A}. \quad (8)$$

3. Application

The proposed model is applied to interpret E_0 , E_{90} and G values of PP at different temperatures. The data and parameters using equations (3), (4) and (6) are given in table 1. The E_P and G_P values are computed using equations (5.14) and (5.16) of Ward (1962). For the crystalline regions of PP the values of $C_{44}^{(c)}$ i.e. $G^{(c)}$ are not available and we have used an estimated value. It is also to be noted that in the absence of any data for $C_{12}^{(c)}$ and $C_{13}^{(c)}$ we have to neglect them in the expressions for E_P and G_P . But as for every polymer $C_{12}^{(c)}$ and $C_{13}^{(c)}$ are very small as compared to $C_{33}^{(c)}$, $C_{11}^{(c)}$, etc the above approximations seem to be justified. The values of E_A are also estimated according to the order of magnitude given by Holliday and White (1971). The G_A values are so estimated to obtain an exact fit at the undrawn state.

As regards the crystallinity values we have used the experimental values of Chan *et al* (1978) for their data at -83°C . For the data at 0°C and 60°C , Leung *et al* (1980) have reported that crystallinity remains constant ($\chi=0.62$) throughout the entire draw ratio range. But there is some uncertainty regarding the crystallinity value for the highest draw ratio ($n=22$) used by them. In order to interpret the data at

Table 1. The input data and parameters

	Temperature (°C)			
	-83	0	60	Room temperature
Elastic constants in GPa				
$E_{\parallel}^{(c)*}$	42	42	42	42
$E_{\perp}^{(c)**}$	4.04	4.04	4.04	4.04
$G^{(c)}$	3.50	3.50	3.50	3.50
E_P	11.48	11.48	11.48	11.48
G_P	2.26	2.26	2.26	2.26
E_A	2.62	2.25	0.91	0.27
G_A	1.65	1.10	0.36	0.15
Parameters				
A	0.35	0.81	0.65	0.35
β	25	50	50	50

*Sakurada *et al* (1966); **Samuels (1965).

0°C and 60°C we have taken χ to be constant as reported. Regarding the room temperature data (Hadley *et al* 1969) there is no information about the crystallinity. However, as the temperature of the experiment is between 0°C and 60°C we assume χ to be constant throughout as reported by Leung *et al* (1980).

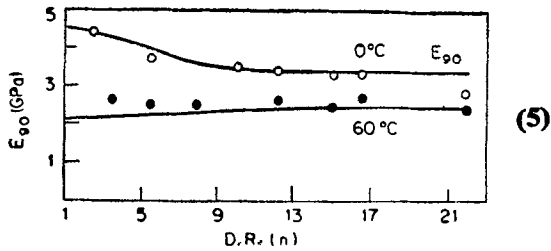
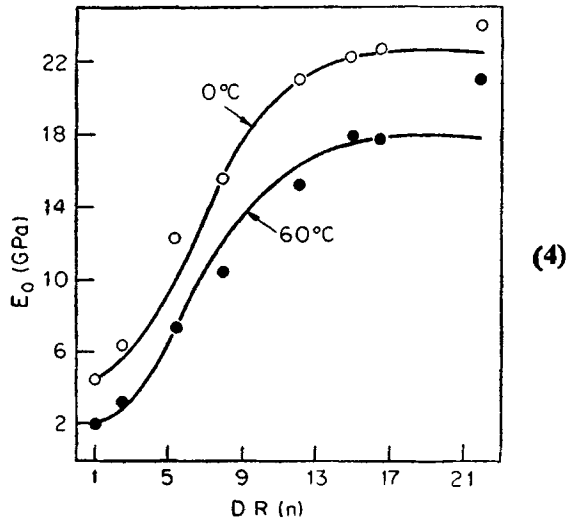
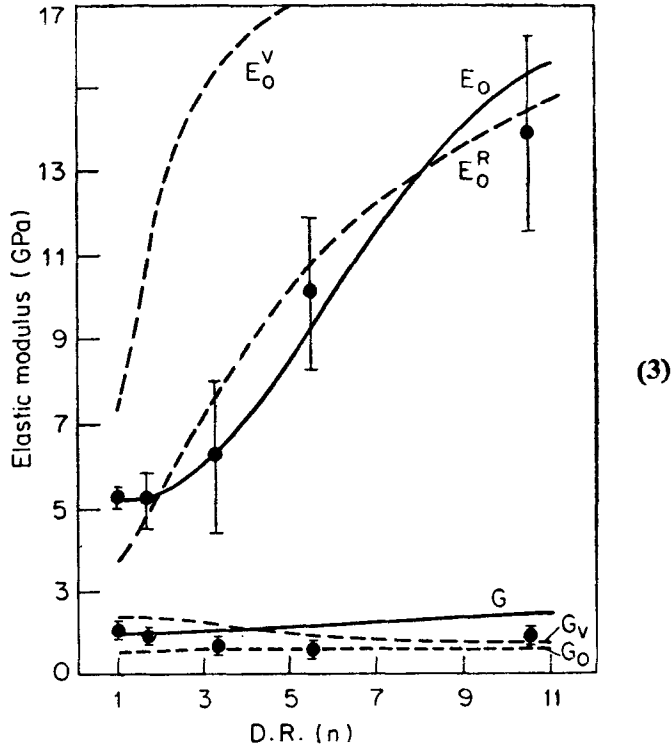
The comparison of the experimental values of E_0 and G (at -83°C) with those predicted by the present model and by the Ward model (E_0^R and E_0^V) is given in figure 3. The predicted values of E_0 , E_{90} and G and the corresponding experimental values (at 0° and 60°C) are shown in figures 4, 5 and 6 respectively.

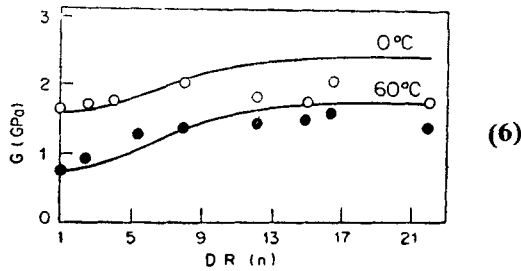
The calculated values of E_0 , E_{90} and G at room temperature and the corresponding Reuss and Voigt bounds by aggregate model are compared with experimental values in figures 7, 8 and 9.

4. Discussion

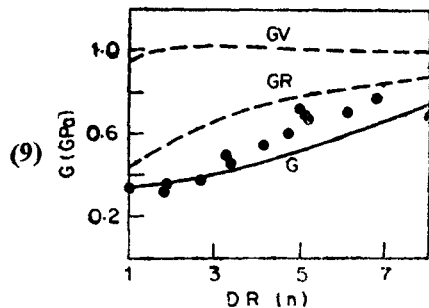
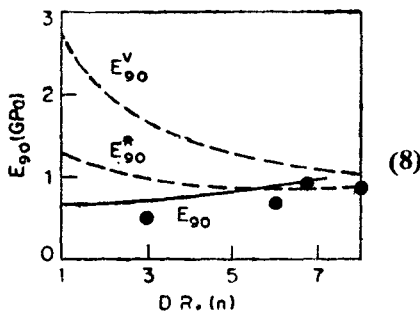
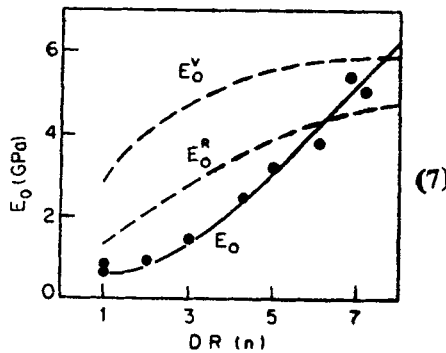
The present results indicate that the quantitative agreement of E_0 and G values is satisfactory at -83°C for the entire draw ratio range. The agreement is quite impressive for E_0 , E_{90} and G values at room temperature. In the case of the predicted values at 0°C and 60°C, the general agreement except at the highest draw ratio (*i.e.* $n=22$) is quite impressive. The disagreement between the predicted values and experimental values at the highest draw ratio is perhaps due to the uncertainty in the crystallinity value reported by Leung *et al* (1980).

The morphology of polymers is, however, so complex that at this stage the model is too approximate to tackle the minute peculiarities in different cases. The broad observation that emerges is that both orientation of chains and crystallinity are equally important in determining the elastic behaviour of the semicrystalline polymers. It is well known that a clear quantitative picture of the different components present





Figures 3-6. 3. Young's modulus in the draw direction and shear modulus (G) at -83°C . Solid curves represent calculated values. E_0^V and E_0^R are the theoretically calculated Voigt and Reuss averages by Ward model using the data of Chan *et al* (1978) 4, 5. Young's modulus at 0°C and 60°C . The solid curves represent the calculated values and indicate experimental values (Leung *et al* 1980). 4. Draw direction 5. along perpendicular to draw direction 6. Shear modulus (G) at 0°C and 60°C (Leung *et al* 1980) (details as in Figure 4.)



Figures 7-9. Young's modulus (Hadley *et al* 1969). Details as in Figure 3. 7. along the draw direction. 8. along the perpendicular to draw direction. 9. Shear modulus (G) at room-temperature (Hadley *et al* 1969) (details as in Figure 3.)

in a semicrystalline polymer and the specific manner in which they are disposed to one another is yet to emerge. Hence it is not surprising that simultaneously conflicting ideas are being used to describe the behaviour of these substances. It has been our motivation to develop a suitable model that will incorporate at least the compelling empirical findings and the obvious inferences drawn on them. Secondly we have cast the model in such a form that it may have some predictability. The assumptions and

the physical picture envisaged in the model may therefore be modified and revised when tested against more refined data to be obtained in future.

Finally we conclude that while the two important models by Ward and Takayanagi are suitable for glassy polymers and high drawn polymers respectively the present model emphasising the role of the morphology and its variation with draw ratio embraces the entire range. It is interesting that at a very high draw ratio when the entire crystalline region will be almost perfectly oriented, the proposed model and the Takayanagi model will be identical.

Appendix

Let us consider an aggregate of elastically anisotropic units possessing fixed elastic constants. These units may be real crystallites or imaginary units as in Ward's model. At the undrawn state these are randomly oriented. From equations (5.13) and (5.15) of Ward (1962), the compliance constants for the randomly oriented phase $S_{33}^{(P)} = S_{11}^{(P)}$ and $S_{44}^{(P)}$ and Young's modulus $E^{(P)}$ and shear modulus $G^{(P)}$ can be calculated.

For the drawn state we can calculate E_0 , E_{90} and G values by using equations (5.17), (5.21) and (5.19) of Ward (1962). In the above procedure we have taken the constant stress *i.e.* Reuss average only. The reason for this has been discussed in detail by Sakurda *et al* (1966). It has been shown by Odajima and Maeda (1966) that for Young's modulus and shear modulus of polycrystalline PE the experimental values are very close to the Reuss average.

We next proceed to calculate the elastic moduli at the drawn state by an alternative procedure. At some intermediate draw ratio when the units have undergone partial orientation we simplify the case by considering the aggregate as a combination of a fraction consisting of fully aligned units along the draw direction and the rest composed of randomly oriented units. If p be the volume fraction of the portion composed of perfectly aligned units, the effective values of $S_{ij}^{(b)}$ of the aggregate will be given by

$$S_{ij}^{(b)} = pS_{ij}^{(u)} + (1 - p)S_{ij}^{(P)}, \quad (\text{A.1})$$

where $S_{ij}^{(u)}$ are the compliance constants for the unit. With the help of (A. 1) we calculate $E_0 = (S_{33}^{(b)})^{-1}$, $E_{90} = (S_{11}^{(b)})^{-1}$ and $G = (S_{44}^{(b)})^{-1}$ for the aggregate.

Now we pose the problem whether we can suggest a relationship between p and n such that the values of the elastic moduli E_0 , E_{90} and G calculated by the two procedures described above have close agreement? By trial we obtain the following relation: $p = [1 - \exp -(n - 1)^{0.7}/1.8]$ which satisfies the above requirement. It can be easily seen that for $n = 1$, $p = 0$ suggesting that the entire assembly consists of randomly oriented units. Also for $n = \infty$, $p = 1$, suggests that the whole aggregate is composed of perfectly aligned units. Both these cases are identical with those of the Ward model. As far as the intermediate draw ratios are concerned we have investigated in the case of real crystallites of PE and nylon and units of PP, PET and PVC and in every case the agreement is excellent. The result in the case of PP is given in figure 10.

We conclude that so far as elastic moduli are concerned we can consider a partial oriented state as a linear combination of a randomly oriented phase and a perfectly oriented phase.

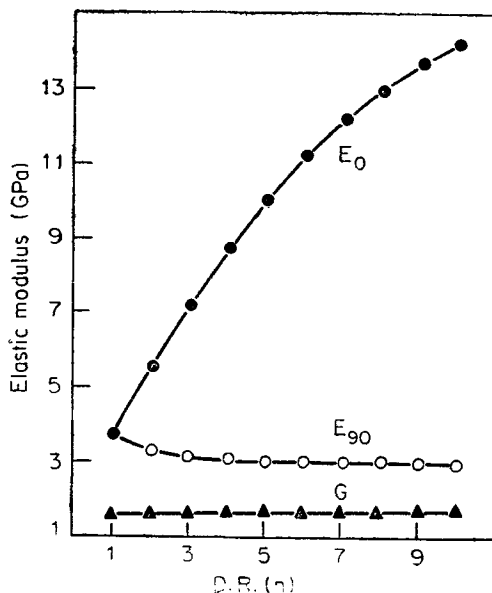


Figure 10. Comparison of calculated values of E_0 , E_{90} and G by Ward's method (solid curve) and by the proposed method (denoted by ●, ○ and ▲) for an aggregate of units. Compliance constants of the units are taken from Chan *et al* (1978).

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