

Effect of Chain Microstructure on Modulus of Ethylene- α -Olefin Copolymers

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SYNOPSIS

A family of copolymers of ethylene and α -olefin resins with homogeneous branching distribution, which behaves as elastomers at high short-chain branching levels and acts as typical thermoplastics at low short-chain branching levels, is now available. Control of this broad range of properties stems from the ability to control the molecular architecture more effectively using Dow's INSITE^{®†} technology than in the past. Due to the unique combination of narrow short-chain branching distribution (SCBD) and narrow molecular weight distribution (MWD), these resins provide a unique opportunity to model structure/property relationships in branched ethylene- α -olefin copolymers. The modulus in branched ethylene- α -olefin copolymers with aliphatic branches is shown to be primarily dictated by crystallinity. It is shown that the branch distribution and the branch type have an insignificant effect on the modulus of ethylene copolymers containing aliphatic branches at a given crystallinity. Modulus data have been successfully modeled in such systems using a lamellar fiber-reinforced amorphous matrix composite model. Switching from aliphatic branches to cyclic branches significantly affected the modulus at similar crystallinities. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

A family of short-chain-branched ethylene- α -olefin copolymers with a homogeneous branching distribution, which behaves as elastomers at high short-chain branching levels and acts as typical thermoplastics at low short-chain branching levels, is now available. Control of this broad range of properties stems from the ability to control the molecular architecture more effectively using Dow's INSITE^{®‡} technology than in the past. Copolymers of ethylene and α -olefins synthesized using conventional heterogeneous (multisite) catalysts yield copolymers with a broad molecular weight distribution and a broad distribution of short-chain branches. Practically all commercial linear low-density ethylene- α -olefin copolymers belong to this category, with variations in short-chain branch type. Recently, using

Dow's INSITE technology, a new set of resins has been synthesized with fairly narrow distributions of short-chain branches (SCBD) and molecular weight (MWD). Typical analytical temperature rising elution fractionation (ATREF) curves of conventional linear low-density polyethylene (LLDPE) and the INSITE technology polymers (ITP), of similar density, are compared in Figure 1. The significant breadth of the ATREF curve for the conventional heterogeneous LLDPE illustrates its broad SCBD.

The unique combination of narrow SCBD and narrow MWD of the ITP resins provides a unique opportunity to model structure/property relationships in branched ethylene- α -olefin copolymers. In this report, the modulus response of various polyethylene resins, including a family of ITP resins, will be discussed. The modeling of the modulus response of semicrystalline polymers in terms of their crystalline and amorphous phase moduli has been attempted several times in the past by various researchers.¹⁻¹⁸ All these modeling efforts considered ethylene- α -olefin copolymers of density 0.90 g/cc (about 32% volume fraction crystallinity) and above. In most of these papers, the amorphous phase mod-

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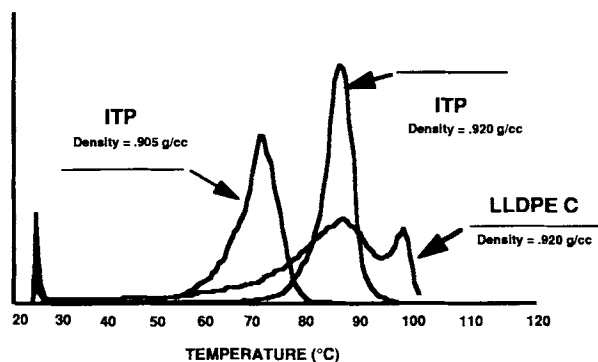


Figure 1 ATREF curves for an LLDPE resin and an INSITE technology resin of similar density.

ulus was assumed to be independent of crystallinity. Boyd¹⁹ suggested that properties of the amorphous layers in the semicrystalline composite could be influenced by its proximity to and its connection to the crystal surfaces. In fact, in the same paper, Boyd also claimed that "the major effect of varying crystallization conditions and crystallinity is to vary the crystal thickness leaving the amorphous layer thickness, and perhaps the properties, relatively constant." Crist et al.²⁰ used the original Tsai-Halpin equation to calculate the amorphous modulus from the total modulus and claimed that the amorphous modulus can increase by 2 orders of magnitude as the volume fraction crystallinity increases from 10 to 70% in ethylene- α -olefin copolymers. The crystal aspect ratio-dependent parameter, ξ , in the Tsai-Halpin equation was arbitrarily taken to be equal to one by Crist et al.²⁰ They justified the strong dependence of amorphous modulus on crystallinity based on mechanical relaxations occurring in ethylene- α -olefin copolymers. Although the concept of an increasing amorphous modulus with increasing crystallinity may make physical sense, an increase of 2 orders of magnitude may not be acceptable. The role of the amorphous fraction and complexities of the chain microstructure on modulus of semicrystalline ethylene- α -olefin copolymers over a very wide range of crystallinity will be addressed in this article.

EXPERIMENTAL

The initial modulus (below 1% strain) and general stress-strain behavior of a family of ITP resins have been experimentally determined. Density (crystallinity) of these resins is the key variable in this study. Variations in melt index (I_2), as measured by ASTM D-1238 condition E, have been introduced in a few cases to study the effect of molecular weight.

To examine the effect of short-chain branch (SCB) type on solid-state properties, a variety of resins with different SCB types was used. These include ITP resins with hexyl branches (octene copolymer), four single-site catalyst resins with ethyl branches (SSE), a high-pressure low-density polyethylene (LDPE) with long-chain branching, and heterogeneous LLDPE resins with hexyl branches. Compression-molded plaques were made out of these resins as follows: Resin, in pellet form, was heaped into the center of a rectangular, metallic mold. The mold was placed between two aluminum foil sheets, sandwiched between two photographic plates, and backed by two steel plates. Molding was done for all specimens under ASTM conditions of a 15°C/min cooling rate. Three air-quenched specimens were also included in the study to verify the effect of cooling rate. Density and melt index (I_2) of all the SCB resins chosen for this study are shown in Table I. The densities were measured on the plaques.

Tensile experiments were done on an Instron Model 1125 primarily following the ASTM D-412 test method. All initial modulus (E_i) measurements were done by pulling each specimen in tension to 5% strain, at test rates of 0.2 in./min, using a 3 in.

Table I Density and Melt Index of Short-chain Branched Ethylene Based Copolymers

Resin Type	Branch Type	Density (g/cc)	Melt Index (I_2)
ITP	Hexyl	0.856	1.0
ITP	Hexyl	0.878	3.6
ITP	Hexyl	0.873	0.6
ITP	Hexyl	0.886	1.0
ITP	Hexyl	0.889	3.4
ITP	Hexyl	0.902	1.1
LLDPE A	Hexyl	0.905	0.8
ITP	Hexyl	0.908	4.7
ITP	Hexyl	0.910	1.0
LLDPE B	Hexyl	0.912	1.0
ITP	Hexyl	0.919	1.0
LLDPE C	Hexyl	0.920	1.0
ITP	Hexyl	0.940	31.6
ITP	Hexyl	0.950	1.0
ITP	Hexyl	0.954	0.9
SSE	Ethyl	0.872	2.8
SSE	Ethyl	0.880	10.0
SSE	Ethyl	0.882	35.0
SSE	Ethyl	0.885	2.2
Cyclic olefin	Norbornene	0.940	—
Cyclic olefin	Norbornene	0.939	—
Cyclic olefin	Norbornene	0.934	—

grip separation. E_i was obtained by determining the slope of a linear fit of the stress-strain data between 0.2 and 1.0% strain. Beyond 5% strain, all samples display extensive nonlinearity at this test rate. All modulus data used in this report are plotted with a 20% error bar estimated from cumulative error analysis. The error bars in the plots represent absolute error. Actual standard deviations for the modulus data were less than 10%.

RESULTS AND DISCUSSION

Figure 2 displays the effect of density on the modulus of the ITP resins for densities ranging from 0.856 to 0.954. Initial modulus increased from 1.5 to 834 MPa in the range of density studied. Since the data in Figure 2 include melt indices ranging from 0.6 to 31.6, it is clear that melt index played an insignificant role on the modulus. As mentioned earlier, the density of these resins is varied simply by changing the comonomer content. The specimens with the highest density have the lowest comonomer content. It is clear that either density or the comonomer content could serve as an independent variable for correlating with the modulus. However, density is more appropriate due to its direct relationship with crystallinity. The effect of density on modulus is clearly nonlinear.

To verify whether this nonlinearity can be described by a single exponential function, the modulus was plotted as a function of density on a semilogarithmic scale (Fig. 3). It is evident from Figure 3 that a single exponent does not describe the modulus

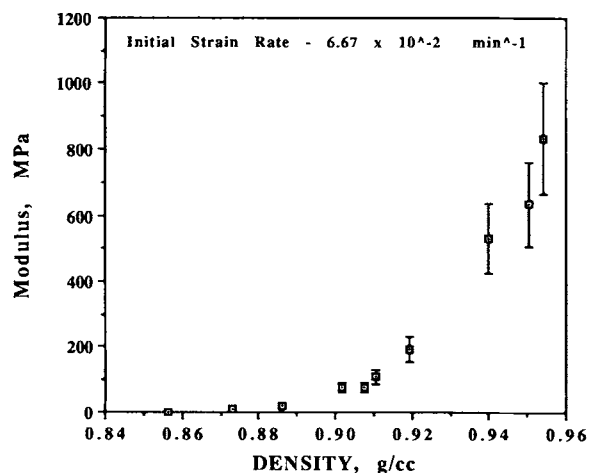


Figure 2 Modulus vs. density of INSITE technology resins on a linear scale.

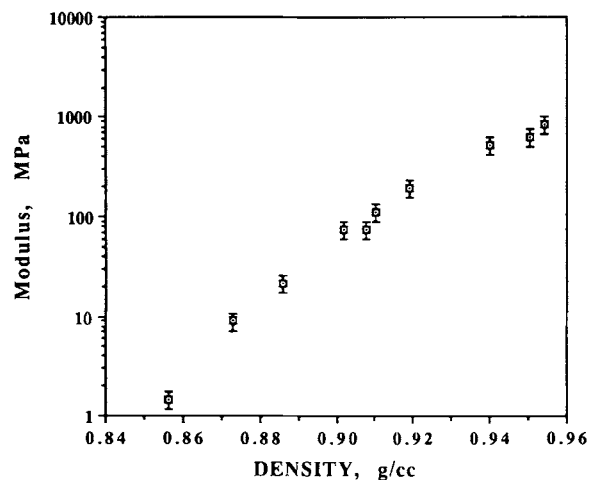


Figure 3 Modulus vs. density of INSITE technology resins on a semilogarithmic scale.

data in the entire density range. In fact, one can argue that there are at least two types of exponential behavior centered around 0.92 density. Figure 3 shows that below 0.92 density the slope of the line is higher than that above 0.92 density, as shown by the two intersecting lines representing the best fit of the data above and below 0.92. Whether this transition is determined by morphology needs to be addressed. First, let us investigate the semicrystalline composition of the ITP resins.

Role of Branches on Overall Density

Since density is the primary variable, it is necessary to examine the chain microstructure that leads to the measured density. The octene in the copolymer results in the formation of hexyl branches. It is well known that the hexyl branches cannot be accommodated in the crystal lattice. Thus, it is expected that the octene content of the resin will directly influence the density, i.e., crystallinity. The relationship between density and wt % octene in the copolymers of similar melt indices is shown in Figure 4. It must be noted that the relationship between octene content and density can also be affected by processing and the molecular weight of the resin. However, in this study, the processing method is held constant by choosing compression molding followed by controlled cooling. Once again, it is noted in Figure 4 that the nature of the density-octene relationship is different above and below 0.92 density. The volume fraction crystallinity can be calculated from the density as follows:

$$X_c = \frac{\rho - \rho_a}{\rho_c - \rho_a} \quad (1)$$

where ρ is the density of polymer; ρ_c , the density of the crystalline fraction; ρ_a , the density of the amorphous fraction, and X_c , the volume fraction crystallinity. To verify whether this relationship is linear, the role of branches on the amorphous density needs to be determined. Direct measurement of amorphous density at low levels of branching is practically impossible, since ethylene- α -olefin copolymers crystallize at a very fast rate, so that at room temperature a completely amorphous polymer cannot be obtained. Experimental approaches based on extrapolation have been employed by several investigators. This type of approach yields an amorphous density of 0.852 g/cc.¹⁻³ However, there is very little literature available on the effect of chain microstructure on amorphous density. Some work has been done on polyisoprene with vinyl branches and on hydrogenated polybutylene (HPB). Hydrogenation saturates the backbone and converts the vinyl branches into ethyl branches. Graessley et al.⁴ reported data on the effect of branching on density in noncrystalline HPB systems. Figure 5 shows a plot of the mol fraction of vinyl vs. density. As expected, the data extrapolate to the amorphous density of linear polyethylene at zero mol fraction.⁴

It is expected that the mol % octene will have a similar effect on the amorphous density. However, octene mol % in the entire range of density (0.96–0.86 g/cc) for ITP resins is between 0 and 20%. Since one can safely assume that the crystallites do not incorporate hexyl branches, all the hexyl branches will be in the amorphous phase. Based on Figure 5, for HPB systems, it will amount to less than 0.4% variation in amorphous density. Thus,

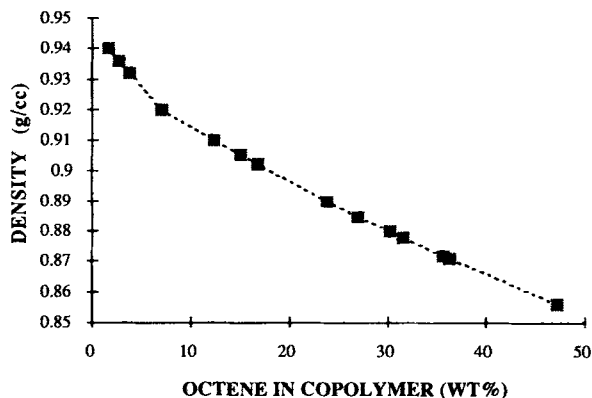


Figure 4 Density vs. wt % octene relationship in Insite technology resins.

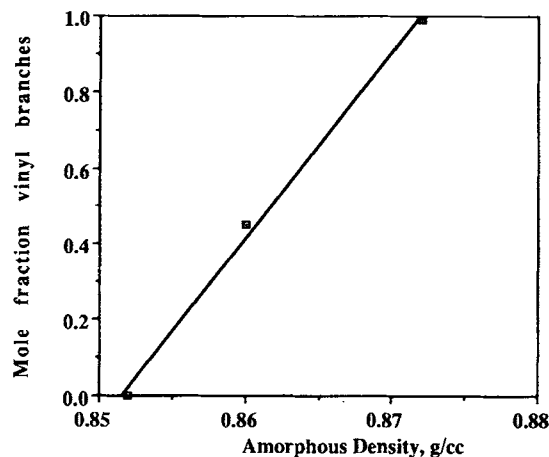


Figure 5 Mol fraction of vinyl branches vs. amorphous density for HPB.

amorphous density can be assumed to be constant equal to 0.852 g/cc. Thus, eq. (1) should provide a fairly good estimate of crystallinity, at least for the density region above 0.87 g/cc. Since the role of branches on amorphous density is practically insignificant, the density variation in ITP resins is dictated by crystallinity. Furthermore, one can confirm the density vs. crystallinity relationship by independent measurement of wt % crystallinity from DSC. Heat of fusion of 100% crystalline polyethylene was taken to be 292 J/g. Figure 6 shows the calculated wt % crystallinity from density against the measured crystallinity from DSC. The error associated with the measurements are within $\pm 5\%$. Good agreement is emphasized with all the data falling along the diagonal.

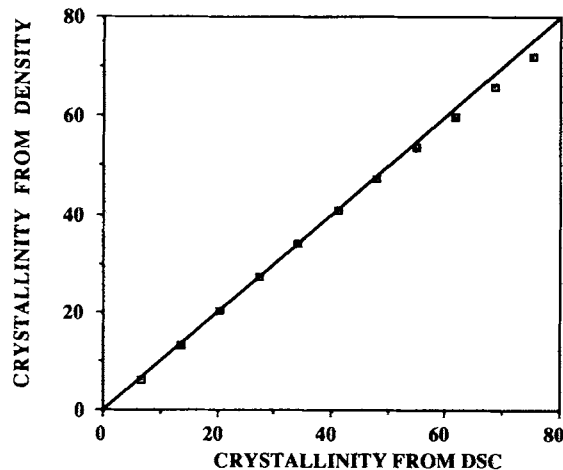


Figure 6 Crystallinity calculated from density vs. crystallinity measured from DSC.

Effect of Branch Distribution and Branch Type on Modulus

Next it was considered whether the modulus–density relationship is affected if the SCB distribution is broad, as in the case of heterogeneous (multisite catalyst) ethylene- α -olefin copolymers. Several heterogeneous ethylene- α -olefin copolymers were included in the modulus studies and compared with the ITP resins. These are LLDPE A (0.905 g/cc), LLDPE B (0.912 g/cc), and LLDPE C (0.92 g/cc). Figure 7 shows the effect of density on modulus, including these specimens, plotted on a semilogarithmic scale. It can be seen that the distribution of branches played an insignificant role on the density–modulus relationship.

There are several possibilities if one considers branch type. For example, if the comonomer type is changed from 1-octene to 1-butene, branch type changes from hexyl to ethyl. In this section, single-site catalyst polyethylene with ethyl branches and ITP resins with hexyl branches are also considered. Additionally, a significant change in the branch type is introduced using norbornene as a comonomer, resulting in cyclic olefin copolymers. It is expected that introduction of norbornene will significantly affect the chain mobility, leading to an increase in amorphous modulus. Note that norbornene units would be totally excluded from the crystallites. Four single-site resins with ethyl branches were used for this study. All four specimens were in the density range between 0.87 and 0.885 g/cc. Moduli of these specimens are included in Figure 8 along with ITP resins to verify the effect of ethyl branches on modulus. It is evident, within experimental error, that

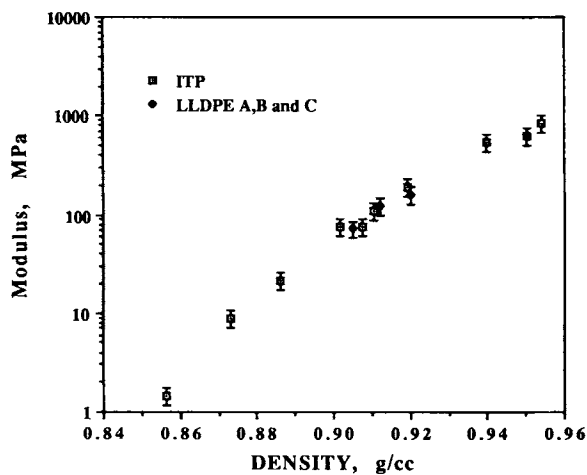


Figure 7 Modulus vs. density for INSITE technology and multisite catalyst polyethylene on a semilogarithmic scale.

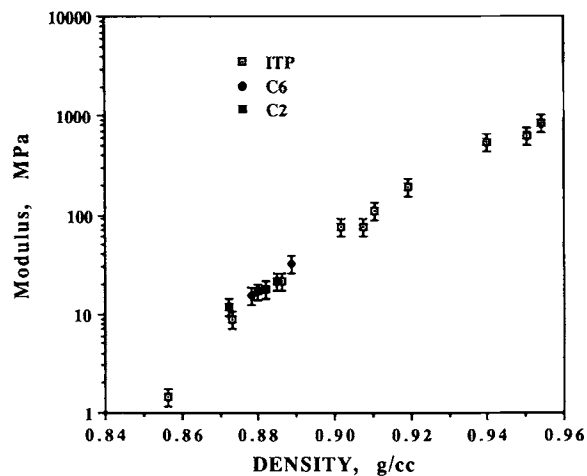


Figure 8 Modulus vs. density of ethylene- α -olefin copolymers with different branch types.

the change in branch type from hexyl to ethyl did not make a significant difference in the modulus–density relationship.

Since single-site resins with ethyl branches used in this study were limited in density range, a comparison of ITP resin modulus data was made with published secant modulus data⁵ of single-site ethyl- and butyl-branched specimens in this range to verify the role of branch type. Below 0.92 density, all modulus data of the ITP resins and single-site resins practically superimposed. However, the published data did not elaborate enough on the experimental technique to make a direct comparison. To further confirm that density (i.e., crystallinity) is the primary variable controlling the modulus of polyethylene based resins, modulus of high-pressure low-density polyethylene (LDPE) with long-chain branches was measured. For an LDPE of density of 0.919 g/cc and a melt index of 0.22, the modulus value is 208.64 ± 20 MPa. This is well within the expectation of the modulus–density relationship discussed so far.

However, if a cyclic structure such as norbornene is used as a comonomer, the amorphous density and the amorphous modulus will be significantly affected over the crystallinity range. In such systems, an increase in density does not always imply an increase in crystallinity, since the amorphous phase density changes with the amount of norbornene comonomer. At wt % crystallinity levels of 14.4, 23.8, and 49, the measured densities of the cyclic olefins were 0.940, 0.9386, and 0.934 gm/cc, respectively. It can be seen from Figure 9 that the modulus of an ethylene–norbornene copolymer at a given crystallinity is slightly higher than that of ethylene- α -olefin copolymers within the limits of experimental error. This is

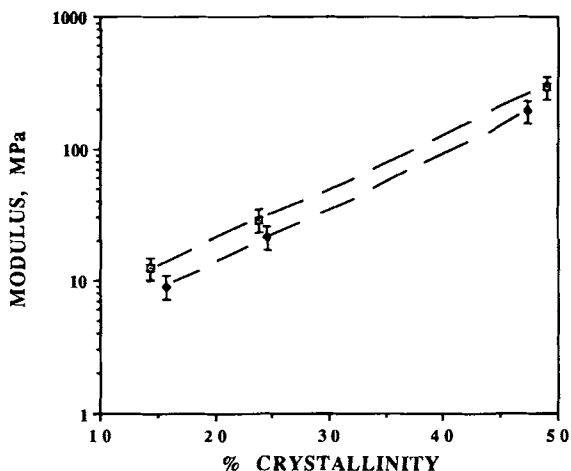


Figure 9 Comparison of modulus vs. crystallinity for the cyclic olefin copolymer and INSITE technology copolymers.

probably due to the higher amorphous modulus of the ethylene–norbornene copolymers. Note that the cyclic branch in the ethylene–norbornene copolymer is more rigid than is the aliphatic hexyl branch in the ethylene–octene copolymer, and both norbornene and hexyl branches are excluded from polyethylene crystallites. Thus, at similar crystallinity, both copolymers would have similar crystal aspect ratio. Also note that the glass transition temperature of the ethylene–norbornene copolymer increases with increasing norbornene content. For example, at 45 mol % norbornene, the copolymer exhibited a glass transition temperature of about 100°C as measured by DSC.

Modeling Modulus Response

Based on these observations, it appears that a composite model of crystalline and amorphous phases is the best way to describe the modulus of ethylene– α -olefin copolymers. To obtain the upper-bound and the lower-bound behavior, two simple combinations of amorphous and crystalline phases are first considered. If X_c is the volume fraction crystallinity, the upper- and lower-bound behavior can be obtained by simple linear combinations of amorphous and crystalline phase moduli as shown below:

Upper-bound behavior (parallel element):

$$E_t = E_c \times X_c + E_a \times (1 - X_c) \quad (2)$$

Lower-bound behavior (series element):

$$\frac{1}{E_t} = \frac{X_c}{E_c} + \frac{1 - X_c}{E_a} \quad (3)$$

where E_a , E_c , and E_t are the amorphous phase modulus, crystalline phase modulus, and total modulus, respectively.

It has been speculated in the past that the rubbery modulus of the amorphous content of the semicrystalline material may not be completely independent of crystallinity.^{19,20} It is believed that the properties of the amorphous material will be influenced by its proximity to and its connection to the crystal surface. Unfortunately, there is no direct measurement for the amorphous modulus to confirm its role.

In the present calculations, the amorphous modulus was assumed to be independent of crystallinity. Extrapolation of the present data to 0.852 density yields an E_a of 1.72 MPa (250 psi). E_c of 1.8 GPa (258,000 psi) from the literature was used in these calculations.⁶ As expected, the actual data points lie in the center of the upper- and lower-bound behavior (Fig. 10). This emphasizes that the actual model describing the modulus response should come from a composite theory. We chose to use a composite theory that considers the crystals as rigid fibers in an amorphous matrix.^{7,21} The model treats the system as randomly oriented plies that individually are unidirectional short-fiber composites. Based on this approach, the modulus of the semicrystalline composite with the b -axis of the crystal oriented in the tensile direction is given by the Tsai–Halpin equation as follows:

$$E_t = \frac{E_a [E_c + \xi(X_c E_c + (1 - X_c) E_a)]}{X_c E_a + (1 - X_c) E_c + \xi E_a} \quad (4)$$

In eq. (4), X_c is the volume fraction crystallinity

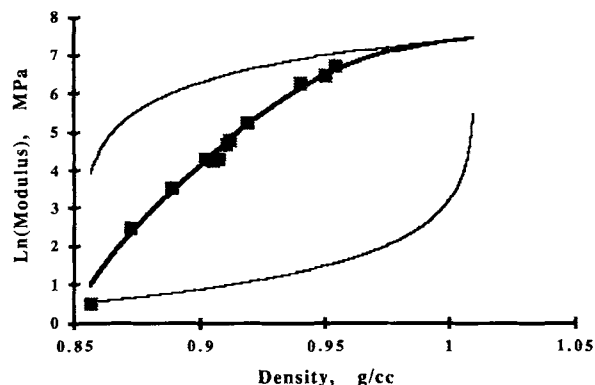


Figure 10 Comparison of predicted modulus using the composite model and the measured modulus as a function of density. Top and bottom curves represent the upper and lower bounds, respectively, whereas the curve in the center displays the fit of the composite model to the actual data points.

and ξ is the crystal aspect ratio-dependent parameter and is equal to $2(L/D)$, i.e., two times the ratio of the length or width of the lamellar fiber and lamellar thickness. It is believed that in the absence of any specific crystallization substrate and if the processing conditions are kept constant the aspect ratio should be a simple function of crystallinity. For simplicity, an exponential increase in the average aspect ratio [of the form $A \exp(BX_c)$, where $A = 4.7$ and $B = 5.5$ are fitting constants with crystallinity was incorporated into eq. (4)]. It can be seen from Figure 10 that the Tsai-Halpin composite model, using aspect ratio-dependent parameter ξ as described and a constant amorphous modulus, adequately describes the modulus data. No attempt was made to verify the assumed aspect ratio as a function of crystallinity. Extensive transmission electron microscopy performed in this laboratory has indicated that the length or width of the lamellar fiber increases much more rapidly than does the thickness with increase in crystallinity for the ITP resins. This lends some credibility to the above assumption of an exponential increase in the aspect ratio with crystallinity. However, for ethylene- α -olefin copolymers, it is extremely tedious and difficult to quantitatively determine the aspect ratio from TEM micrographs or any other combination of scattering techniques. An approximate aspect ratio as measured from these micrographs changed from approximately 1 at 0.856 g/cc to 100 at 0.954 g/cc. Exact experimental determination of this number cannot be accomplished due to curving of lamellae at lower densities. A similar increase in aspect ratio was also assumed by Halpin and Kardos in their attempt to model polyethylene modulus.¹¹

One may question the validity of the approach used earlier by Crist et al.²¹ based on the Tsai-Halpin equation to model the modulus of polyethylene. Crist et al. used the Tsai-Halpin equation to calculate the amorphous modulus from the total modulus and claimed that the amorphous modulus can increase by 2 orders of magnitude as the volume fraction crystallinity increases from 10 to 70% in polyethylene. A two orders of magnitude increase in amorphous modulus is highly improbable. Such a prediction is simply a result of assuming the parameter ξ to be constant throughout the entire density range. The original Tsai-Halpin equation refers to the parameter, ξ , as an aspect ratio-dependent parameter equal to $2(L/D)$. Thus, for morphology with crystal dimensions continuously changing with crystallinity, ξ cannot be assumed constant and must be greater than two. Thus, ξ equal to one used by Boyd¹⁹ and Crist et al.²¹ is also physically impossible.

Another approach to modeling the modulus crystallinity relationship is to use the filled elastomer approach based on hydrodynamic theories. These theories originate from Einstein's viscosity equation. It predicts the modulus of the loaded rubber based on the modulus of the gum rubber. The model implicitly assumes high rigidity of the filler entities; thus, the dimensional changes in the filler due to Poisson's effect is minimum. The semicrystalline ethylene- α -olefin copolymer structure is very analogous, where the crystallites (Lamellar platelets) act as a filler in the rubbery amorphous matrix. Krigas et al.²² actually considered such a model for polyethylene. Assuming crystals to be a spherical entity as required by the Guth-Gold equation for the rubbery matrix, they demonstrated good agreement of the model and the data for small crystallinities.^{22,23} However, the model underpredicted the modulus for high-level crystallinities. The authors expected the failure in predictability because crystalline morphology in polymers is lamellar rather than spherical: Crystallite size and shape must also be determinants of modulus. However, this discrepancy can be effectively removed if one considers the equation by Guth that introduces a shape factor in the original model.²⁴ The original equation then becomes

$$E_t = E_a(1 + 0.6fX_c + 1.62f^2X_c) \quad (5)$$

where f is the aspect ratio of the filler. It is interesting to note that assuming an exponential increase in aspect ratio, eq. (5) predicted the modulus-density relationship as good as did eq. (4). Thus, the role of the crystal aspect ratio changing with crystallinity overlooked by most researchers seems to be very important.

CONCLUSIONS

1. The branch distribution and branch type at similar crystallinities have an insignificant effect on the modulus of ethylene based copolymers containing aliphatic branches.
2. The modulus in branched ethylene- α -olefin copolymers with aliphatic branches over a broad crystallinity range appears to be primarily dictated by crystallinity. This has been successfully modeled in such systems using a lamellar fiber-reinforced amorphous matrix composite model with the crystal aspect ratio-dependent adjustable parameter and using a constant amorphous modulus.

3. Switching from aliphatic branches to cyclic branches as in the ethylene-norbornene copolymer significantly increased the total modulus at similar crystallinities. This is probably due to an increase in the amorphous modulus due to rigid cyclic branches.

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