

## Elastomeric blends of homogeneous ethylene–octene copolymers

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An elastomeric ethylene–octene copolymer was compared with binary blends of ethylene–octene copolymers formulated to have the same crystallinity as the target copolymer. Copolymers having narrow molecular weight distribution, homogeneous comonomer distribution and homogeneous long chain branching structure were prepared by Dow's INSITE<sup>®</sup> constrained geometry catalyst and process technology (INSITE<sup>®</sup> is a trademark of The Dow Chemical Company). A copolymer of higher comonomer content than the target was blended with the appropriate amount of a lower comonomer content copolymer to obtain the target level of crystallinity. Thermal analysis indicated that the components crystallized separately in all the blends. The stress–strain behaviour of the copolymers and their blends was evaluated as a function of temperature. At ambient temperature, the total amount of crystallinity primarily determined the stress–strain relationship regardless of whether the material was a single copolymer or a copolymer blend. Any effects of phase morphology were subtle at ambient temperature. At higher temperatures, where the network junctions started to melt, miscibility of the non-crystalline regions produced a synergistic effect on the tensile strength. However, if the branch concentration of the blended copolymers was too different, the non-crystalline regions were immiscible, and the copolymer blend had a lower tensile strength than the target at higher temperatures. © 1997 Elsevier Science Ltd.

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### INTRODUCTION

The recent development of Dow's INSITE<sup>®</sup> constrained geometry catalyst and process technology has made available copolymers of ethylene with  $\alpha$ -olefins that differ significantly from conventional linear low density polyethylenes (LLDPEs) in having narrow molecular weight distribution, homogeneous comonomer distribution and homogeneous long chain branching structure. This presents an opportunity to probe the limits imposed by branch concentration on miscibility of ethylene copolymer blends. Although solid state structure and properties change gradually with increasing comonomer content, the combined body of observations from melting behaviour, morphology, dynamic mechanical response, yielding and large-scale deformation suggests a classification scheme for the ethylene–octene copolymers prepared with the INSITE<sup>®</sup> technology<sup>1</sup>. Materials with densities higher than 0.93 g ml<sup>-1</sup>, Type IV, exhibit a lamellar morphology with well-developed spherulitic superstructure. Type III polymers with densities between 0.93 and 0.91 g ml<sup>-1</sup> have thinner lamellae and smaller spherulites. Type II materials with densities between 0.91 and 0.89 g ml<sup>-1</sup> have a mixed morphology of small lamellae and fringed micellar crystals, and can form very small spherulites. Type I copolymers with densities less than 0.89 g ml<sup>-1</sup> have no lamellae or spherulites; fringed micellar crystals are

inferred from the low degree of crystallinity, the low melting temperature and the granular, non-lamellar morphology.

An initial blend study focused on binary blends that combined a highly branched Type I copolymer (0.865 g ml<sup>-1</sup>) with a copolymer of approximately the same molecular weight, but of lower branch concentration and higher density<sup>2</sup>. The second component was either another Type I copolymer (0.887 g ml<sup>-1</sup>), a Type II copolymer (0.901 g ml<sup>-1</sup>) or a Type III copolymer (0.913 g ml<sup>-1</sup>). The melting and crystallization behaviour of the copolymer blends suggested that the components crystallized separately in all the blends. Blends of Type I with Types II or III appeared to crystallize from a biphasic melt. In contrast, blends of two Type I copolymers with different branch concentrations appeared to be miscible in the melt. Moreover, dynamic mechanical analysis indicated that the non-crystalline portions of blends of two Type I copolymers formed a single phase, whereas the biphasic nature of the melt in blends of Type I with a Type II or III copolymer extended to phase separation in the non-crystalline regions of the solid state. It was also observed that the stress–strain relationship at ambient temperature was determined by density or total crystallinity regardless of whether the material was a single copolymer or a copolymer blend.

With the INSITE<sup>®</sup> technology, it is possible to polymerize copolymers with crystallinities lower than those of the conventional LLDPEs. These Type I

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copolymers exhibit elastomeric behaviour at ambient temperatures. The structural model proposed for the elastomeric properties consists of a physical network with flexible chain segments linked by fringed micellar crystals that act as multifunctional junctions. The broad melting range of the fringed micellar crystals, which begins near ambient temperature, determines how well the tensile properties are maintained at elevated temperatures. Blending the appropriate copolymers may alter the melting behaviour in a way that extends the elastomeric properties to higher temperatures. This possibility was tested by comparing a target Type I copolymer with binary blends formulated to have the same crystallinity as the target. A copolymer of crystallinity lower than that of the target was blended with the appropriate amount of a higher crystallinity copolymer to obtain a blend with the target crystallinity.

**Table 1** INSITE<sup>®</sup> ethylene–octene copolymers

Polymer designation	Comonomer content <sup>a</sup> (mole %)	Density (g ml <sup>-1</sup> )	<i>I</i> <sub>2</sub> (g/10 min)	<i>I</i> <sub>10</sub> / <i>I</i> <sub>2</sub>
Type IB	14.6	0.865	0.5	≈8.5
Type IT	11.8	0.874	0.5	7.3
Type I	8.5	0.887	1.0	9.2
Type II	5.3	0.901	1.0	9.0
Type III	3.3	0.913	1.0	10.5

<sup>a</sup> Calculated from density<sup>3</sup>

**Table 2** Composition and density of blends and target copolymer

Polymer designation	Blending ratio (w/w)	Density (g ml <sup>-1</sup> )
Type IT	n/a	0.874
Type IB-I	58.3/41.7	0.875
Type IB-II	75.7/24.3	0.875
Type IB-III	81.4/18.6	0.874

## EXPERIMENTAL

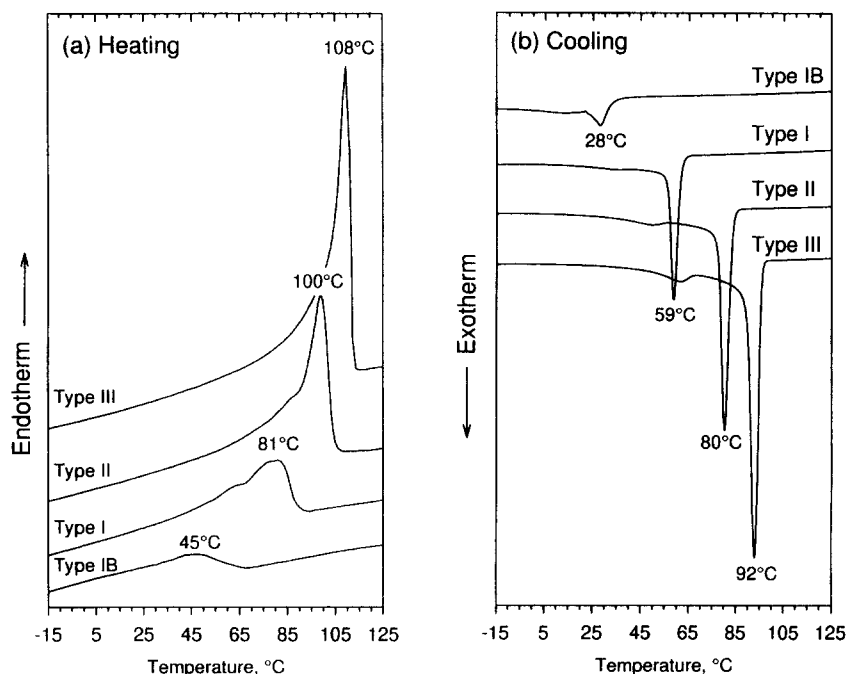
### Materials

Five ethylene–octene copolymers synthesized by the Dow INSITE<sup>®</sup> technology were used in the study. The resins had approximately the same molecular weight, but varied in comonomer content and density. The comonomer content (mol%) (ASTM D2238 Method B), the melt flow index (*I*<sub>2</sub>) and the ratio of melt flow indices at loads of 10 and 2.16 kg (*I*<sub>10</sub>/*I*<sub>2</sub>) (ASTM D1238) given in *Table 1* were provided by The Dow Chemical Company. One of the resins (Type IT) had the target density of 0.87 g ml<sup>-1</sup>. Binary blends with a target density of 0.87 g ml<sup>-1</sup> were prepared from a resin with a density lower than that of the target (Type IB) and three resins with densities higher than that of the target (Types I, II and III). In a previous study, the density of blends of these resins was shown to be additive<sup>2</sup>. The resin densities in *Table 1* were used to determine the blend compositions (w/w) required to obtain the target density. Blend compositions and densities are given in *Table 2*.

### Methods

The copolymers were melt blended in a Haake Rheomix 600 mixing head with 40 ml mixing volume, as described previously<sup>2</sup>. Copolymer blends were processed at 160°C for 8 min at 50 rev min<sup>-1</sup> under dry nitrogen. Single copolymers were processed under identical conditions to give them the same thermal history as the blends. The polymers were compression moulded into 1.4 mm thick plaques for testing. Alternatively, copolymer blends were prepared by dissolving the two components together in xylene (1% by weight of total solids) at 130°C with stirring. After 30 min the solution was precipitated into methanol at –20°C, filtered through sintered glass, washed with acetone and dried under vacuum at ambient temperature for 48 h.

Densities were measured in an isopropanol–distilled water density gradient column calibrated with glass



**Figure 1** Thermograms of component copolymers: (a) second heating scans; (b) cooling scans

floats. The average of three measurements is reported in *Tables 1* and *2*. The accuracy was  $0.0002 \text{ g ml}^{-1}$ .

Thermal analysis was carried out in a Perkin Elmer Model 7 DSC with approximately 5 mg specimens cut from the plaques. The thermograms were obtained with a heating/cooling rate of  $10^\circ\text{C min}^{-1}$ . All materials were held at  $190^\circ\text{C}$  for 10 min before cooling to  $-50^\circ\text{C}$ . The specimens were subjected to a second heating cycle with identical conditions as the first. Crystallinity calculations were based on a heat of fusion of  $290 \text{ J g}^{-1}$  for the polyethylene crystal.

The stress–strain behaviour in uniaxial tension was determined on ASTM 1708 microtensile specimens cut from the compression moulded plaques. The specimens were stretched in an Instron 1123 universal testing machine at a rate of  $10 \text{ min}^{-1}$ . Experiments at temperatures other than ambient were carried out in

an environmental chamber. Specimens were equilibrated at temperature for 10 min before testing.

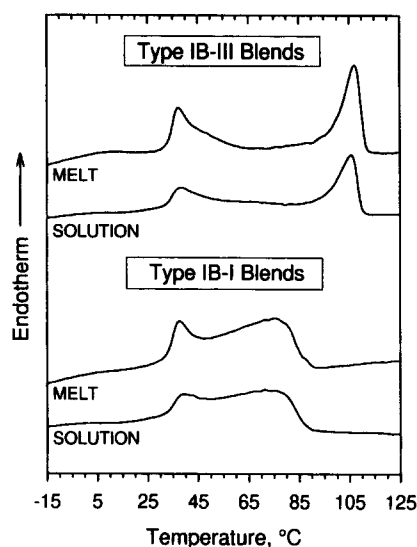
## RESULTS AND DISCUSSION

### Melting and crystallization

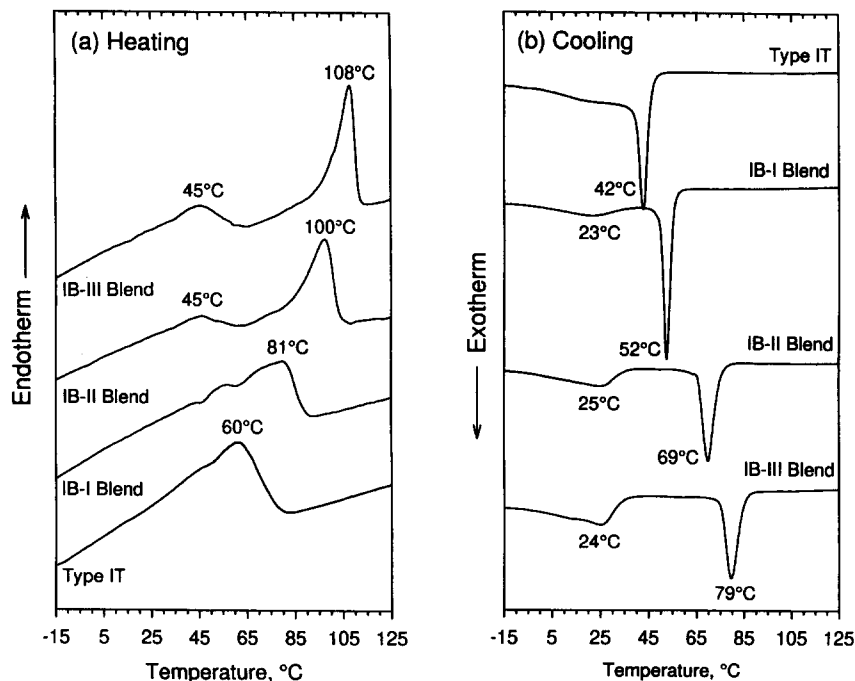
The melting behaviour of the four copolymers used in the blends is illustrated with second heating thermograms in *Figure 1a*. The first heating always exhibited an additional peak at about  $38^\circ\text{C}$ , which was attributed to melting of crystals that formed while the material aged at ambient temperature<sup>1</sup>. All copolymers showed broad melting endotherms with a long low temperature tail. The melting peak shifted to a lower temperature, from  $108$  to  $100^\circ$  to  $81$  to  $45^\circ\text{C}$ , and the melting enthalpy decreased with increasing branching. Cooling thermograms of the copolymers in *Figure 1b* all showed a large crystallization exotherm. Increased branching resulted in a decrease of the crystallization temperature and the crystallization enthalpy. The small low temperature exotherm is often found in the cooling curve of ethylene copolymers with low crystallinity<sup>4</sup>.

The melting behaviour of the solution blends and melt blends is compared using the first heating thermograms in *Figure 2*. The melting endotherms of copolymer blends prepared by solution were very similar to those of melt blends. Crystallization exotherms also exhibited no differences between solution and melt blends. This result is in general agreement with previous studies that describe essentially equivalent mixing by solution and melt blending of other ethylene copolymers<sup>5</sup>.

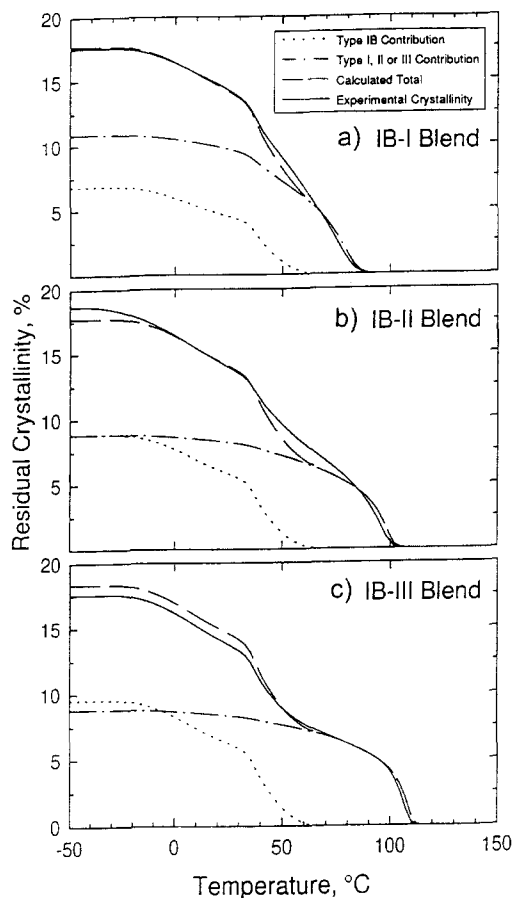
Melting thermograms of Types IB-I, IB-II and IB-III blends and Type IT copolymer are compared in *Figure 3a*. Second heatings were used to avoid the effects of ambient temperature annealing. The Types IB-II and IB-III blends exhibited two distinct melting peaks which corresponded to those of the components. Only the higher temperature melting peak of the Type I component was observed in the Type IB-I blend. Melting



**Figure 2** First heating thermograms of melt blends and solution blends



**Figure 3** Thermograms of melt blends: (a) second heating scans; (b) cooling scans



**Figure 4** Comparison of the residual crystallinity of blends with that calculated from the contributions of the individual components: (a) Type IB-I blend; (b) Type IB-II blend; (c) Type IB-III blend

of the Type IB component was not detectable in this blend, which contained the lowest amount of the low crystallinity Type IB component. The absence of any shift in the melting temperature of the components in the blends indicated that the two components crystallized as separate crystal populations in all the blends. The melting peak of the Type IT copolymer at 60°C fell between the two melting peaks of the blend components.

The crystallization behaviour of Types IB-I, IB-II and IB-III blends and Type IT copolymer is compared using the cooling thermograms in *Figure 3b*. All thermograms of the blends exhibited two crystallization peaks. Unlike the melting peak, the crystallization peak of the higher melting component was significantly lower than the crystallization temperature of the pure component. The shift was 13°C for Type III, 11°C for Type II and 7°C for Type I. Following the previous study<sup>2</sup>, it appears likely that crystallization of the Types IB-III and IB-II blends took place from a biphasic melt. The shift in crystallization temperature in blends with a low amount of the higher melting component may be due to small domains in the biphasic melt that amplified interfacial effects, although slight miscibility of Types II and III with Type I in the melt could also have affected the nucleation kinetics. In contrast, crystallization of the Type IB-I blend probably occurred from a homogeneous melt, and therefore the shift in crystallization temperature was due to the effect of blend composition on the crystallization kinetics of the higher melting component.

The concept of two separate crystal populations in the blends was examined by testing the additivity of the crystallinity. The residual crystallinity as a function of temperature was obtained by integrating the melting endotherms. The residual crystallinities of the two blend components were then added proportionally to obtain the residual crystallinity of the blend. First heating thermograms were used in order to have the same thermal history as the specimens used in tensile tests. The plots in *Figures 4a–c* include the proportional contribution of each component, the calculated crystallinity, which is the sum of the two contributions, and the experimental crystallinity obtained by integrating the heating thermogram of the blend. From the excellent agreement between the calculated curves and the experimental results, it was concluded that the components formed separate crystalline phases in all the blends.

#### Stress–strain relationship

Stress–strain curves of Types IB-I, IB-II and IB-III blends, and Type IT copolymer at three temperatures (25, 45 and 55°C) are shown in *Figures 5a–c*. The curves were typical of elastomeric behaviour with a low initial modulus and at higher strains a gradual increase in the slope. The only exception was the Type IB-III blend, which showed flow characteristics at 55°C. In all cases, there was a trend towards lower stresses and higher fracture strains as the temperature increased.

At 25°C, the stress–strain curves of all three blends and the copolymer corresponded closely up to about 400% strain. This was consistent with the previous observation that stress–strain behaviour at this temperature correlates with density or total crystallinity regardless of whether the material is an INSITE<sup>®</sup> copolymer or a blend of two INSITE<sup>®</sup> copolymers<sup>2</sup>. In the high strain, stress upswing region, the stresses were slightly, but reproducibly lower in the Type IB-II blend and even lower in the Type IB-III blend.

The 45°C stress–strain curves also matched closely up to 400%, but began to diverge more markedly at higher strains. At this temperature, the Type IB-I blend exhibited higher stresses than the Type IT copolymer; in contrast the Type IB-II blend exhibited lower stresses and the Type IB-III blend even lower stresses. The differences were magnified further in the 55°C stress–strain curves. The Type IB-I blend had a considerably higher load-bearing capacity than the Type IB-II blend and the Type IT copolymer at 55°C, even at low strains. Stresses were lowest in the Type IB-III blend. Furthermore, the stress–strain curve of the Type IB-III blend did not exhibit a stress upswing at high strain; instead, the gradually decreasing stress suggested a loss of network connectivity at this temperature.

Ethylene–octene copolymers prepared with the INSITE<sup>®</sup> technology have a broad melting range, and crystallinity changes significantly as temperature is varied within the melting range<sup>1</sup>. The decrease in residual crystallinity with temperature for the Types IB-I, IB-II and IB-III blends and Type IT copolymer is compared in *Figure 6*. All had the same initial level of crystallinity, about 17%, at 0°C where melting began. The Type IT copolymer was completely melted at a lower temperature than any of the blends because the less branched component of the blends imparted some level of residual crystallinity at higher temperatures. The amount of residual crystallinity, and the temperature

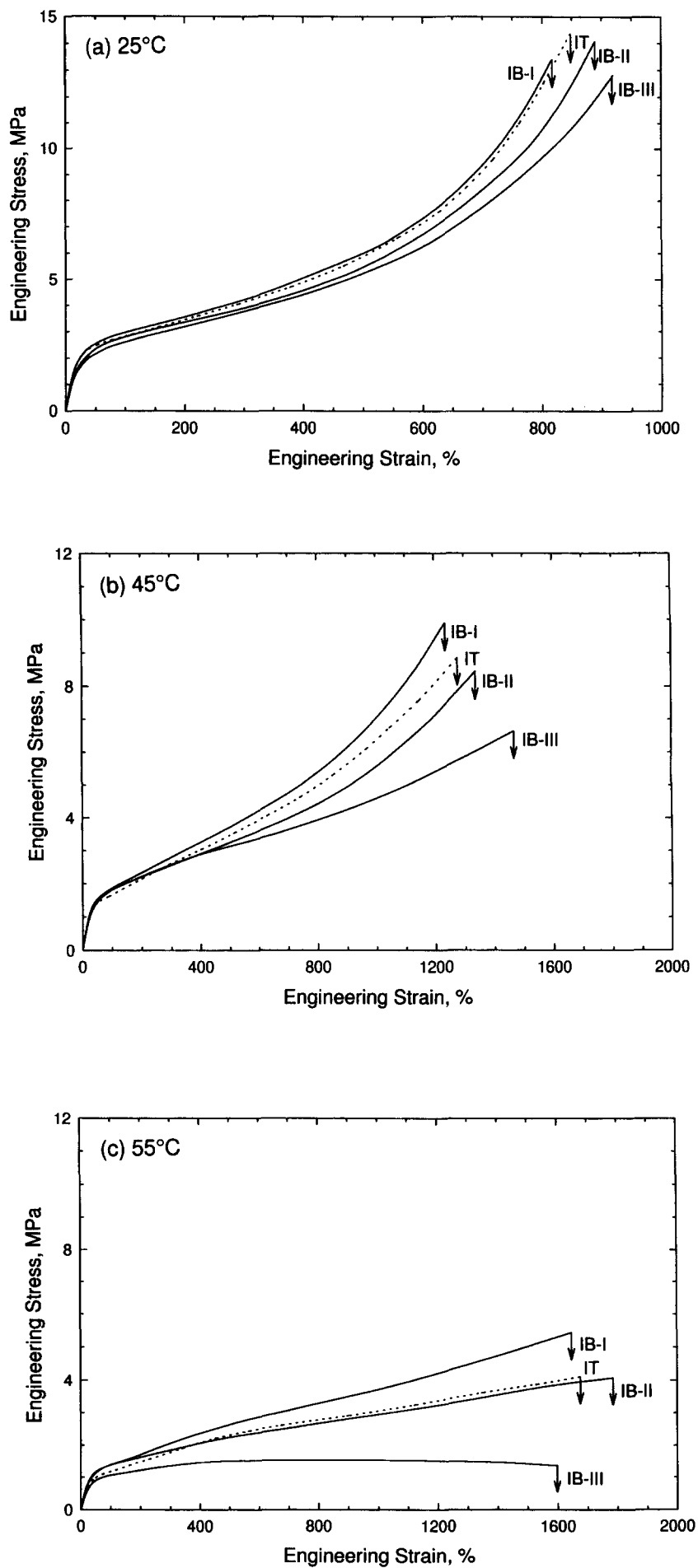


Figure 5 Stress-strain curves of blends and the target copolymer: (a) 25°C; (b) 45°C; (c) 55°C

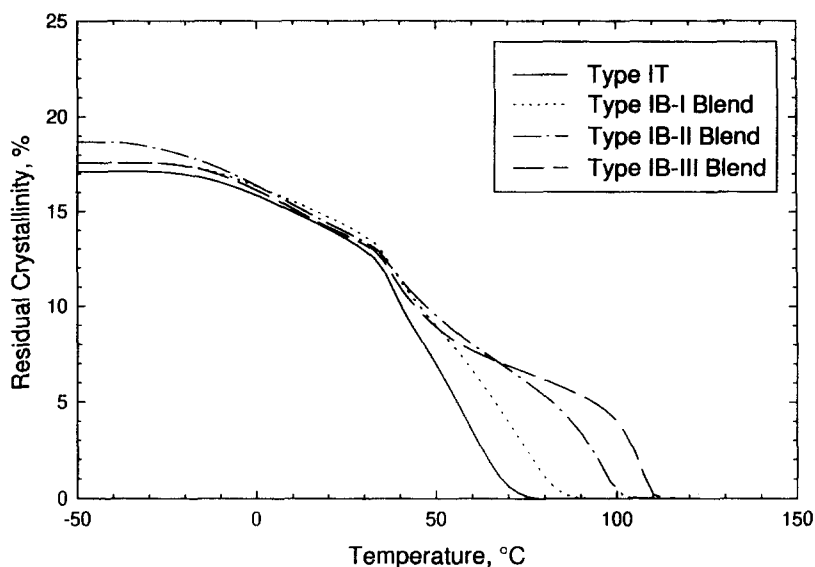


Figure 6 Comparison of the residual crystallinities of Type IT and the blends

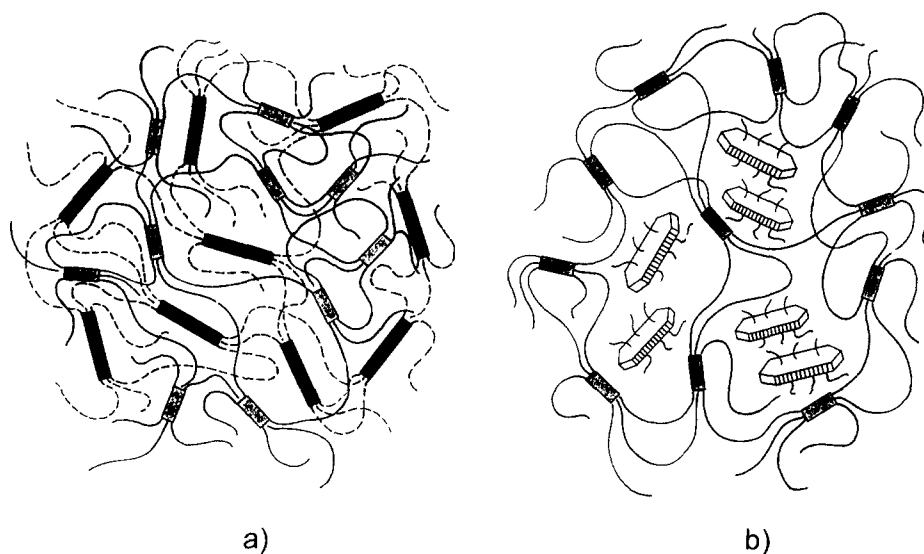


Figure 7 Schematic illustrations of the phase morphology: (a) Type IB-I blend with separate crystalline regions interconnected by a miscible non-crystalline phase; (b) Type IB-III blend with a continuous network of Type IB and phase-separated domains of Type III

required for complete melting, were dictated by the additivity relationship. Thus, the Type IB-III blend required the highest temperature for complete melting, the Type IB-II blend a somewhat lower temperature, and the Type IB-I the lowest temperature of the blends. If it is assumed that crystallinity imparts mechanical integrity to these linear polymers above their glass transition temperature, the results in Figure 6 are inconsistent with the observed stress–strain behaviour. In fact, the trends are reversed, and the blend with the lowest temperature requirement for complete melting, Type IB-I, has the highest load-bearing capacity at 55°C.

The structural model proposed to explain the elastomeric properties of Type I copolymers consists of a physical network with flexible chain segments linked by fringed micellar crystals that act as multifunctional junctions<sup>1</sup>. Gradual melting of the fringed micelles correlates with decreasing stress in the stress–strain curve, including decreasing elastic modulus and fracture stress. It is hypothesized that a blend of two Type I

copolymers forms a homogeneous melt, and the non-crystalline regions remain miscible after crystallization<sup>2</sup>. The resulting structural model for the blend consists of interpenetrating non-crystalline networks with fringed micellar junctions (Figure 7a). The networks are assumed to be co-continuous; it is also possible that they are interconnected by entanglements or by co-crystallization.

This model explains the behaviour of the Type IB-I blend. At ambient temperature, similar levels of crystallinity in Types IT and IB-I translated into similar numbers of junctions and similar mechanical properties. As the temperature increased, the faster melting of the Type IB component compared to Type IT was offset by the slower melting of the Type I component. As a result, the Type IB-I blend had a higher total crystallinity than Type IT at 45 and 55°C and therefore more junctions. This resulted in higher stresses in the stress–strain curve. The importance of the interconnected network was especially clear at 55°C where the Type IB component of the blend had completely

melted. At this temperature, the Type I component accounted for all the residual crystallinity, and the only crystalline junctions possible were those contributed by the Type I copolymer. Continuity of the Type I network made it possible for the blend to retain its elastic properties at temperatures above the melting point of the major component.

A different structural model must be considered for the Types IB-II and IB-III blends. The Type III copolymers form primarily lamellar crystals. Blends of a Type III copolymer with a Type I copolymer are thought to crystallize from a biphasic melt, and the non-crystalline regions are thought to remain immiscible upon cooling<sup>2</sup>. The resulting structural model for the Type IB-III blend where Type IB is the major component consists of a continuous network of Type IB with phase-separated domains of Type III (*Figure 7b*). Only the Type IB network contributed to the elastomeric properties of this blend. When the Type IB was melted at 55°C, the elastomeric behaviour of the Type IB-III blend was lost and the stress–strain curve assumed characteristics of flow.

The Type II copolymers are visualized as intermediate between Types I and III with a mix of lamellar and fringed micellar crystals<sup>1</sup>. Like blends of Type III and Type I, blends of Type II with Type I are also thought to crystallize from a biphasic melt, and the non-crystalline regions are thought to remain immiscible after crystallization<sup>2</sup>. The structural model for the Type IB-II blend is therefore similar to that in *Figure 7b*. However, the stress–strain curve of the Type IB-II blend exhibited elastic character at 55°C even though the fringed micellar junctions of the Type I network were melted at this temperature. This suggested that there existed some interconnectivity of the Type II component with the continuous Type IB network that enabled some of the Type II crystals to function as network junctions. The connectivity was not very efficient, however, because at 55°C the Type IB-II blend had about the same load-bearing capacity as Type IT, and in contrast the total residual crystallinity of the Type IB-II blend was about twice that of Type IT.

In summary, the narrow molecular weight distribution and homogeneous comonomer distribution of INSITE<sup>®</sup> copolymers offer an opportunity to tailor blend compositions to achieve controlled phase morphology and

optimized properties. This study focuses on the elastomeric behaviour of binary blends with extremely low crystallinity. The structural model for the elastomeric properties consists of a physical network with flexible chain segments linked by fringed micellar crystals that act as multifunctional junctions. Because the broad melting range of the fringed micellar crystals determines how well the properties are maintained at elevated temperatures, blending with a higher melting copolymer, i.e. one of lower branch concentration, might extend the properties to higher temperatures. It appears that this approach is successful if the non-crystalline regions of the blend components are miscible. The branch concentrations of the components used in this study are sufficiently different that they crystallize separately in blends. This is not necessarily undesirable if both crystal populations contribute as junctions to the elastic network. However, if the non-crystalline regions also form separate phases, interconnectivity is not achieved and the elastomeric properties are dominated by the network of the continuous component. This has a detrimental effect on the properties especially at higher temperatures as the network starts to melt. In contrast, if the non-crystalline regions are miscible, both crystalline populations contribute to the network and it is possible to achieve synergistic effects on tensile strength by blending with a higher melting component.

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