

The Effect of Short-Chain Branch Structure on the Properties of Low-Density Polyethylene

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Synopsis

In order to determine the effect of the molecular structure of short side branches in low-density polyethylene upon the physical properties of the resin, a study was carried out in which small amounts of various comonomers were added to an otherwise relatively unbranched polymer. It was found that linear short side branches have about the same effect in decreasing stiffness and increasing toughness as the natural short-chain branches of polyethylene have. However, branches containing a *tert*-butyl group increased resin toughness more than linear branches while decreasing stiffness by about the same amount. Thus, by adding a small amount of branched, short side branches, it is possible to obtain an optimum balance of physical properties not obtainable from low-density ethylene homopolymer.

INTRODUCTION

The term "low-density polyethylene" is generally applied to any ethylene homopolymer having a density below about 0.94 g/cc. Generally, these polymers are made at high pressures and temperatures in the presence of a free-radical initiator. A host of different polymer properties can be obtained by adjusting reaction conditions to provide variations in molecular weight, molecular weight distribution, and long- and short-chain branching.

In the course of a detailed study of the effects of molecular variations on polymer properties, we studied not only variations in the amount of short-chain branching but also the effect of the type (molecular shape) of the branch. Both type and amount of short-chain branching (above a low, constant amount of about 0.8 CH₃/100 C spontaneously formed in the reaction) were controlled by addition of small amounts of various comonomers. Resins similar to some covered in this study are marketed today as ethylene polymers although the words "improved" or "modified" are sometimes added to indicate that the resin is not a true homopolymer.

This paper presents the major results and conclusions of the study of the effect of the type of short-chain branch on polymer properties. It will be seen that the type of branch is important in obtaining optimum properties in modified low-density polyethylenes.

EXPERIMENTAL

Polymerization. Polymerization was carried out batchwise at 1360 atm and 130°C in a 240-cc vessel¹ using the previously described general proce-

ture.² Initiator concentration was increased if necessary to get a reasonable rate. Propane concentration was adjusted to give a polymer melt index (MI) close to 1.0. Runs were terminated at low conversion when ethylene consumption indicated that about 5 g polymer had been formed.

Polymer Preparation. Each sample was dissolved in hot xylene, filtered through Whatman no. 1 filter paper in a hot box to remove dirt, gel, and other contamination, precipitated with cold methanol, and vacuum dried at 80°C. It was established using a commercial polyethylene that this method of cleaning up the polymer did not change the polymer properties but only removed contamination which would cause inconsistencies in the results. The purified samples were then melt pressed into 20-ml slabs from which test specimens were die cut.

Sample Evaluation. Because of the limited amount of polymer available from each run, the conventional polyethylene physical property tests had to be modified. All of these modifications have been described in detail elsewhere.³⁻⁵ It was established using a series of commercial polyethylenes that the modified tests showed the same property trends and the same relative ranking of samples as the conventional tests, although the numerical values were not the same.

Elemental analysis (Galbraith Laboratories) was used to determine the amount of comonomer in the various polymers.

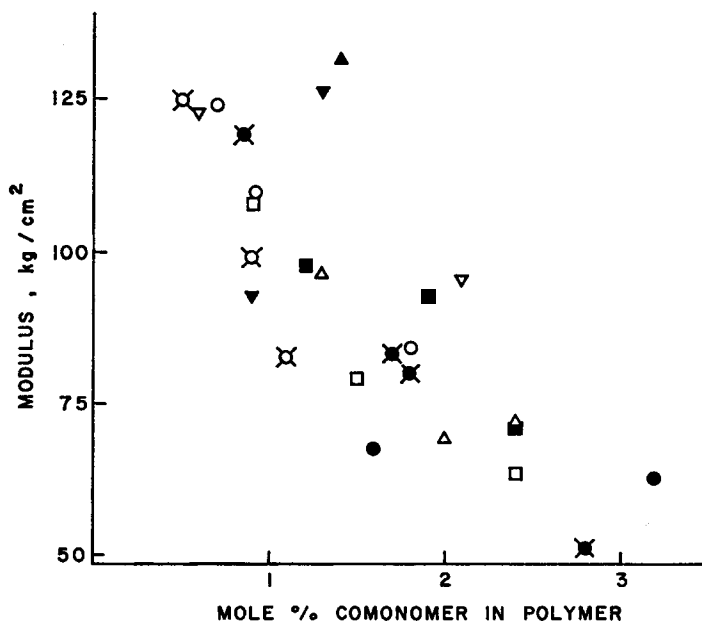


Fig. 1. Effect of branch type on modulus: (Δ) α -cyanoisopropyl acrylate; (\circ (starred)) *tert*-butyl methacrylate; (\circ) *tert*-butyl acrylate; (\square) vinyl pivalate; (∇) *tert*-butylacrylamide; (\blacktriangle) acrylonitrile; (\bullet (starred)) methyl methacrylate; (\bullet) methyl acrylate; (\blacksquare) vinyl acetate; (\blacktriangledown) acrylamide.

RESULTS AND DISCUSSION

The significant data on the strength properties of the various polymers are given in Figures 1 to 3. It may be noted that the filled symbols all refer to monomers which will give essentially linear short side chains in the copolymer, whereas the open symbols denote those monomers which will place a *tert*-butyl group (or its equivalent) at the end of the short side chain. In each group, there is a nitrile-containing monomer (upright triangle), an acrylic amide (inverted triangle), a vinyl ester (square), an acrylate ester (circle), and a methacrylate ester (starred circle). Except for the presence of the comonomer, the basic polyethylene molecular structure was held constant by polymerizing all samples at the same pressure and temperature. To minimize molecular weight effects, only samples having an MI between 0.7 and 6.0 were included in the study.

It is well known that increasing the amount of short-chain branching in polyethylene decreases modulus (stiffness) and tensile strength at yield. It is seen from Figure 1 that branched and linear side chains lower the modulus about the same amount. It might have been expected that the

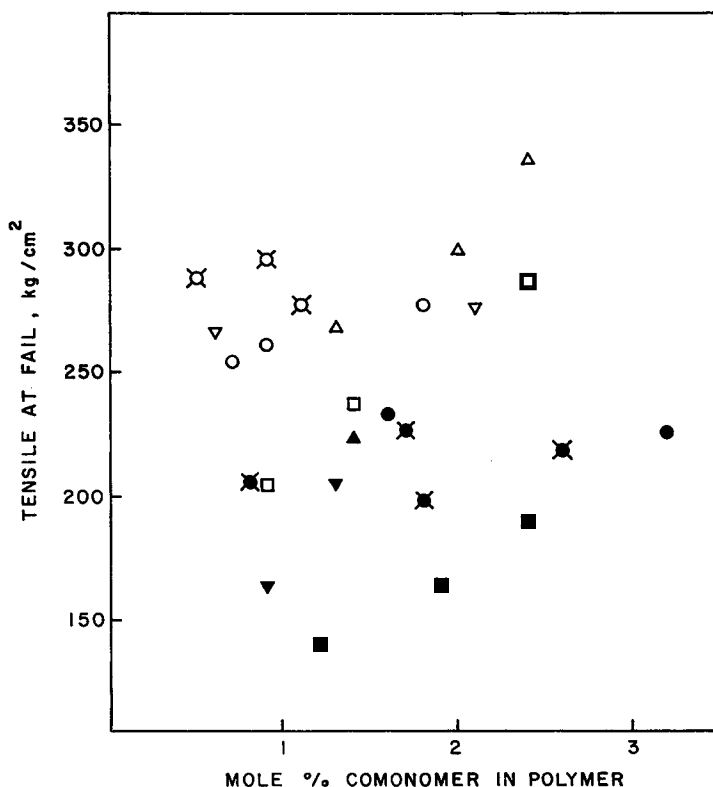


Fig. 2. Effect of branch type on tensile strength at fail. Symbols are the same as in Fig. 1.

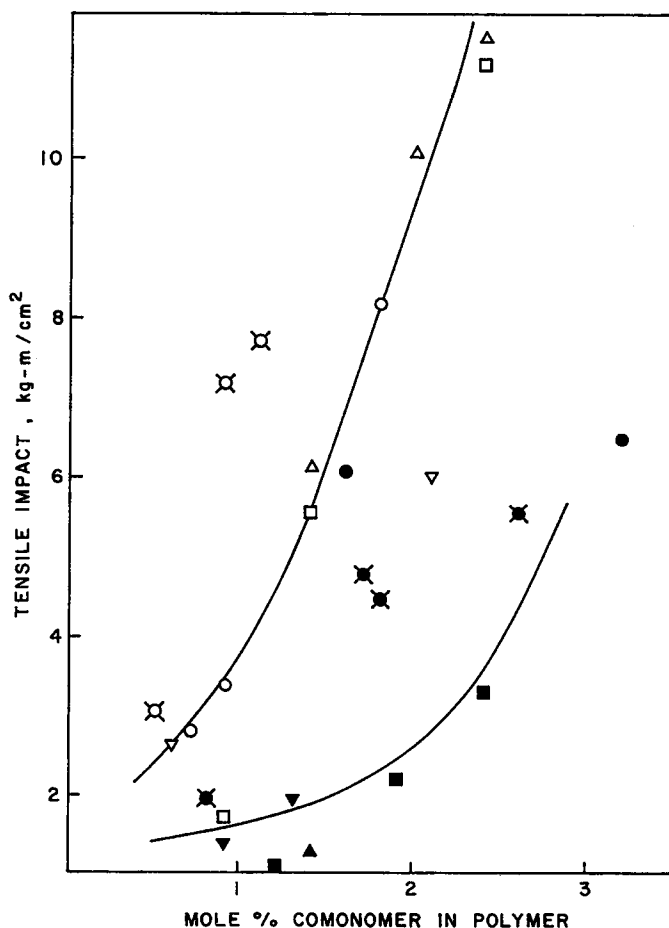


Fig. 3. Effect of branch type on tensile impact. Symbols are the same as in Fig. 1.

branched chains would lower it more at constant molar amount; but if this is so, it is obscured by the scatter in the data. No plot of tensile strength at yield is shown inasmuch as the pattern is the same as for Figure 1.

It is also well known that ultimate tensile strength and tensile impact values increase as short-chain branching increases. Figures 2 and 3 illustrate these trends—but show even more. There is a distinct separation in both figures between the open and closed symbols, showing that property improvement is more pronounced with the branched side chains than with the linear ones. In Figure 3, trend lines for branched and linear side chains have been arbitrarily drawn.

In order to be sure that the effect of branch type was real, three additional comparisons were made. First, plots of tensile strength at fail and tensile impact versus modulus were made in order to be sure that modulus variations alone were not responsible. The separation between the data of the two branch types was as distinct as seen in Figures 2 and 3.

Second, the possibility of a chance combination of molecular weight and modulus differences between samples giving the effect was examined. A number of samples of polyethylene of widely varying MI and modulus were tested, and a regression equation was developed which accurately fit the tensile strength and impact data of all samples using only MI and modulus as input data. Then the regression equation was applied to the copolymer samples. The actual test values for samples containing linear side branches were about the same as or slightly better than predicted by the regression equation, depending upon the specific monomer used. However, the test data for the samples containing branched side branches were substantially better (higher values) than predicted by the equation. Finally, the possibility that the size (rather than shape) of the side chain had an influence was considered. A series of copolymers of *n*-butyl esters of both vinyl and acrylic types were prepared and characterized. In all respects, their property-versus-comonomer content or property-versus-modulus/MI relationships corresponded to the data previously obtained for the other linear side branches.

Thus, it appears that, for a given loss in stiffness, the greatest increase in toughness of low-density polyethylene is obtained when the short side branches on the main chain are highly branched.

The laboratory assistance of L. C. Arnold and helpful advice of C. B. Howard are gratefully acknowledged.

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Received January 12, 1971