Theoretical Prediction of Tie-Chain Concentration and Its Characterization Using Postyield Response

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SYNPOSIS

In the past, relative tie-chain concentration has been semiquantitatively characterized by infrared dichroism on a stretched sample and from brittle fracture strength. The probability of tie-molecule formation has also been theoretically estimated from chain dimensions and the semicrystalline morphology of the polymers. In this article the probability of tie-chain formation of monodisperse and homogeneous single-site ethylene copolymers has been estimated over a range of densities and molecular weights using the model proposed by Huang and Brown. The relative tie-chain concentration is obtained by multiplying tie-chain probability with the volume fraction crystallinity of polymer. A modified rubber elasticity theory is applied to calculate the concentration of chain links between junction points (crystallites) of the INSITE[†] technology polymers (ITPs) from measured rubber modulus. It is expected that the chain-link concentration should relate to the tie-chain concentration. The calculated rubber modulus, or the chain-links concentration, of the ITPs increases with an increase in density in the 0.865 to 0.910 g/cc range and did not change significantly in the density range of about 0.91 g/cc to 0.954 g/cc. Normalized rubber modulus and relative tie-chain concentration data shows that the relative tie-chain concentration predicted by Huang and Brown model and measured using the modified rubber elasticity theory are quantitatively similar below 0.91 g/cc density. However, above 0.91 g/cc density, the measured rubber modulus is influenced by additional tie-chain formation during deformation due to breakdown of crystallites and, hence, the discrepancy exists between the two methods of estimating relative tie-chain concentration. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Consideration of the crystalline domains has long dominated research to explain the properties of semicrystalline polymers such as linear low density polyethylene (LLDPE). Though crystalline domains control low strain properties of semicrystalline polymers such as modulus and yield stress, it has been clearly established by many researchers that large strain properties such as stretchability, impact, tear, failure processes, etc., are also controlled by the amorphous region, particularly by tie-molecules, the amorphous chains that bridge adjacent lamellae.[1-7] However, development of appropriate structure–property relationships in semicrystalline polymers has been perceived to be hindered by the inability to analytically measure relative tie-chain concentration. In the past, relative tie-chain concentration has been semiquantitatively characterized using techniques such as by measurement of the brittle fracture strength,[8] infrared dichroism after deformation, and chlorination of films.[1] The relative tie-molecule concentration has also been estimated from chain dimensions and the semicrystalline morphology (topology) of the polymers.[2-7]

In this report the probability of tie-chain formation of monodisperse, homogeneous ethylene-octene copolymers has been estimated over a range of densities and molecular weights using the model proposed by Huang and Brown.[2] The tie-chain probability calculations have been compared with those done by Hosoda et al. on monodisperse butene

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LLDPE crossfractions.[3] Probability of tie-chain formation alone does not reflect the actual tie-chain concentration in semicrystalline polymers. The relative tie-chain concentration would also depend upon the concentration of "junction points," which would approximately depend upon the volume fraction of the crystallinity. It is proposed that the relative tie-chain concentration can be obtained from the product of tie-chain probability and the volume fraction of the crystallinity.

Additionally, it is proposed that analysis of post-yield true stress–strain data using concepts analogous to rubber elasticity theory can provide an estimate of the concentration of static and dynamic chain links in a semicrystalline network. These include initial tie chains between crystallites (static), entanglements, and new tie chains (dynamic) formed due to lamellar sliding as a result of deformation.

RESULTS AND DISCUSSION

Estimation of Relative Tie-Chain Concentration Using Chain Dimensions and Semicrystalline Morphology

The tie-chain concentration using chain dimensions and morphology can be estimated by the method proposed by Huang and Brown.[2] The basic idea for the calculation is as follows: the molecules, which have an end-to-end distance in the melt equal to or greater than the distance between adjoining crystallites, will probably make a tie molecule. When the end-to-end distance is less than the thickness of the amorphous region between crystallites, a tie molecule will never be formed. This conclusion is supported by comparison of the radius of gyration, obtained using small-angle neutron scattering of polyethylene in the molten state and in the semicrystalline solid state. The comparison revealed negligible differences.[9] The fast crystallization process dominates the transition from the molten state to the semicrystalline solid state, leading to a "freezing in" of entanglements, or topological constraints, in the amorphous regions. Hence, the number of tie molecules that interconnect crystallites can be estimated by relating the lamellar and amorphous layer thickness with the random coil conformation of the chains in the molten state.

In order to make a specific calculation, Huang and Brown[2] initially proposed using $(2L_c + L_a)$ as a critical chain end-to-end distance (L) required to form a tie molecule, where L_c is thickness of crys-

tallites and L_a the amorphous layer thickness. Brown et al.[5] have also used $L = 2L_p = 2(L_c + L_a)$, where L_p is the long period. Yeh and Runt[6] have proposed that the diameter of gyration of a random coil in the melt has to be more than twice the long period L_p $(L_p = L_c + L_a)$ in a given specimen in order to form a tie molecule, because it is unlikely that a molecule will crystallize simultaneously within adjacent crystal blocks if the diameter of gyration is less than twice the long period. Knowing the relationship between radius of gyration and chain end-to-end distance yields $2.45L_p$ as the lower limit for the formation of tie molecules. Note that the absolute value of the calculated tie chain probability depends on the choice of the critical end-to-end distance, but the relative number of calculated tie-chain probability is much less sensitive to the specific choice of the critical distance. The equations for calculating the probability of tie-chain formation are given in Appendix A. Note that the factor $1/3$ was introduced in the probability equation because the other two dimensions of the lamellar crystals are in general much larger than the long period; therefore, the probability of forming tie-chains in these two dimensions can be neglected. This assumption may not be extended to the resins with high comonomer content (below 0.89 g/cc density) where the proposed morphology is fringed micellar.[10,11]

The calculation of the probability requires measurement (or estimation) of crystallite and amorphous layer thickness. The two-phase model of semicrystalline polymers is assumed. The equations to estimate crystallite thickness (from the Thomson-Gibbs equation) and amorphous layer thickness (using the two-phase model) are given in Appendix A. The melting point and wt % crystallinity data of homogeneous ethylene–octene copolymers made using INSITE[†] technology, measured using a Perkin–Elmer DSC-7, are used in the tie-chain probability calculations (Table I). The equilibrium melting point (T_m^o) and end surface free energy (σ_e) were assumed to be independent of density. Weight percent crystallinity of the INSITE[†] technology polymers (ITP) was determined by dividing measured heat of fusion by 292 J/g. The Simpson rule was used to perform integration in our calculations numerically. The numerical procedure was checked for the value of the integral from zero to infinity as the analytical expression is available for those particular limits (see Appendix A). Note that the Huang and Brown model can be extended to account for polydispersity.[6]

The plot of tie-chain probability as a function of wt % crystallinity for different molecular weights of

Table I Melting Point, Crystallinity, and Lamellar and Amorphous Region Thickness Data for Single Site Ethylene Copolymers and Homopolymers

Density (g/cc)	Melting Peak (°C)	L_c (Angstrom) (T-Gibbs)	Wt. Frac. Cryst.	Vol. Frac. Cryst.	L_a (Angstrom)	$2L_c + L_a$ (Angstrom)
0.954	132.2	300	0.722	0.689	135	734.5
0.94	126.6	183	0.633	0.595	125	491.1
0.935	121.4	135	0.600	0.561	105	374.5
0.925	116.8	109	0.533	0.493	112	329.9
0.92	112.2	92	0.499	0.459	108	291.2
0.915	107.7	79	0.465	0.426	107	264.9
0.91	103.1	70	0.431	0.392	108	247.1
0.905	98.5	62	0.396	0.358	111	235.5
0.9	94.5	57	0.360	0.324	118	231.6
0.895	88.1	50	0.325	0.291	122	221.6
0.89	81.8	45	0.288	0.257	129	218.0
0.88	69.1	37	0.215	0.189	157	230.4
0.87	56.3	31	0.140	0.122	225	287.3

monodisperse homogeneous ethylene copolymers is shown as Figure 1. This plot can be compared with the plot of tie-chain probability for monodisperse butene LLDPE crossfractions obtained by Hosoda et al.[3] The shape of the curves in Figure 1 and the plot by Hosoda[3] are different below 40% crystallinity. Hosoda et al.[3] have used a different relationship between melting point and wt % crystallinity, based on their butene LLDPE crossfractions data.[12] However, the lowest x-ray crystallinity of the butene fractions was 41%,[12] while Hosoda calculated tie-chain probability as a function of crystallinity down

to about 20% crystallinity.[3] Note that the probability of tie-chain formation alone does not reflect the actual tie-chain concentration in semicrystalline polymers. The relative tie-chain concentration would also depend upon the concentration of "junction points," which would approximately depend upon the volume fraction crystallinity. The relative tie-chain concentration is obtained here from the product of tie-chain probability and the volume fraction crystallinity. The plot of relative tie-chain concentration as a function of crystallinity for different molecular weights of the monodisperse single

PROBABILITY OF TIE-CHAIN FORMATION
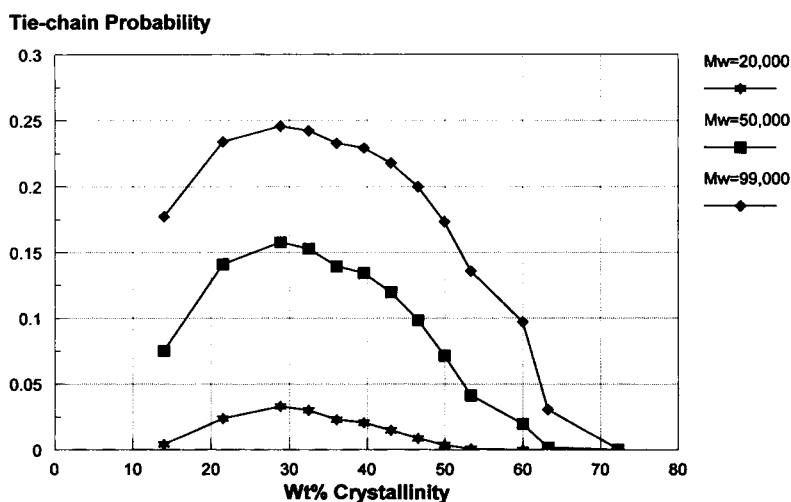### Monodisperse & Homogeneous Polyethylenes

Figure 1 The plot of tie-chain probability as a function of wt % crystallinity for different molecular weights of monodisperse single-site ethylene copolymers.

site ethylene copolymers is shown in Figure 2. Similar data are plotted as a function of density for different molecular weights of the monodisperse single-site ethylene copolymers in Figure 3.

Note that in the calculations of Figures 1 and 2, the value of L_c was estimated from DSC peak melting point and L_a was estimated using a two-phase model. It will be useful to measure L_c and L_a experimentally for various ITPs to see how much the values differ from estimated values and use the measured values in the tie-chain probability calculations.

The tie-chain probability calculations from the Huang and Brown model as shown above suffer from various limitations:

1. The value of the tie-chain probability and relative tie-chain concentration calculated from the Huang and Brown model depends on the value of critical end-to-end distance (L), which depends strongly on the lamellar and amorphous layer thickness. Hence, experimentally measured values of L_c and L_a for a given polymer should preferably be used in the calculations. However, accurate experimental data on L_c and L_a for a given polymer may not be available. Gibbs–Thomson equation used here is valid for lamellar crystallites of large lateral dimensions. For very low density ethylene-α-olefin copolymers, formation of chain bundles or fringed micelles is the dominant crystallization mechanism.[10]

For ethylene-α-olefin copolymers, Gibbs–Thomson equation may not be applicable for calculating crystallite thickness.[13]

2. Different values of the critical end-to-end distance (L) have been used by various authors in the tie-chain probability calculations. Hence, the values of tie-chain probability calculated by various authors should be compared with caution.

3. It has been well established that ethylene copolymers having a higher α-olefin as the comonomer have better mechanical properties such as dart impact, tear, etc., compared to ethylene copolymers having a lower α-olefin comonomer. For example, 1-octene–based LLDPEs are known to have better mechanical properties compared to 1-butene–based LLDPEs. One of the postulates to explain this comonomer effect is that the ethyl branch in a butene copolymer is not as effective in tie-chain formation compared to the hexyl branch in an octene copolymer. The Huang and Brown model considers the effect of comonomer type on tie-chain probability only indirectly, i.e., through its effect on L_c and L_a. This may not be sufficient for accounting the effect of comonomer type such as 1-butene, 1-hexene, 1-octene, etc., on the properties differences. If quantitative measurements of L_c and L_a for each comonomer were available, tie-chain concentration esti-

RELATIVE TIE-CHAIN CONCENTRATION
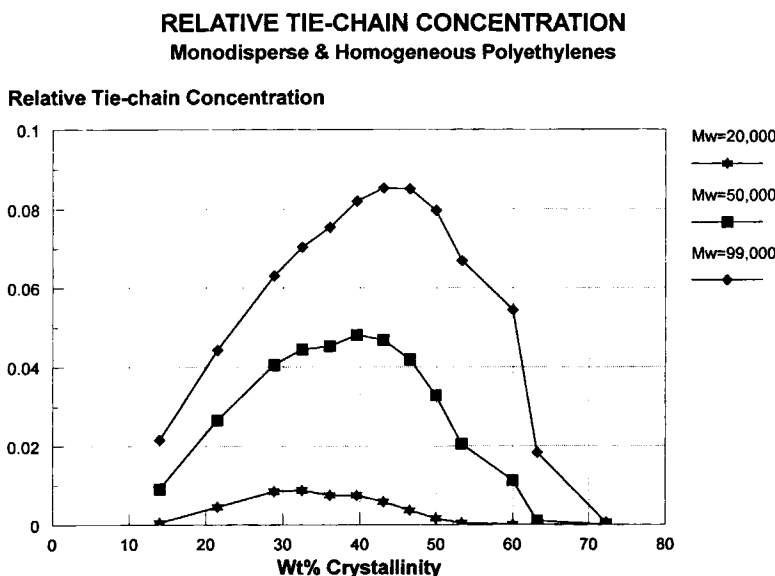### Monodisperse & Homogeneous Polyethylenes

Figure 2   The plot of relative tie-chain concentration as a function of crystallinity for different molecular weights of the monodisperse single-site ethylene copolymers.
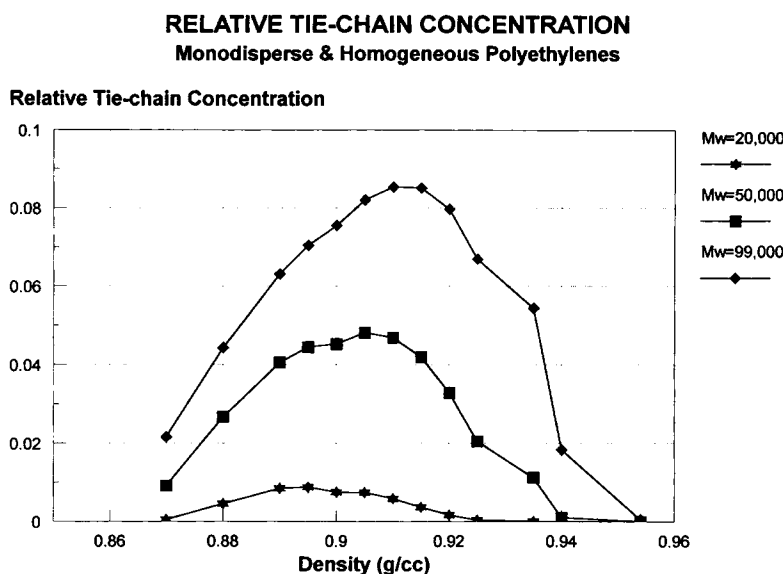
RELATIVE TIE-CHAIN CONCENTRATION
Monodisperse & Homogeneous Polyethylenes

Relative Tie-chain Concentration

Figure 3   The plot of relative tie-chain concentration as a function of density for different molecular weights of the monodisperse single-site ethylene copolymers.

mated using this approach should reflect the role of the comonomer.

4. Critical assumption that probability of tie chain formation can be neglected in the directions orthogonal to the chain axis may not be applicable to the fringed micelle crystal morphology proposed below 0.89 g/cc density.

Characterization of Tie-Chain Concentration Using Uniaxial Postyield Tensile True Stress–Strain Response

As mentioned before, various authors have attempted analytical characterization of tie-chain concentration. Lustiger et al.[1] have proposed using infrared amorphous dichroism on a stretched chlorinated sample to obtain relative concentration of tie-chain molecules. The argument behind the proposal is as follows: the principal component in the amorphous region, which remains oriented after a short initial period of stress relaxation, is the tie molecules, and as a result, an appropriate measurement of amorphous orientation should be directly related to tie-chain concentration. When comparing different polyethylenes, measured dichroism is a function of the degree of orientation (i.e., tie-chain extension) as well as the number of orienting elements (tie-chain concentration). Hence, if the tie-chain extension is kept the same, the measured amorphous dichroism would be proportional to tie-

chain concentration. To obtain an accurate measure of amorphous orientation, Lustiger et al.[1] had to chlorinate the deformed samples, which made the procedure more tedious. Brown and Ward[8] have proposed that variations in brittle fracture strength relate to the tie-chain concentration. Hence, tie-chain concentration can be characterized by measurement of brittle fracture strength. The relationship between brittle fracture strength and tie-molecule concentration is more correlative and lacks clear foundation. However, it is reasonable to conclude that the number of linking molecules should have some influence on the measured engineering fracture strength. In this report we propose a different method, using postyield deformation response of a polymer for characterization of the concentration of static and dynamic junction points (tie chains) in a semicrystalline network.

The mechanical behavior of semicrystalline polymers in the postyield region can be regarded as that of a deformable network of chains linked by crystallites. The tie chains and the entangled chains in the amorphous phase behave like network chains in a crosslinked rubber during deformation.[14] Hence, the rubber elasticity theory can be applied to understand and predict the deformation behavior of semicrystalline polymers during orientation if, and only if, as a result of deformation a subsequent stable state is formed at the applied deformation rate. The stable-necked state in thermoplastics and the strain-hardened state in elastomers are examples of such stable states. In the absence of such a state, failure
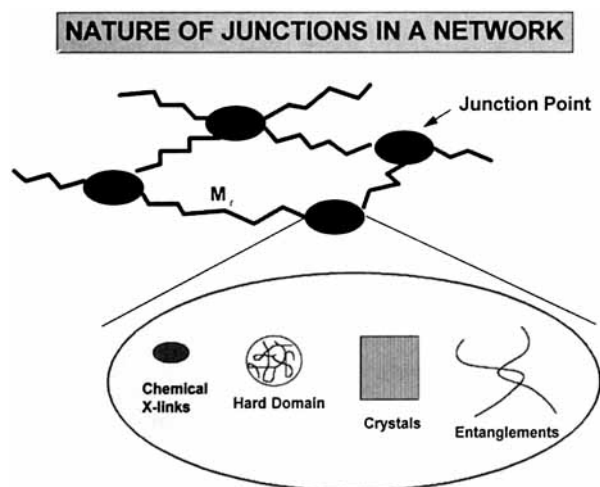
Figure 4   The schematic of nature of various types of junctions in a network.

occurs immediately after necking by continuous thinning down without neck propagation until the true fracture strength is achieved.

In the case of an ideal rubber, chemical crosslinks provide junction points in the network. In the case of styrenic block copolymers, polystyrene hard domains provide junction points in the network. In the case of semicrystalline polymers, crystallites and chain entanglements provide junction points ("crosslink sites") in the network. The schematic of the nature of various types of junctions in a network is shown in Figure 4. Hence, from the deformation behavior of semicrystalline polymers, by invoking the rubber elasticity theory, the number of chains between junction points per unit volume (i.e., tie-chain concentration) can be estimated. Note that chain entanglement density depends on the stretching rate, due to viscoelastic relaxation. In other words, the number of junction points due to chain entanglements can increase with increasing stretching rate.

For uniaxial deformation, the stress–strain relationship from rubber elasticity theory can be written as follows:

$$\sigma_{\text{true}} = G\left(\lambda^2 - \frac{1}{\lambda}\right), \qquad (1)$$

where λ = Extension (draw) Ratio (L/L_o), G = Rubber Modulus = $NkT = \rho RT/M_c$ (N = number of network chains per unit volume or tie-chain concentration, k = Boltzman constant, R = universal gas constant = 8.31 J/mol/°K, ρ = density, T = absolute temperature, °K, M_c = molecular weight between junction points). Thus, according to the rub-

ber elasticity theory, true stress during deformation at a given temperature is a function of draw ratio (i.e., tie-chain extension) and rubber modulus (i.e., chain links or tie-chain concentration). The rubber modulus estimated using the above approach is directly proportional to the concentration of chain links between the junction points. The rubber elasticity theory cannot be applied up to the yielding of crystallites, as deformation up to yielding is based on Hookean (energetic) elasticity. This is based on the hypothesis that the crystals prevent large changes in configurational entropy of the chains. The rubber elasticity theory can be applied to deformation beyond yielding as the deformation occurs due to molecular chain extension (entropic elasticity). The modified rubber elasticity concept is schematically illustrated in Figure 5. The modified rubber elasticity theory can be stated as follows:

$$\sigma_{\text{true}} = \sigma_o + G_p\left(\lambda^2 - \frac{1}{\lambda}\right), \qquad (2)$$

or, in terms of engineering stress,

$$\sigma_{\text{Eng}} = \frac{\sigma_o}{\lambda} + G_p\left(\lambda - \frac{1}{\lambda^2}\right). \qquad (3)$$

As previously noted by Haward,[14,15] eq. (3) has a maximum value at low strain when $\sigma_o/\lambda > 3$, which coincides with the Considere criterion for necking. Haward has applied modified rubber elasticity theory [eq. (2)] to various polymers and has shown that it described the deformation behavior very well.[13,14] However, Haward's approach has overlooked some critical details of the necking process that has been illustrated in recent publications.[16,17]
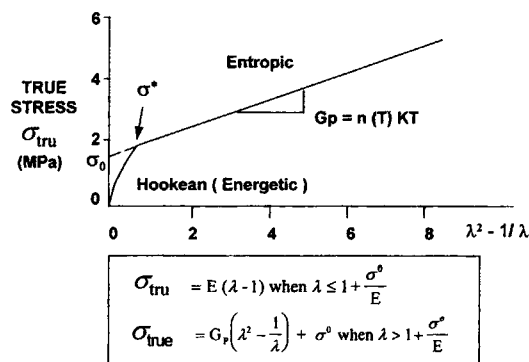

Figure 5   The schematic of the modified rubber elasticity concept.

The true strain in Haward's approach was directly estimated from engineering strain, which cannot be true when the sample exhibits necking, which is a very localized process.

The engineering stress–strain data were obtained on a series of INSITE[†] technology polymers (ITP) of varying densities with melt index equal to one (M_w close to 95,000). A displacement rate of 20 in/min (over a 3 inch grip to grip length) was used in all the measurements. Effect of varying engineering strain rate (0.2 inch/min to 20 inch/min and higher) on stress–strain behavior of ITP resins was investigated in a parallel study. For ITP resins of density below 0.91 g/cc, the effect of strain rate on stress–strain behvaior was insignificant. However, for ITP resin density approaching density 0.955 g/cc, brittle to ductile transition is observed in the strain rate range of 0.04 s^{-1} to 1.1 s^{-1}. However, the measured draw ratio in the case of a stable neck formation was found to be nearly independent of strain rate. Note that true strain rate decreased monotonically during deformation. ITP resins having density greater than 0.90 g/cc exhibited necking while no visible necking was observed for densities less than 0.90 g/cc. For the ITPs exhibiting necking behavior natural draw ratios were measured by marking the specimens. Note that for large deformation, engineering strain ($\Delta L/L_o$) cannot be used to extract any true material parameter such as strain hardening. In large strain measurements, true strain (ln λ) or any suitable measure of true strain, which is a function of draw ratio, λ, should be used. Rubber elasticity theory uses ($\lambda^2 - 1/\lambda$) as a measure of strain or deformation. Also, for ITPs exhibiting necking, the deformation is heterogeneous and the engineering stress–strain curve beyond the yield point has no fundamental significance. For all practical purposes the deformation can be stopped after the neck has developed, as long as one obtains a steady draw stress at the stretching rate. For the ITPs exhibiting necking ($\rho > 0.90$ g/cc) natural draw ratio and draw stress are the two most important large strain parameters and are used to generate the true stress–strain curve. For the ITPs exhibiting homogeneous deformation, the true stress–strain curve can be obtained directly from engineering stress–strain data up to the point of formation of a subsequent rigid state (probably due to strain-induced crystallization). Once the rigid state is formed, a more involved composite analysis should be used.

The true stress–strain data of ITPs of densities 0.8564 g/cc, 0.873 g/cc, and 0.886 g/cc are shown in Figure 6. The best fit of the data in the rubber elastic region is also shown in Figure 6. These ITPs exhibited homogeneous deformation (no necking) up to very high draw ratios. It can be seen that deformation of these ITPs follows the simple rubber elasticity theory up to a draw ratio of about 5. In the case of 0.886 g/cc ITP, stress-whitening was obtained after a draw ratio of about 5 (as indicated by an arrow in Fig. 6), which also coincided with the departure of the true stress–strain curve from the rubber elasticity theory. This departure at the draw ratio of about 5 is thought to be due to stress-induced crystallization between the highly oriented crystal fibers leading to formation of additional junction points. In this region the rubber elastic concept is not applicable, because the oriented frozen state practically does not allow any strain recovery. From these true stress–strain data the rubber modulii of ITPs are obtained from the slope of the best fit line. The intercept gives the value of σ_o. Once the rubber modulus and intercept σ_o are measured as a function of ITP density (<0.90 g/cc) and melt index, the tensile stress–strain curves, over a limited range of deformation, of any ITP can be predicted using modified rubber elasticity theory. The rubber modulus is directly proportional to the concentration of chain links (includes tie chains in the sample and entanglements) between junction points and, hence, can be taken as a relative measure of tie-chain concentration.

As mentioned before, the ITPs having densities greater than 0.90 g/cc exhibited necking. The degree of necking is characterized by the "draw ratio," which is defined as the length of a fully necked specimen divided by the original length. The rubber modulus in such cases was calculated from the measured natural draw ratio and draw stress as follows:
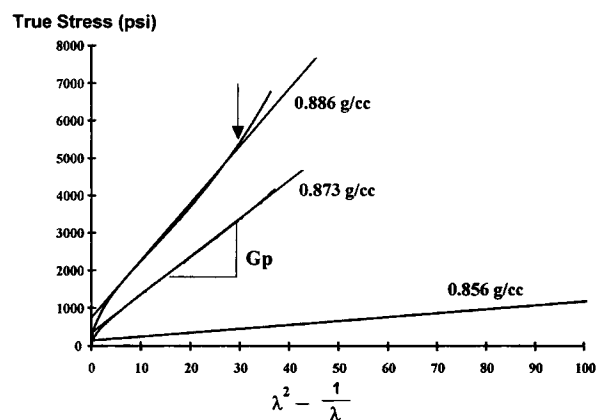

Figure 6 The true stress–strain data of ITPs of densities 0.8564 g/cc, 0.873 g/cc, and 0.886g/cc.

$$G_p = \frac{\sigma_{dr}\lambda_n - \sigma_{dr}}{\lambda_n^2 - \dfrac{1}{\lambda_n}} \qquad (4)$$

where σ_{dr} is the engineering draw stress and λ_n is the natural draw ratio. Natural draw ratio was measured by marking the samples and was the ratio of separation of the marks in the necked and unnecked region. This equation assumes that deformation in the boundary between the necked region and the unnecked region follows the rubber elasticity theory. Note that experimentally it is very challenging to measure the nature of such transition.

The measured rubber modulus data of the ITPs are plotted as a function of density in Figure 7. Note that the rubber modulus estimated using the above approach is directly proportional to the concentration of chain links between the junction points. Rubber modulus or concentration of chain links increases with increase in density in the 0.865 to 0.910 g/cc range. The calculated concentration of chain links did not change significantly from about 0.91 g/cc to 0.954 g/cc. This is in contrast to the calculated tie-chain density from the Huang and Brown model using the Thompson–Gibbs equation (see Fig. 3), in which case tie-chain concentration exhibited a maximum at about 0.91 g/cc density and decreased significantly from 0.91 g/cc to 0.954 g/cc. This difference may be due to formation of additional tie-chains during deformation due to lamellar sliding and breaking down of crystallites for a necked polymer, which is not taken into account in Huang and

Brown's model. Beyond 0.91 g/cc density, failure may also occur prematurely, due to lack of mobility, when true stress on a fracture plane ($\sigma_{dr}\lambda_n$) approaches fracture strength of polyethylene.

Both rubber modulus and relative tie-chain concentration was normalized with respect to their maximum values and plotted as a function of ITP resin density in Figure 8. Figure 8 shows that the relative tie-chain concentration predicted by Huang and Brown model and measured using the modified rubber elasticity theory are quantitatively similar below 0.91 g/cc density. However, above 0.91 g/cc density, the measured rubber modulus is influenced by additional tie-chain formation due to breakdown of crystallites as explained above, and hence, the discrepancy exist between the two methods of estimating relative tie-chain concentration.

SUMMARY AND CONCLUSIONS

The Huang and Brown model for calculating tie-chain probability using chain dimensions is used to calculate tie-chain concentration of monodisperse single site ethylene copolymers. The melting point and wt % crystallinity data of ITP resins, measured using a Perkin–Elmer DSC-7, are used in the calculations. To calculate critical end-to-end distance, L_c was obtained from the melting point–lamellar thickness relationship (Gibbs–Thompson equation) and L_a was obtained using the two-phase lamellar stack model.
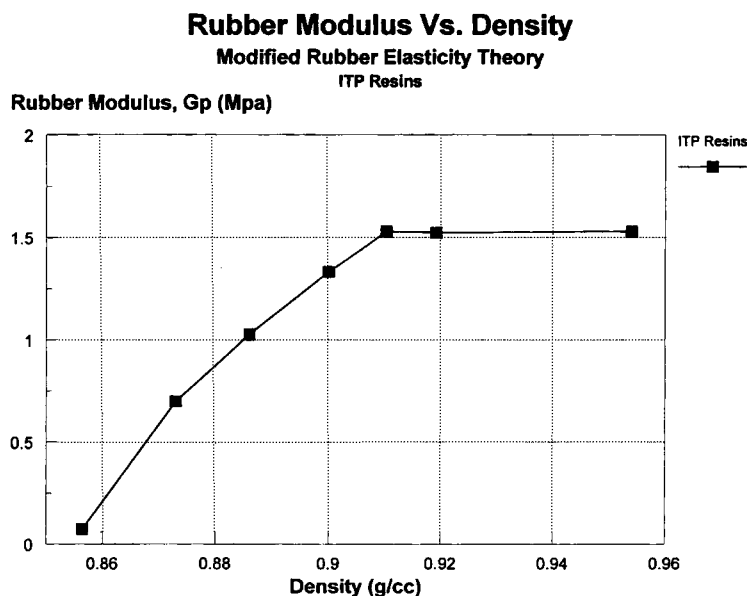
Rubber Modulus Vs. Density
Modified Rubber Elasticity Theory
ITP Resins

Figure 7   The plot of measured rubber modulus of the ITPs as a function of density.

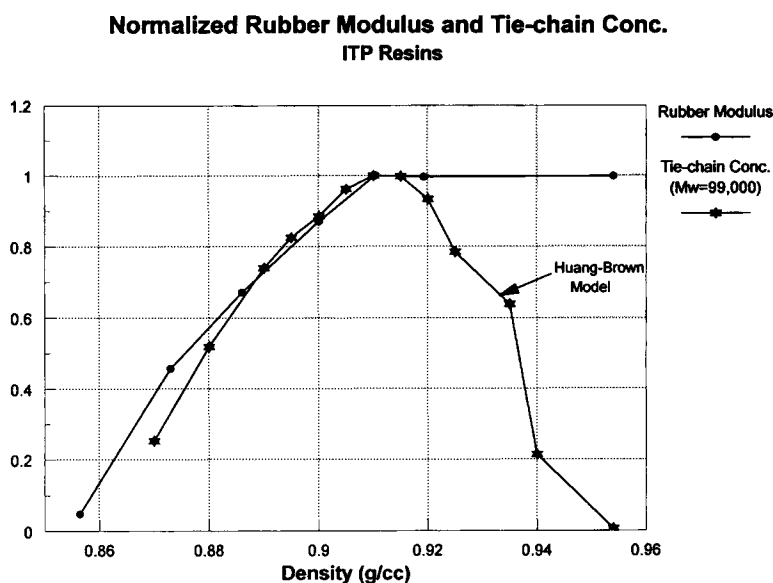**Normalized Rubber Modulus and Tie-chain Conc.**
ITP Resins

Figure 8 The plot of normalized rubber modulus and relative tie-chain concentration as a function of ITP resin density.

To obtain relative tie-chain concentration from probability of tie-chain formation, one needs to take into account the crystallinity of the polymer. The relative tie-chain concentration was calculated by multiplying tie-chain probability with fraction crystallinity of polymers.

The Huang and Brown model considers the effect of comonomer type on tie-chain probability only indirectly, i.e., through its effect on L_c and L_a. This may not be sufficient for estimating the effect of comonomer type such as 1-butene, 1-hexene, 1-octene, etc., on the tie-chain formation and its effect on resultant mechanical properties.

The mechanical behavior of semicrystalline polymers in the postyield region can be regarded as that of a network linked by crystallites. The tie chains in the amorphous region, where the molecules have high local mobility, behave like a rubber phase. Hence, rubber elasticity theory is applied to calculate the tie-chain concentration of semicrystalline polymers from measured rubber modulus. The rubber elasticity theory is modified and is applied to the postyield true stress–strain behavior of various ITP resins. For the ITP resins exhibiting necking ($\rho > 0.90$ g/cc), it is assumed that the deformation in the boundary between the necked region and the unnecked region follows the rubber elasticity theory.

The measured rubber modulus or tie-chain concentration of ITPs increased with increase in density in the 0.865 to 0.910 g/cc range and did not change significantly in the density range of about 0.91 g/cc to 0.954 g/cc. This is in contrast to the calculated

tie-chain density from the Huang and Brown model, in which case tie-chain concentration exhibited a maximum at about 0.91 g/cc density and decreased significantly from 0.91 g/cc to 0.954 g/cc. This difference may be due to formation of additional tie chains during deformation due to lamellar sliding and breaking down of crystallites for a necked polymer, which is not taken into account in Huang and Brown's model.

Normalized rubber modulus and relative tie-chain concentration data shows that the relative tie-chain concentration predicted by Huang and Brown model and measured using the modified rubber elasticity theory are quantitatively similar below 0.91 g/cc density. However, above 0.91 g/cc density, the measured rubber modulus is influenced by additional tie-chain formation due to breakdown of crystallites, and hence, the discrepancy exist between the two methods of estimating relative tie-chain concentration.

APPENDIX A

Huang–Brown Model: probability of tie-chain formation for a monodisperse polymer is given by

$$P = \frac{1}{3} \frac{\int_{L}^{\infty} r^2 \exp(-b^2 r^2) dr}{\int_{O}^{\infty} r^2 \exp(-b^2 r^2) dr} \quad (A)$$

$$b^2 = \frac{3}{2\bar{r}^2} \quad (B)$$

$$\bar{r}^2 = (Dnl^2) \quad (C)$$

where

P = Probability of tie-chain formation
L = Critical distance = $2L_c + L_a$
L_c = Lamella thickness
L_a = Amorphous layer thickness
D = Chain extension factor in melt = 6.8 for polyethylene
n = Number of links
l = The link length = 1.53 A° for polyethylene

The lamellar thickness was calculated from the Thomson–Gibbs equation as follows:

$$T_m = T_m^o \left(1 - \frac{2\sigma_e}{\Delta H_f L_c} \right) \quad (D)$$

Where, the parameters used are as follows:

T_m^o = Equilibrium melting point of polyethylene = 414°K
σ_e = Surface free energy = 93 erg/cm^2
ΔH_f = Heat of fusion = 2.92 × 10^9 erg/cm^3

The amorphous layer thickness was calculated using $L_a = \rho_c L_c (1 - X_c)/\rho_a X_c$, where X_c is the wt % crystallinity, ρ_c = crystalline density = 1.00 g/cc, ρ_a = amorphous density = 0.852 g/cc.

Gamma Function

An analytical solution is available for the following integral,

$$\int_0^{\infty} X^{2n} \exp(-aX^2) dX$$

$$= \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}$$

Comparing with eq. (A), $n = 1$ and $a = b^2$. Hence,

$$\int_0^{\infty} r^2 \exp(-b^2 r^2) dr = \frac{\sqrt{\pi}}{4b^3}$$

For $n = 6000$, $D = 6.8$, and $l = 1.53\, A°$, $b^2 = 3/(2Dnl^2)$ gives $b = 3.963E-03$ and the value of the integral from zero to infinity is 7119387. From numerical integration using the Simpson rule, value of 7119306 was obtained, which matched very well with the analytical value.

REFERENCES

1. A. Lustiger and N. Ishikawa, *J. Polym. Sci., Polym. Phys.*, **29**, 1047 (1991).
2. Y. Huang and N. Brown, *J. Polym. Sci., Polym. Phys.*, **29**, 129 (1991).
3. S. Hosoda and A. Uemura, *Polym. J.*, **24**, 939 (1992).
4. L. L. Bohm, H. F. Enderle, and M. Fleibner, *Adv. Mater.*, **4**, 234 (1992).
5. N. Brown, X. Lu, Y. Huang, I. P. Harrison, and N. Ishikawa, *Plast. Rubber Compos. Proc. Appl.*, **17**, 255 (1992).
6. J. T. Yeh and J. Runt, *J. Polym. Sci., Polym. Phys.*, **29**, 371 (1991).
7. Z. Zhou, X. Lu, and N. Brown, *Polymer*, **34**, 2520 (1993).
8. N. Brown and I. M. Ward, *J. Mater. Sci.*, **18**, 1405 (1983).
9. E. W. Fisher, K. Hahn, J. Kugler, U. Struth, and J. Born, *J. Polym. Sci., Polym. Phys.*, **22**, 1491 (1984).
10. Y. C. Hwang, S. Chum, R. Guerra, and K. Sehanobish, *ANTEC '94*, 3414 (1994).
11. S. Bensason et al., proceedings of SPE ANTEC, Boston, 1995.
12. S. Hosoda, *Polym. J.*, **20**, 383 (1988).
13. L. Lu, R. G. Alamo, and L. Mandelkern, *Macromolecules*, **27**, 6571 (1994).
14. R. N. Haward, *Macromolecules*, **26**, 5860 (1993).
15. R. N. Haward, *Polymer*, **28**, 1485 (1987).
16. Z. Zhou, A. Chudnovsky, C. P. Bosnyak, and K. Sehanobish, *Polym. Eng. Sci.*, **35**, 304 (1995).
17. G. Buisson and K. Ravi-Chander, *Polymer*, **31**, 2071 (1990).