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Tensile Properties of Mixtures of Linear Polyethylene and Random Ethylene Copolymers Having Similar Molecular Weights

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ABSTRACT: The stress-strain curves of mixtures of linear polyethylene and random ethylene-1-alkane copolymers have been studied. The molecular weights in each series were closely matched so that complications due to polydispersity and chain length differences were avoided. The pertinent variables were the composition, counit content, and crystallization mode. Comparison would be made of mixtures of the same molecular weight, depending on whether on whether or not cocrystallization took place. The characters of the stress-strain curves were found to be different for these two different situations. The small-deformation properties, such as the initial modulus and yield stress, were found to depend only on the total core crystallinity irrespective of crystallization mode and composition. On the other hand, ultimate properties such as the draw ratio break are very dependent on the phase structure of the system. In an important observation, which has other implications, it was found that crystallinity levels and ultimate properties were the same in the mixture and pure copolymers when comparison was made at the same nominal branch content.

Introduction

The deformation behavior and tensile properties are very important characteristics of semicrystalline polymers. The polyethylenes have been extensively studied in this connection. The stress-stain curves and tensile properties of linear polyethylene[1-18] and branched and random copolymers[19-31] have certain general features in common. However, each of these polymer types displays some distinctive features of their own. When examined carefully, quantitative differences in the key tensile parameters can be discerned between the two classes.[18,31] There have not, however, been controlled studies of the tensile behavior of mixtures of these two species that are chemically very similar but structurally so different. It is, therefore, of interest to examine the tensile behavior of selected mixtures of these different species to learn how one influences the other. Our main purpose here is to establish the experimental base for mixtures of this type. Consequently, we have focused our attention on the influence of phase structure and limited our observations to one draw rate and one deformation temperature.

In studying this problem cognizance must be taken of the fact that molecular weight has an important influence on the tensile properties of both homopolymers and copolymers. Hence, in order to assess the influence of mixture composition, the molecular weights of the pure species need to be close to one another. In our investigation of the tensile properties of such mixtures, we have taken care to assure that the molecular weights of the pure species are very close to one another. In addition, we have used either fractions or samples with narrow molecular weight distributions. If this is not done it is very difficult to separate the influence of polydispersity and molecular fractionation from the inherent crystallization behavior.[32] In the crystallization of mixtures, where the polymers can cocrystallize, it is important to establish whether or not the two species cocrystallize or not. Therefore, we have also established crystallization conditions under which cocrystallization occurs.

With this background we report the results of a study of the stress-strain characteristics and key tensile parameters of the individual pure species and the mixtures. Our mixtures include a linear polyethylene and a hydrogenated polybutadiene fraction, as well as linear polyethylenes and ethylene-hexene copolymers, each of which has most probable molecular weight and narrow composition distributions.

Table I. Characterization of Polymers

polymer	M_w	M_n	M_w/M_n	mol % branch units
A	119 600	100 500	1.19	
B	138 800	60 100	2.31	
C	39 900	21 200	1.88	
D	71 400	32 160	2.22	
E	108 000	82 400	1.31	2.2
F	121 000	55 000	2.20	1.65
G	48 800	26 100	1.87	1.21
H	68 000	32 000	2.13	1.1

All of the pure random ethylene copolymers studied here undergo ductile deformations under the experimental conditions. Depending on molecular weight and crystallization conditions, the pure linear polyethylenes are either ductile, brittle, or in the transition region between them.[33]

Experimental Section

The characteristics of the sample used in this work are given in Table I. Samples A-D are linear polyethylenes. Sample A is an NBS reference standard. The other three homopolymers have most probable molecular weight distributions.

The hydrogenated polybutadiene, designated as P108, was obtained from the Phillips Petroleum Co. and has been used in previous studies reported from this laboratory.[34,35] It is designated as sample E and is characterized by M_w = 10 8000 and M_n = 82 400 with 2.2 mol % of ethyl branches randomly distributed. The ethylene-hexene copolymers all had most probable molecular weight and narrow composition distributions. The method of synthesis of these copolymers has been described previously.[35] The copolymer compositions were determined by ^{13}C NMR in the conventional manner.[34,36-38] A set of ethylene-butene-1 random copolymers were also used as reference in this work. Their synthesis and characterization has also been described.[35] These copolymers also possess most probable molecular weight and narrow composition distributions.

Mixtures over the complete composition range were made with homopolymer A and copolymer E; homopolymer B and copolymer F; homopolymer C and copolymer G, and homopolymer D and copolymer H. These mixtures are designated as series I-IV, respectively.

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Characterization. The core crystallinity was determined from either the enthalpy of fusion or the analysis of the Raman internal modes. It has been demonstrated that the same results are obtained by either method.[39] Heats of fusion were measured in a Perkin-Elmer DSC-2 calibrated with indium. Specimens of about 2 mg were sealed in aluminum pans and heated over the range 280–450 K at 10 K/min. The melting endotherm was defined by drawing a straight base line from the onset to the conclusion of melting. The area of each endotherm was determined by planimetry. The degree of crystallinity from the calorimetric data, $(1 - \lambda)_{\Delta H}$, was calculated using 69 cal/g for the completely crystalline polyethylene.[40]

The crystallinity levels of the samples were also determined by analysis of the Raman internal mode spectra based in the method of Strobl and Hagedorn[41] as further refined in our laboratory.[42-44]

Procedures. Mixtures were prepared following procedures that have previously been described in detail, which have been shown to result in homogeneous systems.[45-47] In essence, the two species in the required proportion are dissolved in a dilute solution of *p*-xylene at 125 °C and then quench precipitated. After washing and drying, the powdered mixture was used to prepare the film for the tensile measurements.

Films of the mixtures were prepared by compression molding at 160 °C in a Carver press. The samples were molded between 0.9-mm-thick copper plates spaced with a 0.2-mm-thick brass sheet.

Each of the mixtures was crystallized from the melt under two different conditions: quenching to −78 °C or isothermal crystallization at a predetermined temperature. The quenching process was carried out by plunging the plates from the press into a dry-ice-saturated solution of isopropyl alcohol. The isothermal crystallizations of the mixtures were carried out in an oil bath capable of holding a given temperature within ±0.1 °C. Upon removal from the press the plates were placed in a container previously placed in the oil path. The crystallization process was carried out in a nitrogen atmosphere to prevent the oxidation of the samples. After a period of time, the plates were removed from the oil bath and transferred rapidly to a dry-ice-saturated solution of isopropyl alcohol. Isothermal crystallizations were carried out at 120 and 125 °C for series I and 120 °C for series II and IV. The times for the isothermal crystallizations were 2000 and 3000 min for the crystallizations at 120 and 125 °C, respectively. For reasons that will become apparent, mixtures in series III were only quenched.

Small, dumbbell-shaped specimens having a gauge length of 4 mm were stamped from the films using a mallet handle die. Sample thicknesses were in the range 0.15–0.20 mm. The force–length studies were carried out using an apparatus that was designed and built in our laboratory. Its design, construction, and performance have already been described in detail.[31] The samples, in this study were deformed at ambient temperature (24–26 °C) at the draw rate of 1-in./min. Because of the rise in temperature that takes place during the deformation,[47a] the observations were not carried out at exactly the same temperature. The deformation was carried out to failure. Prior to deformation, the width and thickness of the gauge region of each specimen was measured to ±2.5 μm. Equidistant fiducial marks were placed on the unreformed samples in order to facilitate the measurement of the draw ratio during elongation and after break. Seven to ten force–elongation curves were recorded for each sample. Any sample that failed at the grips was not considered in the analysis. The mean and standard deviations were calculated for each of the parameters that was measured. The standard deviation is in the range 5–15% for the initial modulus; it is in the range 2–8% for the yield stress; it is in the range 4–8% for the draw ratio at break; for the ultimate tensile stress the standard deviation range is 5–20%.

The key tensile parameters of interest are defined in the following manner. The initial modulus, *E*, is the stress divided by the strain at very low deformation levels. It was calculated from the initial slope of the force–elongation curve at a strain of 3%. The yield stress, YS, is defined as the yield force divided by the initial cross-sectional area. The draw ratio after break, λ_B, is defined as the spacing of the fiducial marks after break divided by their initial spacing. The true ultimate tensile stress, TUTS, is defined as the ultimate tensile force multiplied by the draw ratio at break and divided by the original cross-sectional area.

Results and Discussion

Characterization. The quenched and isothermally crystallized mixtures were examined for cocrystallization by both DSC measurement and selective extraction at appropriate temperatures.[47b] The extraction temperature selected was between those of the pure, quenched species.

The quenched mixtures of series I, II, and IV displayed only one endothermic peak. Selective extraction of the individual species could not be accomplished over the complete composition range for all the mixtures studied. The results for the linear polyethylene–hydrogenated polybutadiene mixtures were the same as those previously reported.[47b] All of the mixtures of the linear polyethylene–ethylene–hexene copolymers behaved in a very similar manner. Only a very small percentage of material, about 2%, could be removed by selective extraction. A typical set of DSC endotherms for mixture II is given in Figure 1a. It is quite clear that only one endothermic peak is observed for these mixtures and is consistent with the inability to selectively extract the individual species. These results gave strong evidence for cocrystallization over the range of composition studied.

In contrast to the results for the quenched samples, all of the isothermally crystallized mixtures, over the complete composition range, give two distinct endothermic peaks. These correspond to those of the individual species. Selective extraction could be quantitatively carried out with all of the isothermally crystallized samples. The extraction resulted in the removal of a fraction of the material which corresponded to the mass fraction of the copolymer in the mixture. A typical set of DSC endotherms for specimens of mixture II, crystallized isothermally, are given in Figure 1b. In contrast to the thermograms in Figure 1a, two endothermic peaks, which compared to the melting temperature of the pure species, are observed in this case. Thus, the isothermally crystallized samples do not cocrystallize. Some type of fractionation, or segregation, takes place under these conditions. We, thus, have available for study in each of series I, II, and IV two sets of mixtures, having the same composition but crystallized in such a manner as to yield quite different phase structures. Series III, whose mixtures were only quenched, served a special purpose in this study.

The level of core crystallinity is plotted against the composition in Figure 2 for the mixtures in all of the series. For either of the crystallization modes the crystallinity level changes continuously from the extreme of one pure species to that of the other. As would be expected, the isothermally crystallized samples have higher crystallinity levels than the quenched ones. The difference in crystallinity level increases progressively with increasing proportion of the linear component.

In Figure 3 the core crystallinity levels of the series I mixtures are compared with those of pure ethylene–butene copolymers of narrow composition distribution with similar weight-average molecular weights. Here, the crystallinity level is plotted against the nominal concentration of branch points, i.e., the concentration as if the branches were uniformly distributed among all the molecules. When plotted on this basis, we find, quite surprisingly, that the crystallinity levels of the mixtures and of the pure species all fall on the same curve. For the nonequilibrium situation being studied here the melt structure plays a major role in determining the crystallinity level. In the melt, both homopolymers and copolymers are profusely intercon-

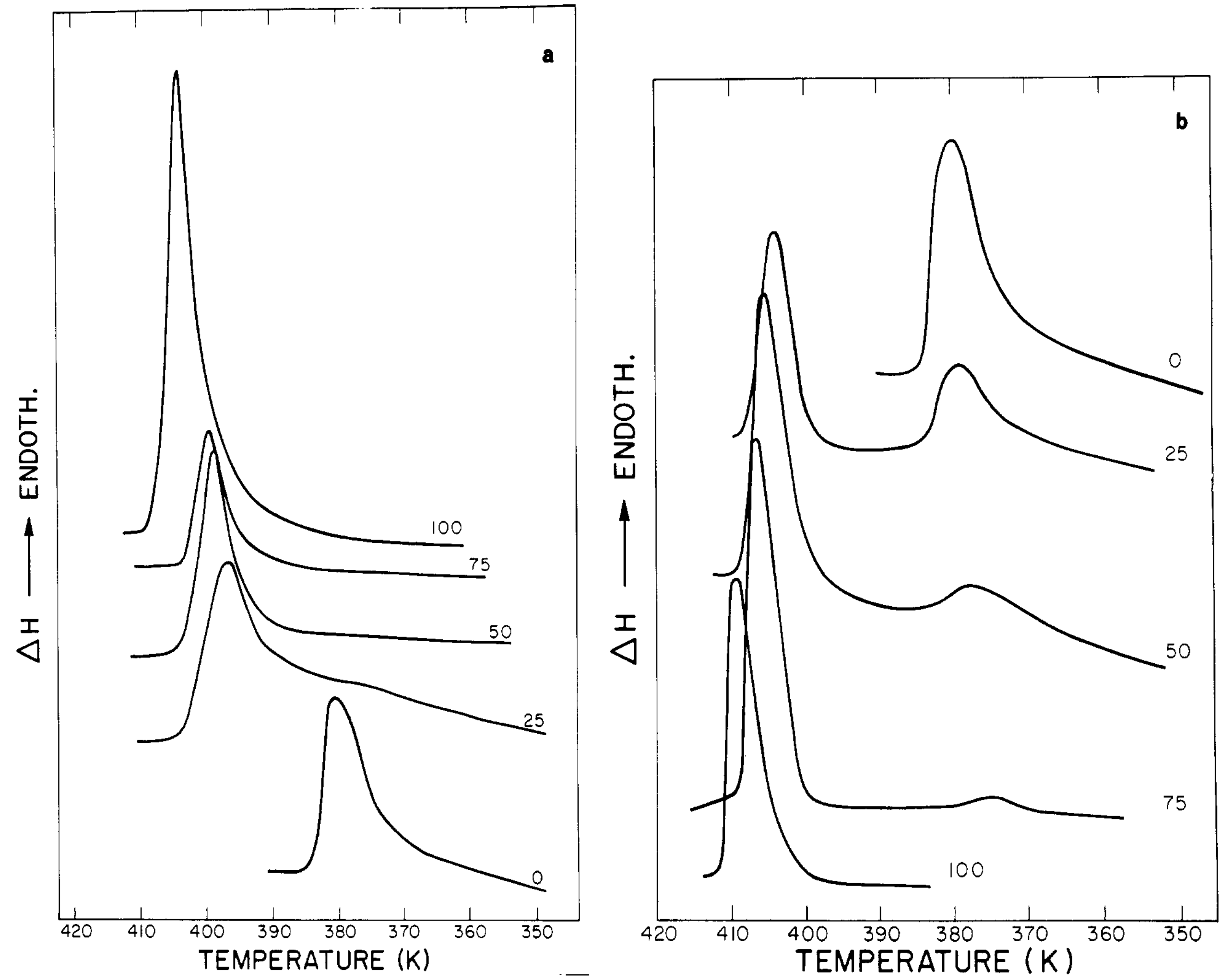

Figure 1. DSC thermograms of series II mixtures: (a) quenched; (b) isothermally crystallized at 120 °C for 2000 min. The numbers represent the percentage of linear polymer B in the mixtures.

nected, one with the other.[48,49] The results in Figure 3 indicate that the specific way that the counits are distributed among the molecules is not crucial in specifying the melt structure. This original observation with respect to the melt structure could have important implications to other crystalline properties of similar mixtures.

A similar comparison could not be made with the mixtures containing the ethylene–hexene copolymers since an adequate number of reference samples were not available.

Tensile Properties. A composite set of stress–strain curves for the quenched samples of series I are given in Figure 4. Cocrystallization occurs in all these mixtures. There is an obvious difference in the yield stress between the two pure species which will be discussed subsequently. In addition, the general characters of the stress–strain curves of the pure species are also quite different. The pure copolymer is characterized by a rather strong upswing in the stress–strain curve, the so-called "strain hardening" region, as compared to the linear polymer of the same molecular weight. At the smaller deformations the nominal stress for all of the mixtures clusters about the value of the pure copolymer; i.e., the stress does not vary significantly with composition. The stress values of the mixtures do not vary through most of the deformation. However, prior to failure the curves separate from one another. At this point the character of the 75/25 mixture resembles that of the linear polymer at lower stress level, while the 25/75 mixture begins to display the strain hardening characteristics typical of the pure copolymer. Through the major portion of the deformation the stress level and general characteristics of all the mixtures are similar to one another and to that of the pure copolymer. Significant differences are only observed toward the end of the deformation process.

The stress–strain curves of the isothermally crystallized mixtures of series I, which do not cocrystallize, are illustrated in Figure 5. Major differences between these mixtures and the quenched ones are readily apparent. We do not show a curve for the isothermally crystallized pure copolymer because only a very small amount of crystallinity develops under isothermal crystallization conditions.[50] Hence, most of the crystallinity that is observed is formed during the cooling from the crystallization temperature. We have therefore represented this sample with the force–length curve of the quenched sample.

Differences are found in both the shape and magnitude of the yield stress between the isothermally crystallized mixtures. The yield region of the pure linear polymer is very sharp when compared with either the quenched homopolymer or the isothermally crystallized mixtures. When diluted with the copolymeric component, the yield process becomes progressively more diffuse. Most importantly, the nominal stress levels of the curves progressively change with composition. This behavior is to be contrasted with the plots in Figure 4 where the stress–strain curves of the mixtures and the copolymer are virtually coincident over the major portion of the deformation process. There are, therefore, significant differences in the character of the stress–strain curves, de-

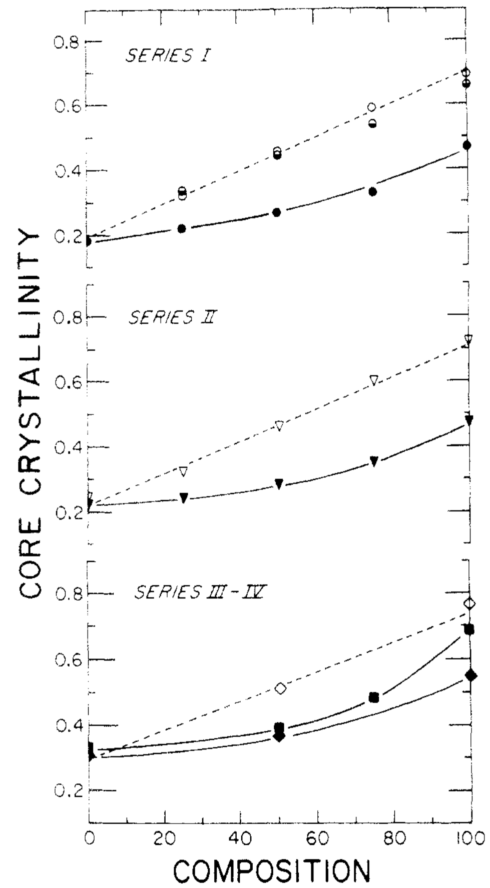

Figure 2. Plot of core crystallinity against percent of linear polymer in the mixtures. Series I: (●) quenched; (○) crystallized at 120 °C; (◒) crystallized at 125 °C. Series II: (▼) quenched; (▽) crystallized at 120 °C. Series III: (■) quenched. Series IV: (◆) quenched, (◇) crystallized at 120 °C.

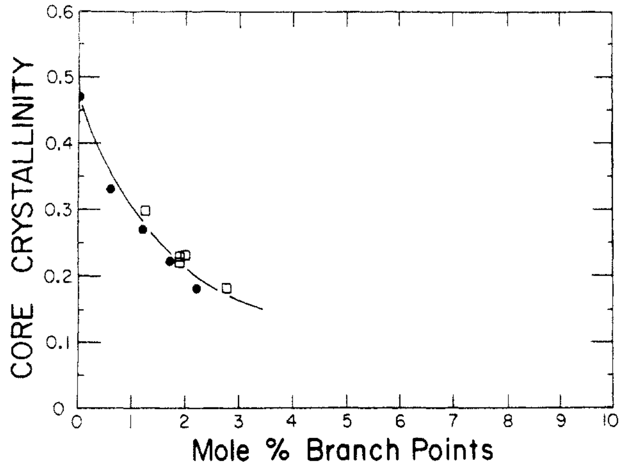

Figure 3. Plot core crystallinity against nominal percent of branch points for rapidly crystallized samples: (●) series I mixtures; (□) ethylene–butene copolymers.

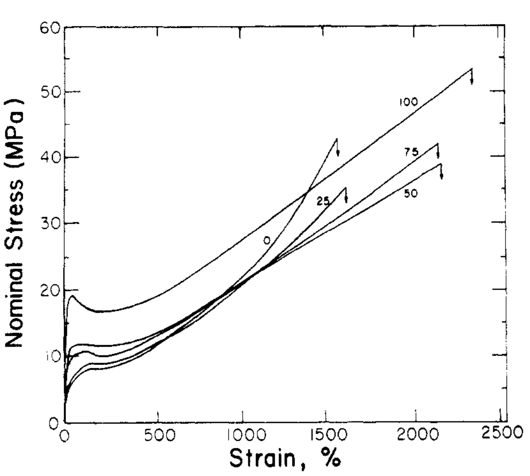

Figure 4. Stress–strain curves for quenched samples of series I mixtures. The numbers represent the mass percent of linear polymer A in the mixtures.

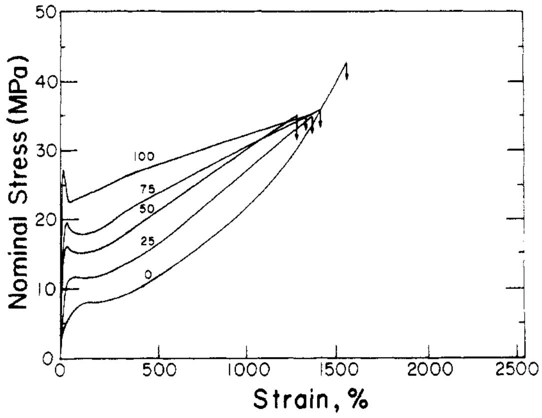

Figure 5. Stress–strain curves for series I mixtures crystallized at 120 °C. The numbers represent the mass percent of linear polymer A in the mixtures.

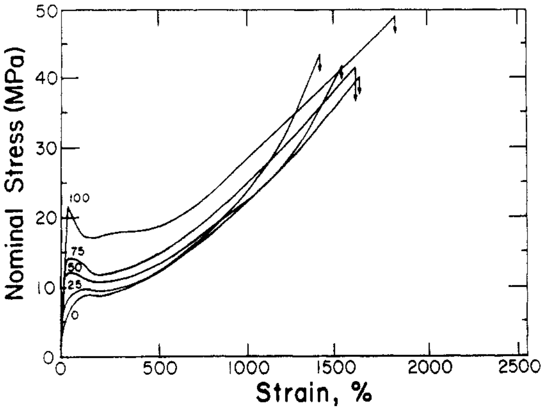

Figure 6. Stress–strain curves for quenched samples of series II mixtures. The percent numbers represent the mass of linear polymer B in the mixtures.

pending on whether the individual species do or do not cocrystallize.

The results of similar studies with mixtures of series II are given in Figures 6 and 7 for quenched and isothermally crystallized samples, respectively. The results for the quenched samples are essentially the same as those for series I. Characteristically, at the smaller deformations the nominal stress of all the mixtures clusters around the value of the pure copolymer and the stress–strain curves are very close to one another. At higher deformations the curves separate from one another in the order of their composition. Although the main results for the isothermally crystallized samples of series II are very similar to those of series I, there are small differences due to the stress–strain behavior of the pure homopolymers. The reason is that under these crystallization conditions the deformation of the pure homopolymer of series II is in the transition region between ductile and brittle. In this case, after yielding, the neck that is formed did not propagate steadily along the gauge length. For different specimens of the homopolymer fracture may occur either just after necking or after the neck has propagated through a portion of the gauge length. This last situation is respresented by the stress–strain curve drawn for the homopolymer in Figure 7. There is, therefore, a large scatter in the results for the ultimate properties of this isothermally crystallized

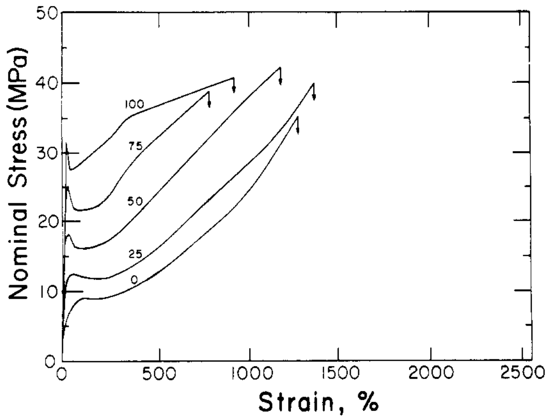

Figure 7. Stress–strain curves of series II mixtures crystallized at 120 °C. The numbers represent the mass percent of linear polymer B in the mixtures.

homopolymer. However, the characteristics of the stress–strain curves of the mixtures are the same as those in series I.

The stress–strain curves for the quenched samples of series III differ in many aspects from the other quenched series. There is a major difference in tensile behavior between the pure, quenched linear component (sample C) and those in the other series since it displays brittle behavior. Its stress–strain curve is characterized by a very sharp yield which is immediately followed by fracture. On the other hand, at small deformations the characteristics of copolymer G in this series are similar to those of the other copolymers. There is, however, a difference in the strain-hardening process. The increase in the stress in the last part of the deformation is continuous, but it is very small compared to the other copolymers. This is due to the lower molecular weight of the copolymer.[10,14] The quenched mixtures display intermediate behavior between the pure components. The addition of the copolymer to the linear component causes a change from brittle to ductile through a transitional behavior. Thus, the 75/25 mixture behaves in a transitional manner. It displays a very sharp yield region with a yield stress level considerably lower than the linear component, polymer C. The 50/50 mixture still shows a sharp yield region. After yielding, the stress increases very slowly until failure. There are, therefore, very marked differences in the features of the deformation curves between the quenched samples of series III and the other quenched series. The yield stress, as well as the shape of the yield region, changes with the composition in a manner that closely resembles that of the isothermally crystallized samples of series I and II.

The results for the quenched samples of series IV are essentially the same as those for series I and II. The isothermally crystallized samples of series IV present the same situation as the quenched series III. The linear component, polymer D, is brittle under this crystallization condition, and its stress–strain curve has the same characteritics as the quenched polymer C. Therefore, the isothermally crystallized mixtures of series IV follow the same pattern as the quenched ones of series III.

The initial modulus is plotted against the weight percent of the linear component in Figure 8. All of the mixtures display a very similar behavior. When compared on this basis, the moduli for a given mixture depend on the mode of crystallization. The quenched samples have lower values at the same composition. The differences in moduli become greater as the pure homopolymer is approached. This behavior might be expected since we have already noted that the isothermally crystallized samples have higher crystallinity levels than the quenched ones. The structural factors contributing to the initial modulus complex are not completely understood. However, the level of crystallinity makes an important contribution to this quantity.[18,31] Examining this data solely on a composition basis can be misleading, as is shown in Figure 9. Here the initial moduli of all the mixtures are plotted against the core crystallinity level. Within experimental error a unification of the data occurs when the moduli data are examined on this basis. The data from both crystallization modes now delineate the same curve. The core level of crystallinity is thus the unifying factor bringing the different types of mixtures, from all the series, in concordance with one another. The modulus–core crystallinity curve of Figure 9 follows the lower portion of the S-shaped curve that was previously reported for single species copolymers and homopolymers that encompassed

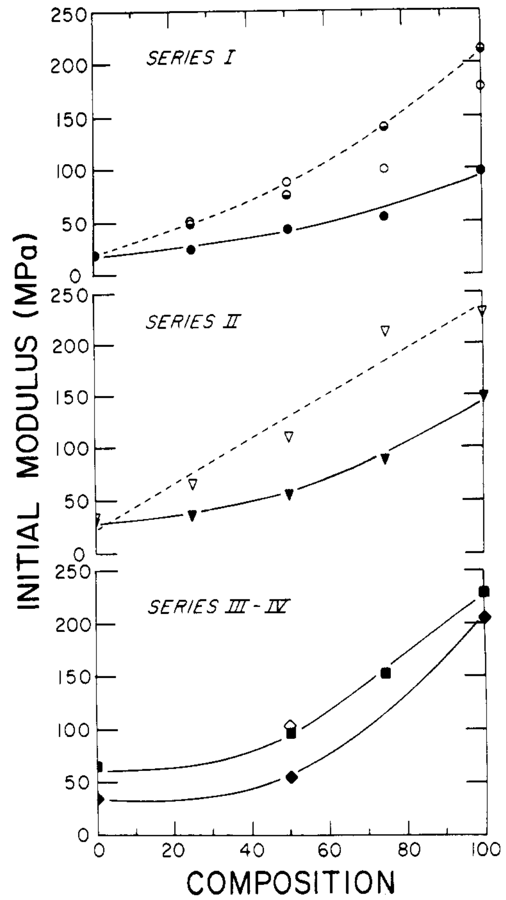

Figure 8. Plot of initial modulus against percent of linear polymer in the mixtures. Symbols are the same as in Figure 2.

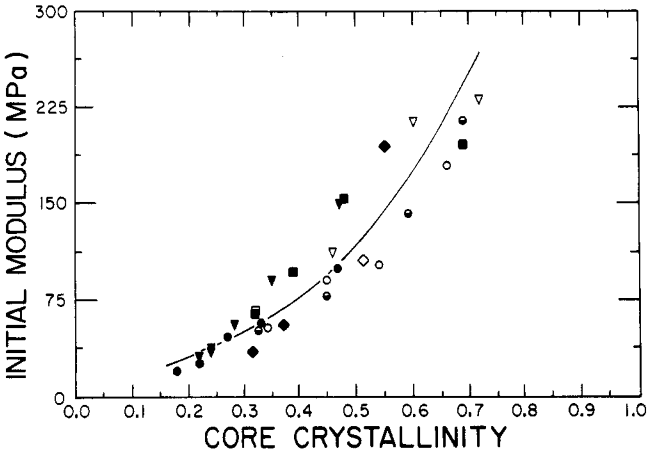

Figure 9. Plot of initial modulus against fraction core crystallinity. Symbols are the same as in Figure 2.

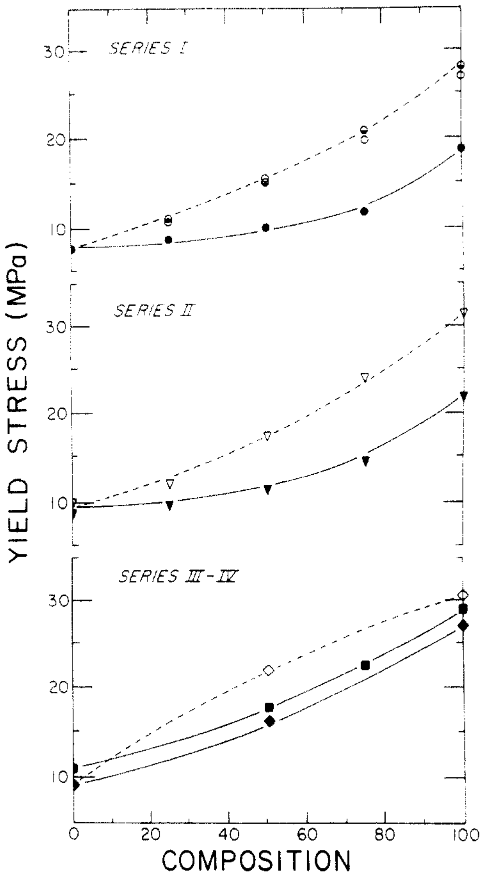

Figure 10. Plot of yield stress against percent of linear polymers. Symbols are the same as in Figure 2.

a very wide range in structural parameters.[18,31] The modulus values reported here are slightly lower than those previously reported for a series of unfractionated copolymers.[31]

The yield stress is plotted against the composition in Figure 10 for all of the mixtures. There is a continuous increase in the yield stress with increasing concentration of the homopolymer component for both the quenched and isothermally crystallized samples. However, the yield stress of the isothermally crystallized samples is substantially greater than that of the quenched ones at the same composition. This result in itself is not unexpected since it has been well established[18,20-23,31] that yield stress depends on the crystallinity level. However, what is surprising is that, when the yield stress is plotted against the total level of core crystallinity, as is shown in Figure 11, the results for the different series, are indistinguishable from one another. A linear relation extrapolating to the origin, is observed over the entire crystallinity range. The data for the single species ethylene–butene copolymers also fall on the same straight line. The yield stress is also independent of the chemical nature of the counit. These results are very similar to those reported for a set of unfractionated random ethylene copolymers,[2] that are indicated by the dashed line in the figure. It follows from the plot in Figure 11 that the reduced yield stress is a constant.

The fact that the yield stress only depends on the total core crystallinity, irrespective of the crystallization mode, composition, or type of copolymer, is not easily explained. Small-angle neutron scattering experiments have shown that the yield in linear polyethylene is the result of a partial melting–recrystallization process.[51] The data for the quenched samples, where cocrystallization occurs, are consistent with this conclusion. However, the isothermally crystallized samples, which do not cocrystallize, should consist of two different types of crystallites. The contribution of each would be expected to be independent of one another. In the analysis given, the contributions of each type have been added to give the net crystallinity level. Therefore, we conclude that the yield stress is the result of the additive contribution to two crystallite types that have different thicknesses and interfacial structures.

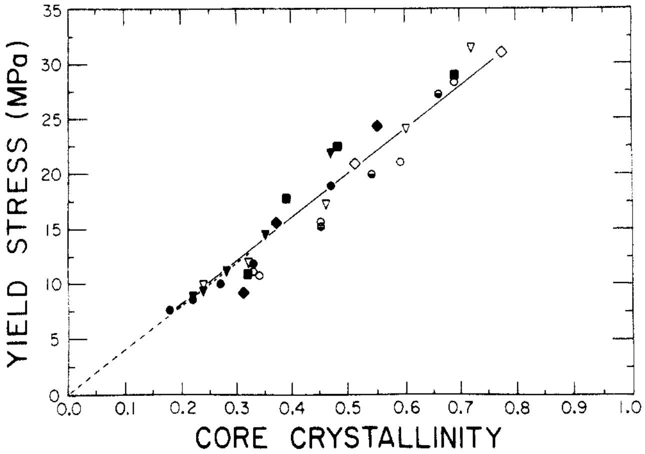

Figure 11. Plot of yield stress against the fraction core crystallinity. Symbols are the same as in Figure 2.

When compared at the same composition, the major characteristics in the range of small deformation, i.e., the initial modulus and the yield stress, appear to differ between the isothermally crystallized and quenched samples. However, these differences are more apparent than real. When these quantities are examined on the basis of the total core crystallinity, the results between the different crystallization modes are indistinguishable. Hence, on this basis there are no differences between a cocrystallized mixture and one with a different phase structure.

We next examine the dependence of the ultimate properties on the crystallization mode and the copolymer type and composition. We are particularly interested in the draw ratio at break and the true ultimate tensile strength. For the pure species, in the ductile range, the draw ratio at break, λ_b, is less for copolymers than for linear polymers.[18,31,52] In the ductile region λ_b is independent of the crystallinity level for the linear polyethylenes.[18,52] For the linear polyethylenes studied here, polymer A is in the ductile region for the quenched sample and the sample isothermally crystallized at 120 °C. However, when isothermally crystallized at 125 °C, the deformation is in the transition region for this polymer. Therefore, as is indicated in Figure 12 the sample crystallized at 124 °C has a lower λ_b value than those of the same polymer crystallized under the other conditions. The λ_b value for the transitional sample has a large error because it represents the average of a broad distribution of values. Sample B, of series II, is also in the transition region. The quenched pure linear polyethylene sample C (series III) is brittle, as indicated by $\lambda_b = 1$. In series IV, the pure linear polymer, sample D, is ductile when quenched but brittle when crystallized isothermally. The different deformation characteristics are reflected in the plots of λ_b against mixture composition. The difference between the curves in the various series can be attributed to the altered deformation characteristics of the pure homopolymers, i.e., whether they are ductile, brittle, or in the transition region. For example, the decrease in λ_b that is observed at the higher composition for the isothermally crystallized samples in series I and II can be

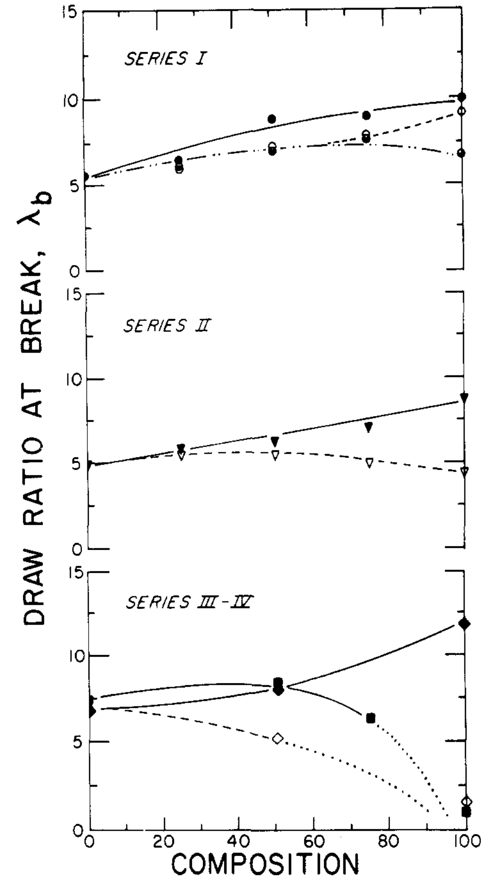

Figure 12. Plot of draw ratio after break, λ_b, against percent of linear polymers. Symbols are the same as in Figure 2.

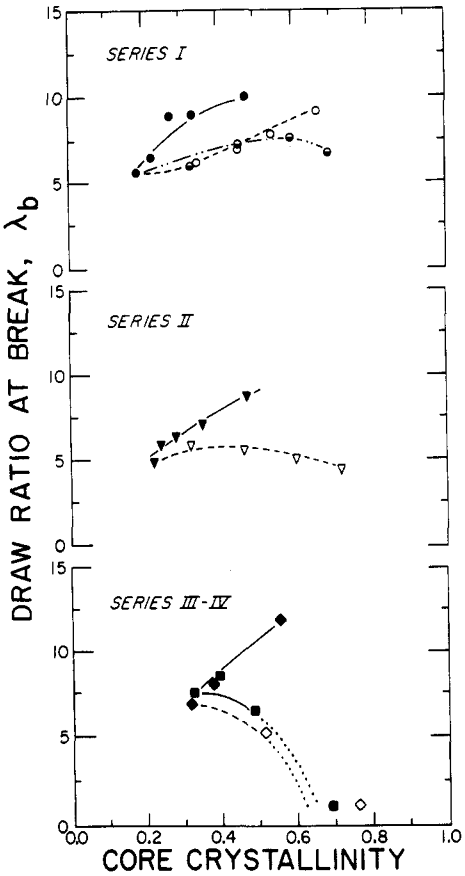

Figure 13. Plot of draw ratio after break, λ_b, against fraction core crystallinity. Symbols are the same as in Figure 2.

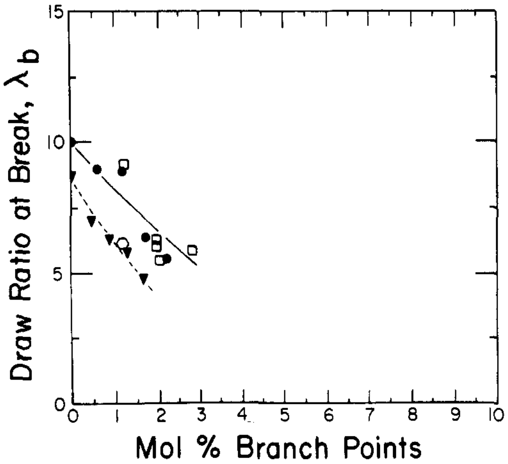

Figure 14. Plot of draw ratio after break, λ_b, against nominal mole fraction of branch points for samples rapidly crystallized: (●) series I mixtures; (□) ethylene–butene copolymers; (▼) series II mixtures; (○) ethylene–hexene copolymer.

attributed to the fact that the pure linear polyethylene is in the transition region. This effect is much more pronounced in the quenched series III and isothermally crystallized series IV. Here both homopolymers are brittle. In contrast, the quenched samples in series IV show an increasing λ_b with composition because under these circumstances the linear polyethylene component is ductile. We note that coincidentally for the 50/50 mixtures λ_b is the same for quenched samples of series III and IV. However, for a mixture at a given composition there is a definite difference in λ_b for the different crystallization modes.

These differences become clearer in Figure 13 where λ_b is plotted against the core crystallinity level. In series I and II, except at the very lowest crystallinity levels, λ_b is greater for the quenched samples when the comparison is made at the same level of core crystallinity. For the quenched samples in these series there is a monotonic increase of λ_b with crystallinity. The increase in λ_b with crystallinity is retarded for the isothermally crystallized sample mixture when the pure linear polymer is ductile. When the pure linear polymer is in the transition region (series I crystallized at 125 °C; series II crystallized at 120 °C), there is a slight increase and then decrease in λ_b with crystallinity. The quenched homopolymer of series III and the isothermally crystallized one in series IV are brittle and of approximately the same molecular weight. A slight increase in λ_b with crystallinity is observed, followed by a very rapid decrease as the composition of pure polymer is approached.

Another way of examining the influence of composition is illustrated in Figure 14. Here λ_b is plotted against the nominal branch content for the quenched mixtures of series I and the ethylene–butene copolymers and the quenched mixtures of series II and a pure ethylene–hexene copolymer. The data delineate two separate curves depending on the nature of the branch. The decrease in λ_b from about 10 for the pure homopolymer to about 5 for the pure hydrogenated polybutadiene is clear. The values for the blends falls smoothly in between. The pure ethylene–butene copolymer data fall on the same curve. Their λ_b values are virtually coincident with the blends when compared at the same nominal branching content. From the data in Figure 3 we concluded that the melt structure was essentially the same for the pure copolymers and mixtures when comparison is made at the same nominal composition. Thus the similarity in λ_b values in Figure 14 points out once again the importance of the residual melt structure in determining the ultimate properties.[18,31,53] A complete set of pure ethylene–hexene copolymers with

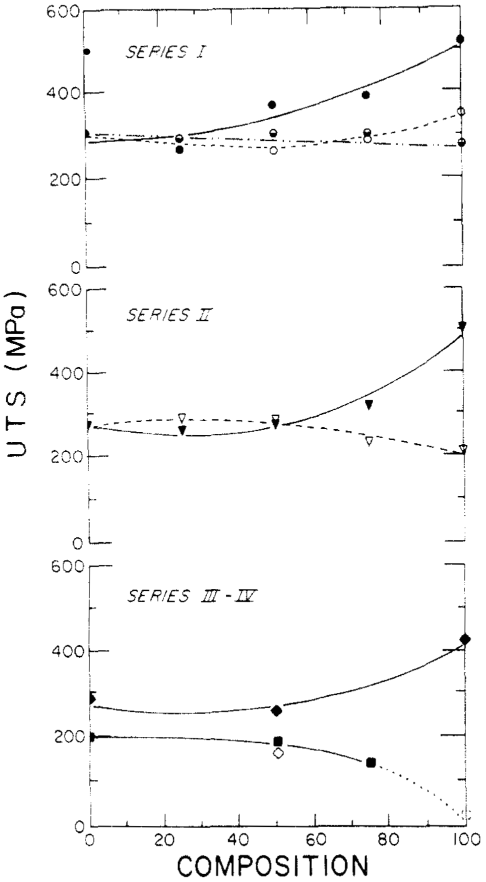

Figure 15. Plot of true ultimate tensile stress against percent of linear polymers in the mixtures. Symbols are the same as in Figure 2.

which to make a similar comparison is not available. However, a pure ethylene–hexene copolymer that has the same molecular weight as those in series II, and containing 1.1 mol % branch points, gives a λ_b value that falls on the same curve. The λ_b values for the series II mixtures are slightly below those of series I. This difference can be attributed to the nature of the side group when samples having narrow molecular weight and composition distributions are studied.

The true ultimate tensile stress is plotted against composition in Figure 15. When the data are plotted on this basis, there is a clear distinction between the two crystallization modes. The pattern with composition follows that expected from the draw ratio data. The differences between the quenched samples of series III and IV are very striking. The contrasting behavior is due to the different deformation characteristics of the pure homopolymers. The differences become more accentuated when the data are plotted against the core crystallinity as in Figure 16. The true ultimate tensile stress increases monotonically with homopolymer content for all the cocrystallized mixtures that undergo a ductile deformation. The values range from about 250 to 500 MPa over the complete composition range for these mixtures. The other mixtures, when the pure homopolymer component is brittle, display a decrease in ultimate tensile stress. However, the total stress range covered in this situation is fairly limited.

In this comprehensive experimental study of the tensile properties of mixtures of linear polyethylene and random ethylene copolymers we have found that the results depend not only on the molecular constituents of the individual mixtures but also on whether or not the system cocrystallizes. For each set of mixtures studied the components were chosen as that the molecular weight was essentially constant, while crystallization could be controlled by the mode of crystallization. The general character of the stress–strain curves depends on whether or not the two components cocrystallized. However, the small deformation properties, such as the initial modulus and the yield stress, depend only on the total level of core crystallinity. They are independent of whether or not cocrystallization occurred, the molecular nature of the mixtures, and the composition. These results would indicate that these properties are additive in terms of crystallite types. They would indicate that these props are additive in terms of crystallite types. They depend on the crystallite and local noncrystalline structure and are independent of the character and amount of each crystallite type.

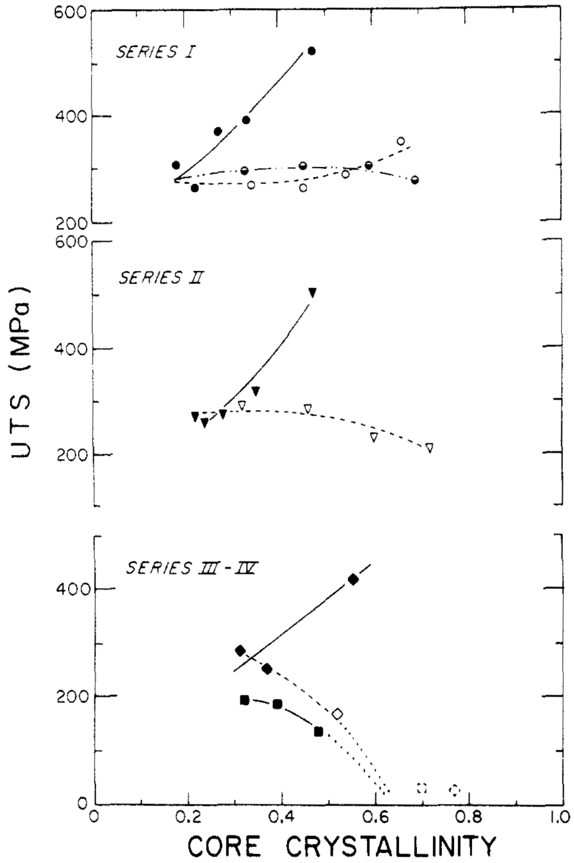

Figure 16. Plot of true ultimate tensile stress against the fraction core crystallinity. Symbols are the same as in Figure 2.

In contrast, the ultimate properties, such as the draw ratio at break and true ultimate tensile stress, are dependent on whether or not the system cocrystallizes. When compared at either the same composition or crystallinity level, cocrystallized mixtures have significantly higher values of both λ_b and the ultimate tensile stress. Since these properties are governed primarily by the interlamellar regions,[52,53] these results would indicate that the contributions from the different interlamellar regions are not additive. For the systems that do not cocrystallize, the structures of the interlamellar regions will not be uniform. The different, disordered regions will contribute in a different manner to the ultimate properties. For the cocrystallized mixtures, with only one type of crystallite present, the interlamellar region is uniform.

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