Physical Properties of Some Ethylene Polymers

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Synopsis

Various physical properties of 43 experimental ethylene–1-olefin copolymers and ethylene homopolymers produced by the Ziegler route were subjected to a statistical analysis. Correlations obtained indicate that the density of these polymers is a function almost solely of the number of branches introduced by the comonomer, regardless of their length. Similarly, tensile modulus and yield strength are shown to depend primarily on density, and to be independent of branch length. Physical properties of commercial resins produced by both low- and high-pressure processes are shown to follow the same relationships. Examination of homopolymers of widely different melt indexes indicates that vinyl unsaturation is not a reliable measure of number-average molecular weight.

Introduction

During the last 15 years, the effect of molecular structure on the physical properties of semicrystalline polymers has been the subject of many publications. In 1953, a comprehensive series of papers appeared which discussed the origin, determination, and significance of branching in polyethylene produced by the high-pressure process.[1-5] It was apparent at that time that two types of branches occur in these polymers. The most common is short-chain branching, in which most of the branches are believed to be four carbon atoms in length while, in addition, there are a few long branches which presumably are of about the same length as the main carbon chain.

When low-pressure coordination catalysts were developed, the production of linear polymers of ethylene became possible. Also, the copolymerization of ethylene with various 1-olefins allowed control of both the length and the amount of short chain branching. Recently Folt published a study of a group of copolymers of ethylene and four different 1-olefins,[6] in which he concluded that the number of branches, and not their length, controlled density and hence the yield and ultimate tensile strengths of these resins. He also found that the tensile strengths of the copolymers were the same as those for high-pressure resins of the same density.

During the operation of a Ziegler process pilot plant elsewhere in the company, we have obtained samples of ethylene polymers ranging in density from 0.920 to 0.965 g./cc. and in melt index from 0.3 to 16 dg./min. Density control was achieved with a variety of 1-olefins, including

propylene, 1-butene, and a variety of 1-olefin distillation fractions up to a C_{18}–C_{20} cut. The physical property data for these resins have been subjected to a statistical analysis which confirms and extends the observation of earlier workers.[5,6] Data obtained in the same manner for a variety of commercial resins produced by both high- and low-pressure processes are also included.

Test Methods

Physical properties for all samples were obtained by using the ASTM procedures indicated in Table I. Test specimens were prepared by compression molding, followed by annealing in either boiling water or an air oven at 120°C. The compression molding procedure was carefully controlled as to mold temperature and pressure, molding time, and rate of cooling in order to obtain reproducible specimens. Tensile bars were die-cut from the molded sheets and pulled on a Baldwin tester with an extensometer at a draw rate of 2 in./min.

TABLE I
Test Procedures

Property	ASTM method
Melt index	D-1238-62T
Density	D-1505-63T
Tensile properties	D-638-61T

The number of methyl and vinyl groups was determined from infrared spectra obtained on a Perkin-Elmer 421G spectrophotometer by using essentially the procedures of Lomonte.[7]

Statistical analysis of 43 data sets was carried out by using a stepwise regression procedure on a Burroughs 5000 computer. Included in this group of polymers were 10 homopolymers and 33 ethylene–1-olefin copolymers. Of the latter, 22 contained a C_6–C_7 1-olefin cut as the comonomer, two contained 1-butene, one contained propylene and the balance a variety of 1-olefin cuts up to a C_{18}–C_{20} fraction. Additional copolymers prepared with propylene and 1-butene for which certain data were not obtained could not be included in the statistical analysis, but are used in certain portions of the balance of this paper.

Correlations and Discussion

The first correlation considered was that between the number of branches, and the density and melt index. The regression analysis indicated the following:

$$\log MC = 0.0176I_2 - 40.1\rho + 38.4 \tag{1}$$

where MC is the methyl count expressed in CH_3/1000C atoms, ρ is the density in grams per cubic centimeter, and I_2 is the melt index in deci-
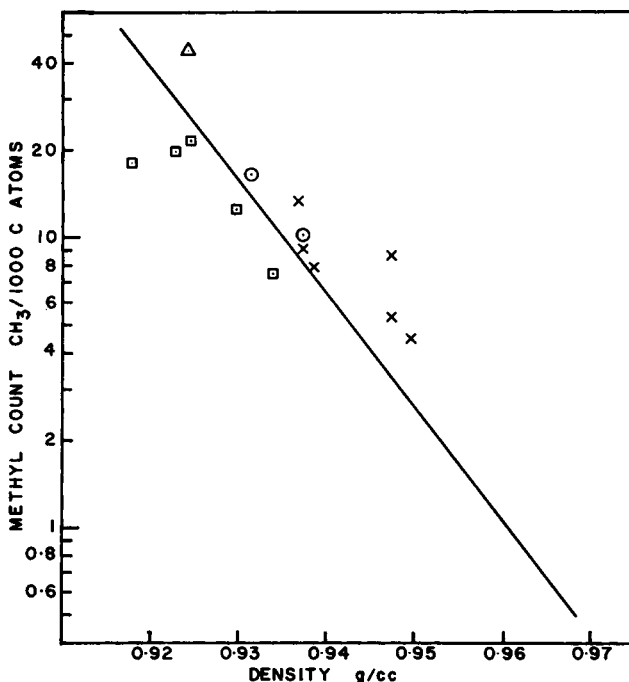
Fig. 1. Relationship between density and branching: ($\triangle$)C_2 copolymers; ($\odot$)C_4 copolymers; ($\times$) > C_8 copolymers; ($\square$) high-pressure process polymers; (———) correlation line.

grams per minute. The coefficient of correlation, R^2, for eq. (1) is 0.88, indicating that 88% of the variance in log MC is accounted for by the equation. An indication of the significance level of the terms in eq. (1) is obtained from the ratios of the coefficients to their associated standard errors. In this case the ratios are 2.0 for the coefficient of I_2 and 17.5 for that of ρ. Since, for this number of data sets, a number greater than 3.5 indicates less than a 0.1% probability of the correlation being due to chance, the correlation of branching with density is obviously very good. The effect of melt index, however, is of marginal statistical significance. The correlation line for methyl count as a function of density, at a melt index of 5, is shown in Figure 1. Points are shown which represent copolymers produced with comonomers other than the C_6–C_7 1-olefin fraction. Since no distinct trend of density with branch length at a given branching frequency is apparent, it can be concluded, in agreement with Folt,[6] that only branch frequency, and not branch length, affects density. Also included in Figure 1 are data points for five high-pressure resins, all of which fall somewhat below the correlation line. Smith et al.[8] have expressed the view that there are fewer branches in high-pressure resins than in ethylene–propylene copolymers of the same density. The precision of the present work, however, is not adequate to extend this conclusion to copolymers containing higher molecular weight 1-olefins.
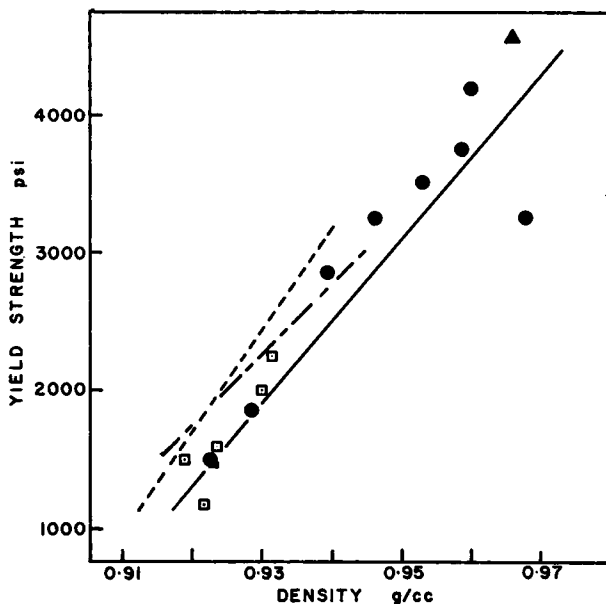
Fig. 2. Relationship between density and yield strength: (●) Ziegler process; (▲) Phillips process; (□) high pressure process; (——) correlation line; (- - -) data of Sperati et al.;[5] (– - –) data of Folt.[6]

The second correlation obtained was:

$$Y = 59,400\rho - 58.1I_2 - 53,300 \tag{2}$$

where Y is the yield strength in pounds per square inch.

The value of R^2 is 0.85, while the ratios of the coefficients to the associated standard errors are 17.2 for ρ and 3.96 for I_2. Again, density is the more important parameter while the melt index term, although statistically significant, amounts to only a minor correction. The dependence of yield strength on melt index, however, is unexpected, since neither Sperati[5] nor Folt[6] observed any melt ndex dependence in their data.

For purposes of comparison, the relationship found in this work, at a melt index level of 5, is plotted in Figure 2 together with the similar lines proposed by Sperati and by Folt. Since both of these previous studies used a strain rate 10 times faster than employed here, the shift of their data to higher values compared with the present work is to be expected. Otherwise, the agreement among the three sets of data is reasonably good. Included in Figure 2 are data points for a variety of resins produced by the three major commercial processes. The points follow the same relationship as the experimental polymers in the present study.

Absence of an effect of branch length on yield strength is apparent in Figure 3, where data for a variety of copolymers containing monomers other than 1-hexene are shown superimposed on the regression analysis
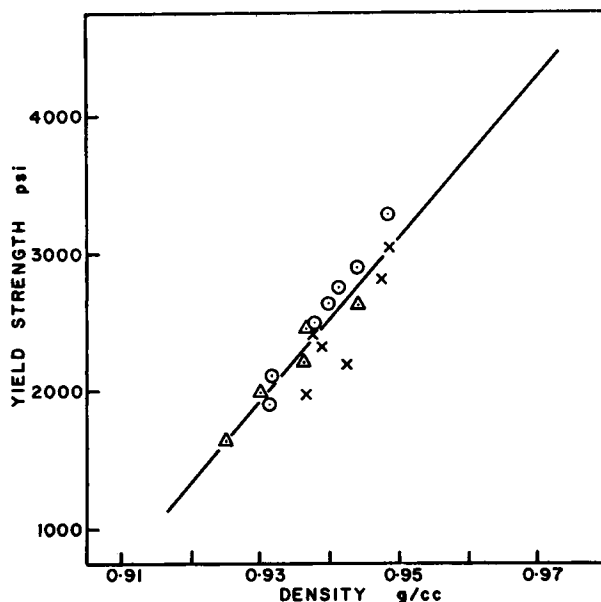
Fig. 3. Effect of branch length on yield strength–density relationship: (△)C$_3$ copolymers; (⊙)C$_4$ copolymers; (✕) > C$_8$ copolymers; (———) correlation line.

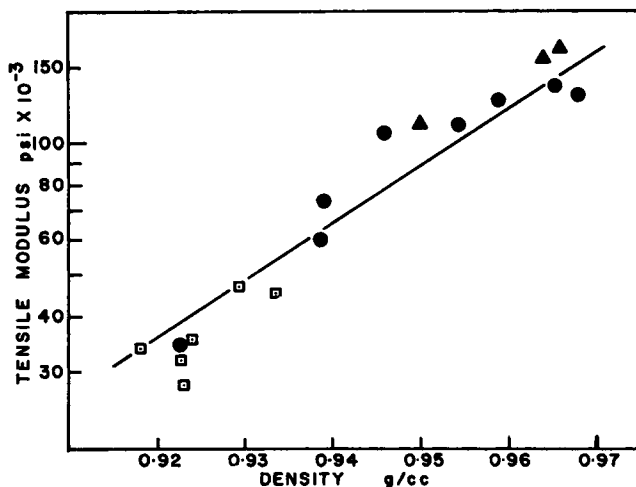Fig. 4. Relationship between density and tensile modulus: (●) Ziegler process; (▲) Phillips process; (□) high-pressure process; (———) correlation line.

line. Thus tensile strength depends primarily on density and is independent of branch length and of the process by which the polymer was made.

Further evidence for this view is provided by a study of 2% tensile modulus. Regression analysis indicates the following:

$$\log M = 13.15\rho - 7.55 \tag{3}$$

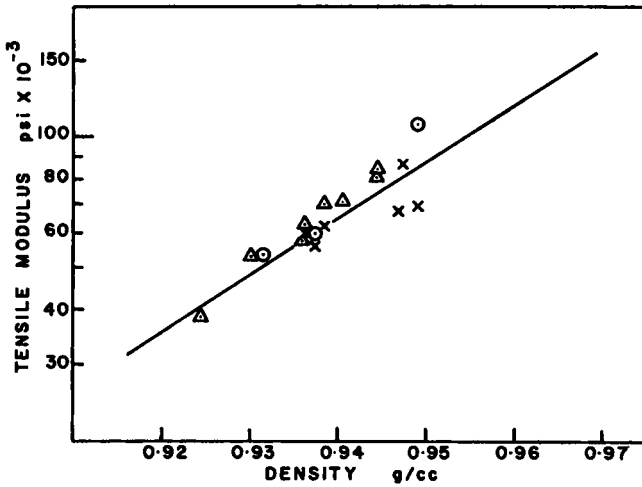where M is the 2% secant modulus in pounds per square inch.

Fig. 5. Effect of branch length on tensile modulus–density relationship: (△)C$_3$ copolymers; (⊙)C$_4$ copolymers; (×) > C$_8$ copolymers; (———) correlation line.

In this case, the value of R^2 is 0.94 and the ratio of the coefficient to its standard error is 25.2, indicating an excellent correlation. This line is plotted in Figure 4, together with data points for the same commercial resins mentioned above. Again, the points fall in a reasonably consistent manner about the line, indicating that the stiffness of the polymer is a function only of its density and hence the number of branches, and not of the method of manufacture. The absence of an effect of branch length is apparent in Figure 5, where data for copolymers of different branch lengths are included with the main correlation line.

As both Sperati[5] and Folt[6] previously indicated, there must be curvature in the proposed relationships for tensile modulus and tensile yield strength versus density in order to accommodate values for amorphous rubbers. The samples studied here, however, are over a sufficiently narrow density range that straight lines represent the data in a satisfactory manner.

TABLE II
Variation of Vinyl Group Analysis with Melt Index

I_2, dg./min.	Vinyl/1000C
0.66	0.58
1.04	0.52
1.17	0.37
5.12	0.26
5.53	0.34
7.39	0.44
7.92	0.32
15.1	0.23
15.6	0.42
16.2	0.27

Vinyl unsaturation has been determined on a series of ethylene homopolymers covering a 25-fold range in melt index, corresponding to at least a twofold range of viscosity-average molecular weight. Such measurements of unsaturation have been used as a measure of the number-average molecular weight of low-pressure polyethylenes. As the data in Table II indicate, however, the level of unsaturation does not increase with increasing melt index in this group of samples. Thus vinyl unsaturation must be used with caution as a measure of number-average molecular weight.

Conclusions

The density of ethylene–1-olefin copolymers is dependent almost exclusively on the number of branch points in the polymer chain and is independent of the length of the branches. The tensile modulus and yield strength in turn are dependent on the density of the polymer and hence ultimately on the number of branch points. Commercial polymers produced by both high- and low-pressure processes show no significant deviation from the correlations obtained for the series of experimental polymers. Finally, no correlation between vinyl group analysis and melt index was found.

References

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Résumé

Plusieurs propriétés physiques de 43 copolymères d'éthylène–et d'oléfine-1 et d'homopolymères d'éthylène produits à la façon de Ziegler, sont sourmises à une analyse statistique. Les corrélations obtenues indiquent que la densité de ces polymères est seulement fonction du nombre de branches introduites par le co-monomère, sans tenir compte de leur longueur. De la même façon le module de tension et de la force globale dépendent en premier lieu de la densité et sont indépendants de la longueur des branches. Les propriétés physiques des résines commerciales obtenues à basse ou haute pression suivent les mêmes relations. L'étude des homopolymères possédant des indices de fusion très différents montre que l'insaturation vinylique n'est pas une mesure adéquate de détermination du poids moléculaire moyen en nombre.

Zusammenfassung

Verschiedene physikalische Eigenschaften von 43 nach dem Ziegler-Verfahren hergestellten Äthylen–1-Olefin-Versuchscopolymeren und Äthylenhomopolymeren wurden einer statistischen Analyse unterworfen. Die erhaltenen Korrelationen zeigen, dass die Dichte dieser Polymeren fast nur von der Zahl der durch das Comonomere eingeführten Verzweigungen ohne Rücksicht auf ihre Länge abhängt. In ähnlicher Weise wird gezeigt, dass Zugmodul und Zugfestigkeit primär von der Dichte abhängen und unabhängig von der Verzweigungslänge sind. Die physikalischen Eigenschaften von technischen, nach Nieder- und Hochdruckverfahren erzeugten Harzen befolgen die gleichen Beziehungen. Die Untersuchung von Homopolymeren mit stark verschiedenem Schmelzindex zeigt, dass der Vinylgruppengehalt kein verlässliches Mass für das Zahlenmittelmolekulargewicht bildet.