

Influence of Branching Characteristics on Thermal and Mechanical Properties of Ziegler-Natta and Metallocene hexene-LLDPE blends with LDPE

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ABSTRACT

The effect of branch content (BC) and composition distribution (CD) of LLDPE on the thermal and mechanical properties of its blends with LDPE were studied. All blends and pure resins were conditioned in a Haake PolyDrive blender at 190°C and in the presence of adequate amount of antioxidant. Two metallocene and one Ziegler-Natta (ZN) hexene LLDPEs were melt blended with the same LDPE. The effect of BC was investigated by blending two hexene m-LLDPEs of similar M_w and MWD and of different BC with the same LDPE. The effect of CD was studied by using a ZN and a m-LLDPE of similar M_w , BC and comonomer type. Low-BC m-LLDPE blends showed separate crystallization while cocrystallization was observed in the high-BC m-LLDPE-rich blends. However, ZN-LLDPE/LDPE blends showed separate crystallization together with a third population of cocrystals. Influence of crystallization behavior was reflected on the mechanical properties. The BC has influenced the modulus, ultimate tensile strength and toughness. Addition of small amount of LDPE to a low-BC m-LLDPE resulted in major improvement of toughness, while the results for the high-BC pair followed additivity rule. ZN-LLDPE blends with LDPE blends were found to be more compatible and exhibited superior mechanical properties compared to m-LLDPE counterparts of the same M_w and BC. All mechanical properties of ZN-LLDPE blends follow linear rule of mixtures. However, CD was observed to have stronger influence on mechanical properties in comparison to BC.

Keywords: LLDPE/ LDPE blends, mechanical properties, DSC, branch content, composition distribution

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1. Introduction

Linear low-density polyethylene (LLDPE) is a copolymer of an α -olefin such as 1-butene, 1-hexene or 1-octene and ethylene produced by Ziegler-Natta (ZN) or more recently by metallocene catalysis. LLDPEs were reported to have superior mechanical properties like high tensile strength, high elongation at break and better tear and impact strength¹⁻⁸. However, they show poor processability (sharkskin effects and melt fracture at high rates). On the other hand, low-density polyethylene (LDPE) is characterized by good toughness and flexibility^{1,3}. Moreover, LDPE exhibits excellent processability due to the presence of long chain branching (LCB). LLDPE is usually blended with LDPE to combine the superior mechanical properties of the former with the ease of processing of the latter^{1,3,6,9-11}. Further, blending LDPE into LLDPE gives excellent optical properties and better bubble stability in blow molding applications due to the increase in melt strength^{1,9,12}. Blends of LLDPE and LDPE find applications in the film and blow molding industries.

However, the improvement in properties of the melt or solid state is determined by compatibility of the blend. Blends of LLDPE and LDPE were reported to phase separate in the melt^{4,13-17}. On the other hand, complete melt homogeneity of these blends was reported^{6,11,12}. However, LLDPE/LDPE blends are suggested to be immiscible (incompatible) in the solid state^{1,6,13,14,16,17}. This phase separation is usually dictated by molecular parameters such as M_w , MWD, branch content (BC), composition distribution (size and structural heterogeneity) and blend composition^{11-13,15,18-20}. Whereas the melt miscibility/immiscibility is governed by the mismatch of conformations of blend

components^{10,15,21,22} the solid-state behavior is controlled by separate or co-crystallization.

Muller et. al.⁷ observed separate crystal populations in ZN-LLDPE/LDPE blends with some degree of cocrystallization in the LLDPE-rich blends. However, good interaction between the phases was concluded since the tensile properties indicated that the blends were mechanically compatible. Kyu et al.²³ used DSC and light scattering to study slowly cooled blends of ZN-LLDPE/LDPE blends. It was observed that ZN-LLDPE crystallized first forming skeletal spherulites within which LDPE had crystallized. Separate crystallization in LLDPE/LDPE blends was also reported by others researchers^{1,14,16}. However, ZN-LLDPE is known for its structural heterogeneity, mainly inter and intra-molecular heterogeneities²⁴⁻²⁶ which makes isolation of molecular parameters very difficult, if not impossible.

Recently, blends of metallocene LLDPE (m-LLDPE) and LDPE were investigated. Thermal fractionation measurements of Chen et. al.¹² suggested *cocrystallization* at all compositions of m-LLDPE/LDPE blends, whereas, DSC data of Yamaguchi and Abe¹¹ suggested *separate crystallization*. The effect of BC was reported to be critical on the crystallization behavior of blends of linear and branched PE^{18,19,20,24,25,27}. The critical BC for separate crystallization was reported to be much less in the m-LLDPE/HDPE blends compared to ZN-LLDPE/HDPE blends^{20,24}. However, no such investigation was carried out for LLDPE/LDPE blends.

Also, composition distribution (CD) is an important parameter that determines the crystallization behavior of polyethylene blends. Recently, Xu et al.¹³ reported higher degree of cocrystallization in ZN-LLDPE/LDPE blends compared to m-LLDPE/LDPE

blends for the same BC and comonomer type. However, other researchers suggested no effect for CD^{25,27} (usually referred to in these publications as branch distribution).

Many studies have appeared on mechanical characteristics of polyolefin blends^{2,5-7, 29-34}. La Mantia and coworkers^{5,34} investigated the effect of comonomer type and M_w on the rheology and mechanical characteristics of ZN-LLDPE/LDPE blends. Comonomer type was found to influence the mechanical properties only slightly. On the contrary, mechanical properties were a strong function of M_w . Cho et al.⁶ observed that ZN-LLDPE/LDPE blends show synergistic effects on the yield strength and elongation at break while the strength at break varies linearly with composition. The mechanical properties of blends of different LLDPE/LLDPE resins of uniform branch distribution were found to be a function of total crystallinity rather than the type of crystallinity³³. Recently, the authors showed that both BC and CD of LLDPE influence its melt miscibility with LDPE²². Here, the investigation is extended to the solid state and the influence of BC and CD of LLDPE on the thermal and mechanical properties of LLDPE/LDPE blends is studied.

2. Experimental

2.1 Materials and Sample Preparation

Two commercial samples of m-LLDPE, one of high BC (BC= 32.2 CH₃/1000 C) and another one of low-BC (BC= 14.4 CH₃/1000 C) and a LDPE were used. The three resins were ExxonMobil products. The ZN-LLDPE was provided by SABIC, Saudi Arabia (ExxonMobil technology). All LLDPEs were hexene-based copolymers. The BC of LLDPE was obtained from ¹³C NMR. Table 1 provides characterization data such as density at room temperature, melt index (MI) at 190°C as provided by the manufacturer.

The M_n , M_w as well as polydispersity (PD) were obtained by Waters 2000 GPC instrument. Trichlorobenzene was used as solvent ($T=135^\circ\text{C}$) and standard polystyrene samples were utilized for calibration. The label 1 denotes the m-LLDPE with low BC as m-EH1 (metallocene Ethylene-Hexene copolymer) and the resin with high BC was labeled m-EH2. The ZN-LLDPE is labeled as ZN-EH. The same LDPE was used in all of these blends. The effect of BC of LLDPE was investigated by studying blends of m-EH1 and LDPE and results were compared to those obtained by blending m-EH2 and LDPE. Samples m-EH1 and m-EH2 were chosen in a way that BC would be the only primary molecular parameter in this comparison. As shown in Table 1, m-EH1 and m-EH2 were of the same branch type (hexene), similar M_w and MWD, and both LLDPEs were metallocene resins. Hence, comparison of m-EH1 and m-EH2 blends with LDPE is expected to reveal the effect of BC on the thermal and mechanical characteristics of m-LLDPE/LDPE systems. Similarly, the comparison of m-EH1 and ZN-EH blends with LDPE is likely to show the influence of CD, since BC and M_w were similar.

The LDPE and LLDPE resins used in this study were conditioned (or blended) in a Haake PolyDrive melt blender. Conditions and details of melt blending and sample preparation of dog-bones for thermal and mechanical analyses were discussed in a previous publication aimed at studying the melt miscibility of these samples¹⁵.

2.2 Differential Scanning Calorimetry (DSC)

Thermal analysis was performed with a TA Instruments DSC 2910 equipped with Thermal Analyst 2200 software, and nitrogen gas flow was used as a blanket. 5-10 mg samples were sliced and then compressed into aluminum pans for testing. The samples were heated from 25°C to 200°C at $10^\circ\text{C}/\text{min}$ to remove the thermal history, held at

200°C for one minute and then cooled to 25 °C at the same rate. All samples were subjected to a second identical heating cycle. Crystallinity calculations were based on a heat of fusion of 290 Jg⁻¹ for the polyethylene crystal³⁵.

2.3 Mechanical Testing

Dog-bone samples were prepared according to ASTM D638 (type V). The tensile tests were performed on the Instron 5567 tensile testing machine at 25°C. The gauge length was kept at 25 mm with a crosshead speed of 125 mm/s. All samples ruptured within 0.5 to 5 min of testing time. All the reported mechanical parameters are based on an average of a minimum of five samples.

3. Results and Discussion

3.1 Thermal Analysis

DSC melting endotherms for the low-BC m-LLDPE (m-EH1) blends with LDPE together with pure resins are given in Figure 1a. The second heating curves were used for comparison to avoid the effects of ambient cooling^{12,20,33}. LDPE showed the highest melting point (T_m), which shifts to a lower value as the amount of m-EH1 increases in the blend. Further, all LDPE rich blends showed a single and sharp melting peaks. However, the m-EH1 and 90% m-EH1/LDPE blends displayed two distinct melting peaks. The double peak in the pure m-EH1 signifies the bimodal nature of this resin and is a clear indication of different crystal populations²⁰. Also, the peaks of m-EH1-rich blends are relatively broader than that of LDPE-rich blends. In an attempt to obtain further information on crystallization mechanism the DSC cooling-run measurements were also performed. Figure 1b shows the DSC crystallization thermograms obtained at a cooling

rate of 10 °C /min. In contrast to the heating curves, only single peaks were observed. The LDPE showed the highest crystallization temperature (T_c) that decreased systematically as the m-EH1 component increased in the blends. The influence of blending was further examined by comparing the observed crystallinities to those obtained by adding the component crystallinities in the same proportion in which they appear in the blend. The DSC crystallinities of each polymer will be an additive in the blend if blends crystallize in the same manner as in pure polymers. Whereas, a low or high crystallinity of the blend compared to the pure components was taken as an argument in favor of separate or co-crystallization^{12,20,33}. It can be very clearly seen from Figure 2a that all blends follow the linear additivity rule. Hence, it could be easily concluded that these blends form separate crystals. These results are in agreement with previous observations of Yamaguchi and Abe¹¹ obtained for m-LLDPE/LDPE blends. The percentage crystallinity for all blends was given in Figure 2 for ease of comparison and will be discussed in the following sections.

Figure 3a shows the melting endotherms for the blends of m-EH2 with LDPE. Once again LDPE showed the highest T_m while m-EH2 the least, which is due to the large number of short chain branches in m-EH2. The depression in T_m for increasing comonomer incorporation is explained by the occurrence of shorter ethylene sequences between short chain branches (SCB) in the sample containing high amounts of comonomer²⁰. The LDPE-rich blends show sharp peaks whereas the m-EH2-rich blends melt over a broad range. The crystallization peaks are shown in Figure 3b. A shift in T_c is broad compared to that seen in the m-EH1 blends. Again the observed crystallinities were compared with those calculated from the additivity rule (Figure 2b). For blends with $\phi \geq$

30%, the observed crystallinities are less than those calculated by the additivity rule. As discussed before, this observation suggests co-crystallization. Although high-BC is expected to hinder co-crystallization, the opposite is observed. This is likely to be due to structural heterogeneities of m-LLDPEs^{20,25}. Also, it was found that the comonomer distribution is more homogeneous in samples containing low BC compared to samples containing higher BC²⁰. Hence, the cocrystallization is suggested to take place between the less branched segments of m-EH1 and similar fractions of the LDPE. In fact, temperature rising elution fractionation (TREF) analysis of blends of LLDPE and LDPE suggested that fraction containing similar branches were more likely to cocrystallize than fractions with different BCs^{12, 37}. The left over highly branched fractions were suggested to form separate crystal populations.

Finally, DSC melting peaks for the ZN-LLDPE (ZN-EH) are shown in Figure 4a. LDPE and ZN-EH exhibit sharp melting peaks while all blends display multiple peaks over a broad range of temperatures. The presence of multiple peaks in ZN-EH/LDPE blends is interesting as no such peaks were observed in the metallocene LLDPE blends. Take for instance the 30/70 blend in Figure 4a. The peak at 109.5°C most probably represents the LDPE or more precisely the LDPE-rich phase whereas the peak at 124.6°C exhibits the presence of ZN-EH-rich crystals. So, what does the third peak at 120.56°C represent? It is likely for co-crystals of ZN-LLDPE and LDPE. In fact, similar multiple peaks were observed by other researchers for the ZN-LLDPE/LDPE blends^{7,12,37}. Xu et al.¹³ working with ZN-LLDPE and LDPE blends reported similar melting peaks in the 50/50 blend. It was suggested that these peaks represent three different crystal populations in the blend namely, LDPE or more accurately LDPE-rich crystals, segregated cocrystals and ZN-

LLDPE-rich crystals. Compared to the low-BC LLDPE (m-EH1), which has almost the same branch content, ZN-EH displays a higher melting temperature, even higher than LDPE. The linear fractions of ZN-EH can really form thicker lamellas, melting at high temperatures (see Fig. 59 on p. 372 of Ref. 35). The DSC cooling curves for the ZN-EH blends are shown in Figure 4b. To assess the degree of cocrystallization once again measured crystallinities were compared to those calculated by assuming completely separate crystallization (Figure 3c). A very symmetric trend is observed around the 50% composition, which shows crystallinity less than that calculated by the additive rule. For all other compositions, the observed crystallinity is higher than that calculated assuming separate crystallization. The increase in crystallinity could be explained as: the summation of separate crystals composed of LDPE-rich and ZN-EH-rich blend are equal to the crystallinity predicted by additive rule while the separately existing co-crystals population contributes an additional value to the observed crystallinity.

Hence, in summary the branch content and distribution of LLDPE were found to influence the solid-state morphology of LLDPE/LDPE blends. Blends containing high-BC m-LLDPE showed some cocrystallization in the LLDPE-rich blends i.e. improved compatibility. However, in the case of low-BC m-LLDPE blends with LDPE only separate crystallization was observed. This is contrary to the behavior reported for linear and branched PEs where higher branching leads to separate crystallization (18-20,24). However, the ZN-LLDPE blends behaved quite differently. Multiple peaks suggesting three different populations of crystals were observed to exist at all compositions. These observations indicate that ZN-LLDPE/LDPE blends were more compatible than m-

LLDPE/LDPE blends. The heterogeneity of ZN-EH, especially the presence of linear PE may have helped in the co-crystallization with the long chain branches present in LDPE.

3.2 Mechanical Properties

The tensile moduli as function of composition for m-EH1/LDPE are shown in Figure 5a. In the following figures the error bars show standard deviation of the results for at least five specimens. The modulus for LDPE is 145.9 MPa while that of m-EH1 is 78.65 MPa. Moduli for the blends were observed to be lower than that calculated by the linear rule of mixtures. The moduli for the m-EH1-rich blends were even less than that of pure constituents. The modulus for m-EH2 is 23.68 MPa. This is due to the high comonomer content and the resulting low crystallinity. The moduli for m-EH2-rich blends were found to be very close to those predicted by the rule of mixtures. This is attributable to the cocrystallization observed in these blends in contrast to separate crystallization in m-EH1/LDPE blends (see Figure 2 a & b). However, LDPE-rich blends show negative deviation from linear rule of mixtures although single melting peaks were observed for these blends (Fig. 3a). Figure 5c shows the moduli for ZN-EH blends. The modulus for ZN-EH is 119.73 MPa, which is almost twice the modulus of more homogeneous m-EH1 polymer of similar BC. All moduli for ZN-EH/LDPE blends show linear variation with composition. Again, cocrystallization is suggested as the reason for the compatibility of these blends. Comparison of Figures 5a and 5c suggests that CD influences the modulus, especially m-LLDPE-rich blends. Hence both BC and CD have influenced the modulus; however, the effect of CD is stronger for LDPE-rich blends.

Strength at yield for the three blend systems under investigation is shown in Figure 6. Blends of m-EH2 with LDPE follow a behavior similar to that of the modulus. For blends

of m-EH1 with LDPE, only the LDPE-rich blends showed similar behavior to the modulus. Figures 6a and 6b show the effect of BC on yield strength. For LDPE-rich blends, the strength at yield displayed weak negative deviations from linear rule of mixtures, whereas LLDPE-rich blends followed the rule. Also, the strength at yield followed approximately the rule of mixture regardless of BC. Strength at yield of ZN-EH/LDPE blends again exhibits a linear relationship with respect to composition (Figure 6c) similar to the modulus. Strength at yield of ZN-EH is comparable to that of m-EH1 with similar BC. Hence, both BC and CD have little influence on strength at yield.

Ultimate tensile strength for the above blends studied is displayed in Figure 7. In all cases the strength at break for the LLDPE is higher than that of LDPE of the same M_w , which is consistent with previous reports^{6,35}. Ultimate tensile strength of m-EH1/LDPE blends increases linearly with the addition of m-EH1 (Figure 7a). The strength at break for m-EH1 was 30.88 MPa, and that for m-EH2 was 23.26 MPa. This shows that increasing the BC has negative effect on ultimate tensile strength. Further, the ultimate tensile strength values of the m-EH2/LDPE blends show synergistic effect (Figure 7b). The 30% and 50% m-EH2 blends with LDPE show values comparable to the strength at break of pure m-EH2 while those of the m-EH2-rich blends are even higher. On the other hand, ZN-EH/LDPE followed a linear trend with respect to composition (Figure 7c). Similar behavior for ZN-LLDPE/LDPE blends was reported by Cho et al.⁶. Comparison of Figures 7a and 7b shows the strong effect of BC on ultimate tensile modulus. Also, Figures 7a and 7c suggest the influence of CD on ultimate strength with ZN-LLDPE following closely linear additivity. Here, the effect of BC on ultimate strength is stronger than that of CD especially for m-LLDPE-rich blends.

The elongation at break for different blend systems is given in Figure 8. Similar to the strength at break values, elongation at break for LLDPE's was found to be higher than LDPE irrespective of BC or synthesis type. As seen in Figures 8a and 8b the low-BC and high-BC m-EH blends with LDPE display similar trends, although m-EH2 shows a higher elongation at break. Elongation at break for blends was always higher the predictions of rule of mixtures. However, the ZN-EH/LDPE blends show a linear increase in elongation at break as the ZN-EH fraction increases in the blend (Figure 8c). Also, ZN-EH shows elongation at break twice that of m-EH1 of similar BC and M_w , which is likely due to the presence of the linear fractions in ZN-LLDPE²⁴. Hence, for elongation at break the influence of CD is stronger than that of BC and synergistic effects were obtained in all m-EH blends.

Finally, area under the stress-strain curve which is proportional to the toughness of material is given in Figure 9. For m-EH1/LDPE and m-EH2/LDPE blends, two regions were detected: the LDPE-rich ($\phi < 0.5$) and the LLDPE-rich ($\phi > 0.5$). Similar trend is observed in the LDPE-rich blends ($\phi < 0.5$) with 30% LLDPE blend showing maximum toughness. However, in the LLDPE-rich blends ($\phi > 0.5$) tremendous enhancement in toughness is observed for m-EH1/LDPE blends while the m-EH2 blends exhibit toughness close to the estimations from additivity. The ZN-EH is almost twice tougher than m-EH1. The toughness of ZN-EH blends vary linearly with the addition of the tougher component (ZN-EH). On the other hand, addition of a small amount of LDPE to m-EH1 has resulted in major improvement of toughness. Again, the effect of CD of m-LLDPE on the toughness of m-LLDPE/LDPE blends was observed to be stronger than the influence of BC.

The above discussion can be summarized as follows:

- ◆ For the same M_w the three LLDPEs: m-EH1, m-EH2 and ZN-EH exhibited different mechanical properties. In the linear elastic range, ZN-EH showed the maximum modulus while strength at yield was comparable for ZN-EH and m-EH1. The high-BC m-EH2 displayed the lowest properties. Also, the properties were observed to be associated with the degree and type of crystallization in these polymers. At large deformations, m-EH2 displayed the highest ultimate tensile strength whereas ZN-EH exhibited maximum elongation at break and toughness.
- ◆ Influence of BC on blends was observed in modulus, ultimate tensile strength and toughness. m-EH2/LDPE blends displayed synergistic effect in ultimate tensile strength while m-EH1-rich blends with LDPE were found to be tougher than m-EH2 rich blends. BC had little or no significant influence on elongation at break and strength at yield. The influence of BC on ultimate strength is stronger than that of CD.
- ◆ In general, the effect of CD on the mechanical properties prevailed over that of BC.

4. Conclusion

Blends of three different LLDPEs (two metallocene-based and one Ziegler-Natta based) with similar M_w were melt blended with the same LDPE. The LLDPEs were selected to study the effect of branch content and composition distribution, one variable at a time. Effects of both the BC and the CD on thermal and mechanical properties of LLDPE/LDPE were investigated. Low-BC m-LLDPE blends with LDPE showed separate crystallization while co-crystallization was observed in the high-BC-rich blends

of m-LLDPE with LDPE. However, ZN-LLDPE/LDPE blends showed separate crystallization together with a third population of cocrystals. Influence of crystallization behavior was reflected on the mechanical properties. BC and CD of LLDPE were observed to influence the mechanical properties of LLDPE/LDPE blends. In general, the influence of CD was enormous. Addition of a small amount of LDPE to m-LLDPE resulted in major improvement of both toughness for low-BC m-LLDPE/LDPE blends and ultimate tensile strength of low and high-BC blends. Further, ZN-LLDPE/LDPE blends were found to be most compatible and exhibited superior mechanical properties compared to metallocene counterparts. All mechanical properties of ZN-LLDPE/LDPE blends can be predicted by the simple rule of mixtures.

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Table 1: Characterization of Resins

Resin	Density g/cm ³	MI g/10 min	M _w kg/mol	PD=M _w /M _n	Branch Content CH ₃ /1000 C
m-EH1	0.912	1.2	102	2.14	14.4
m-EH2	0.883	2.20	97	2.02	32.2
ZN-EH	0.917	2.80	107	4.01	16.7
LDPE	0.923	1.2	100	4.14	11*

*Total number of short and long branches

Legends for Figures:

Figure 1a. DSC Heating scans for m-EH1/LDPE blends

Figure 1b. DSC Cooling scans for m-EH1/LDPE blends

Figure 2. Percentage crystallinity as a function of composition.

Figure 3a. DSC Heating scans for m-EH2/LDPE blends

Figure 3b. DSC Cooling scans for m-EH2/LDPE blends.

Figure 4a. DSC Heating scans for ZN-EH/LDPE blends.

Figure 4b. DSC Cooling scans for m-EH1/LDPE blends.

Figure 5. Tensile modulus as a function of composition.

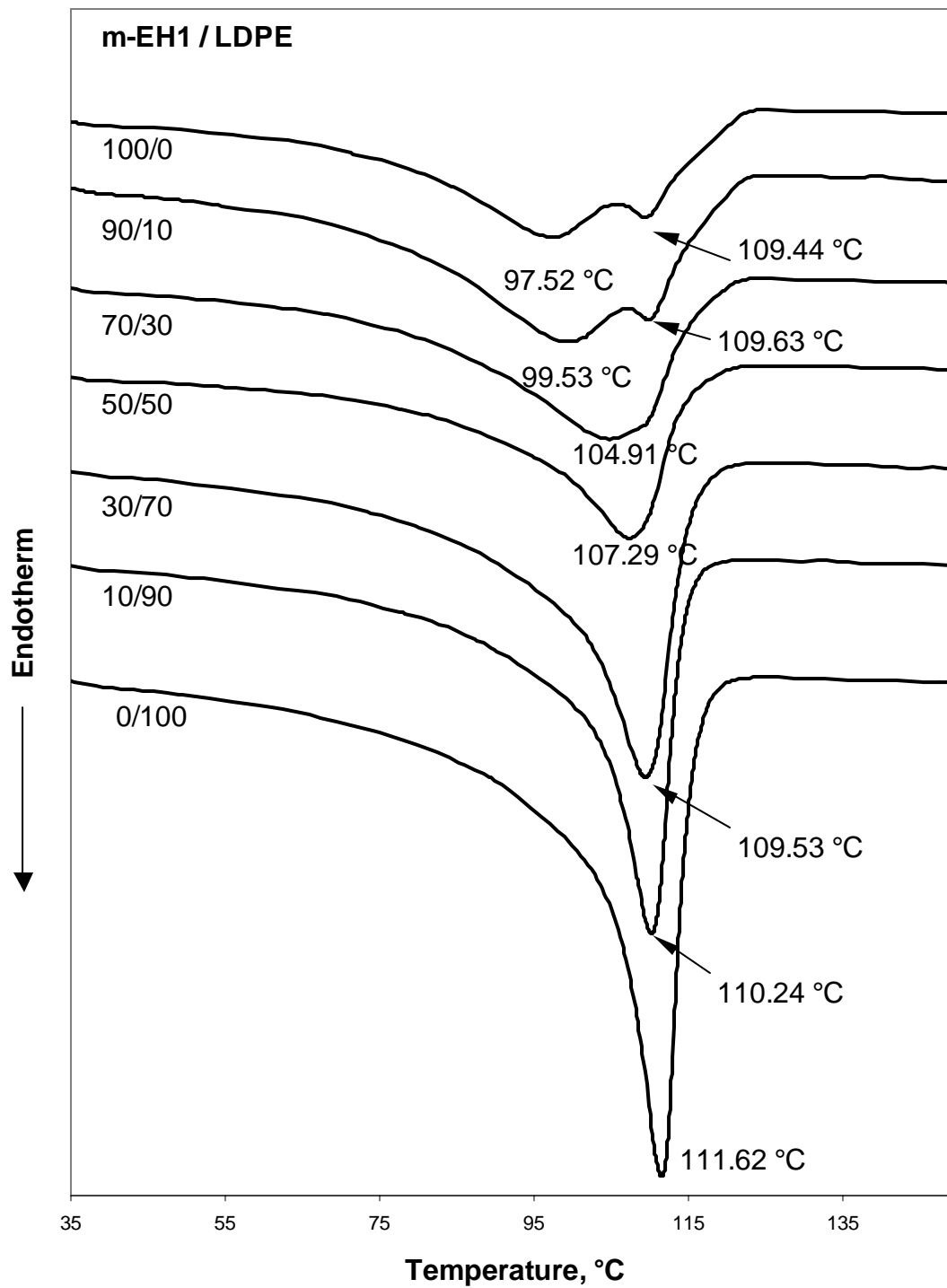
Figure 6. Strength at yield as a function of composition.

Figure 7. Ultimate tensile strength as a function of composition.

Figure 8. Elongation at break as a function of composition.

Figure 9. Work of rupture as a function of composition.

Figure 1a. DSC Heating scans for m-EH1/LDPE blends



**Figure 1b. DSC Cooling scans form-
EH1/LDPEblends**

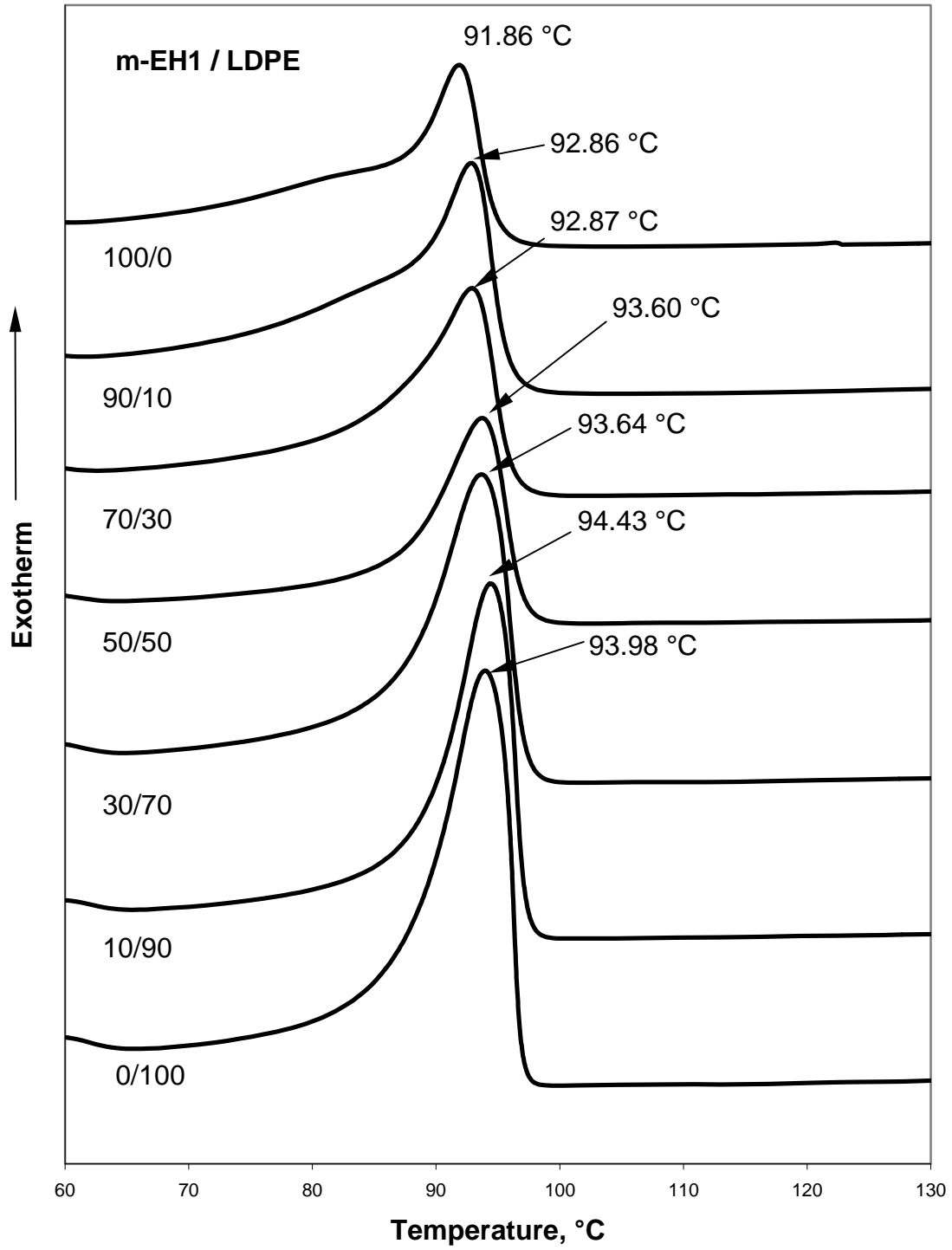


Figure 2. Percentage crystallinity as a function of composition

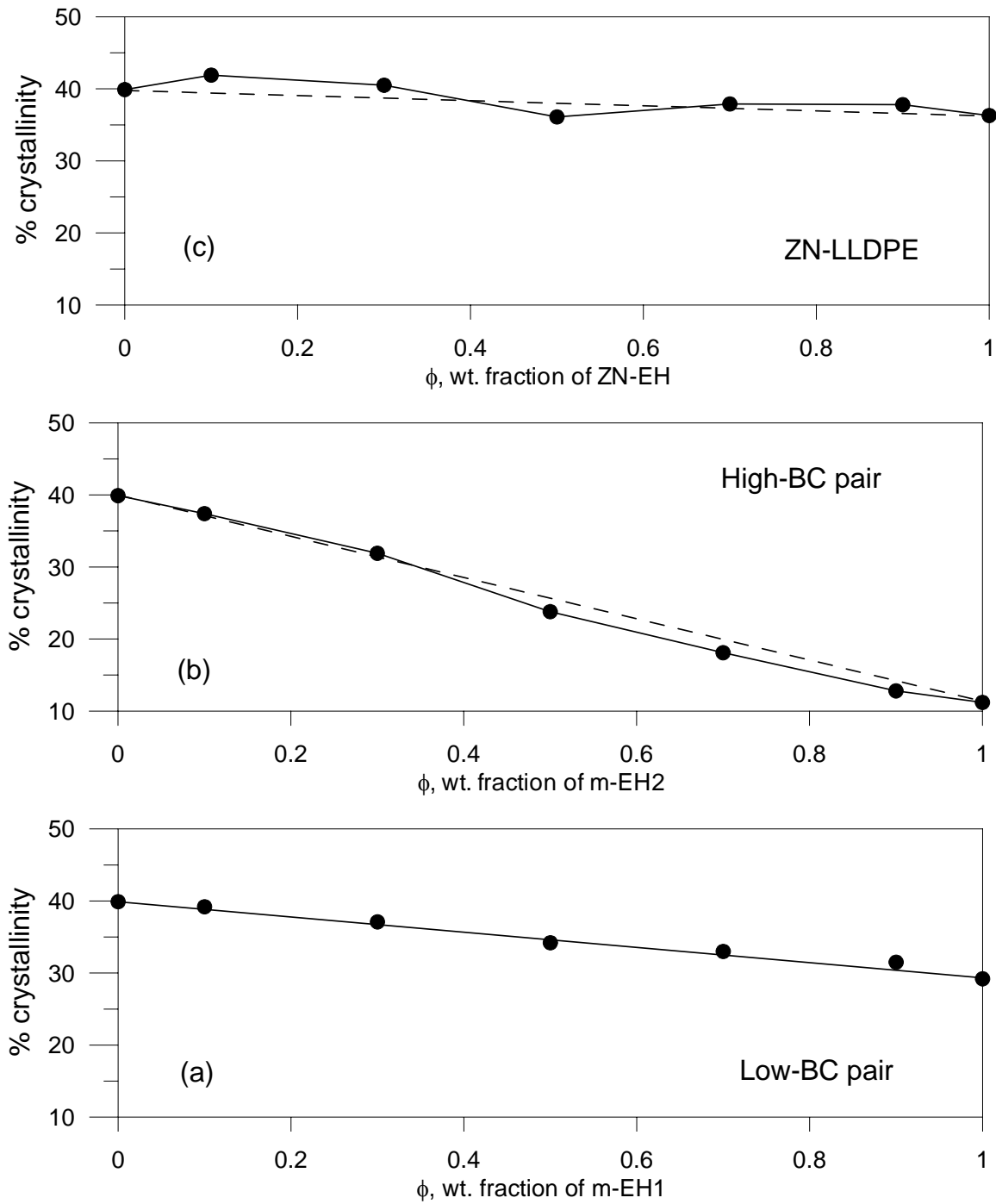


Figure 3a. DSC Heating scans for m-EH2/LDPE blends

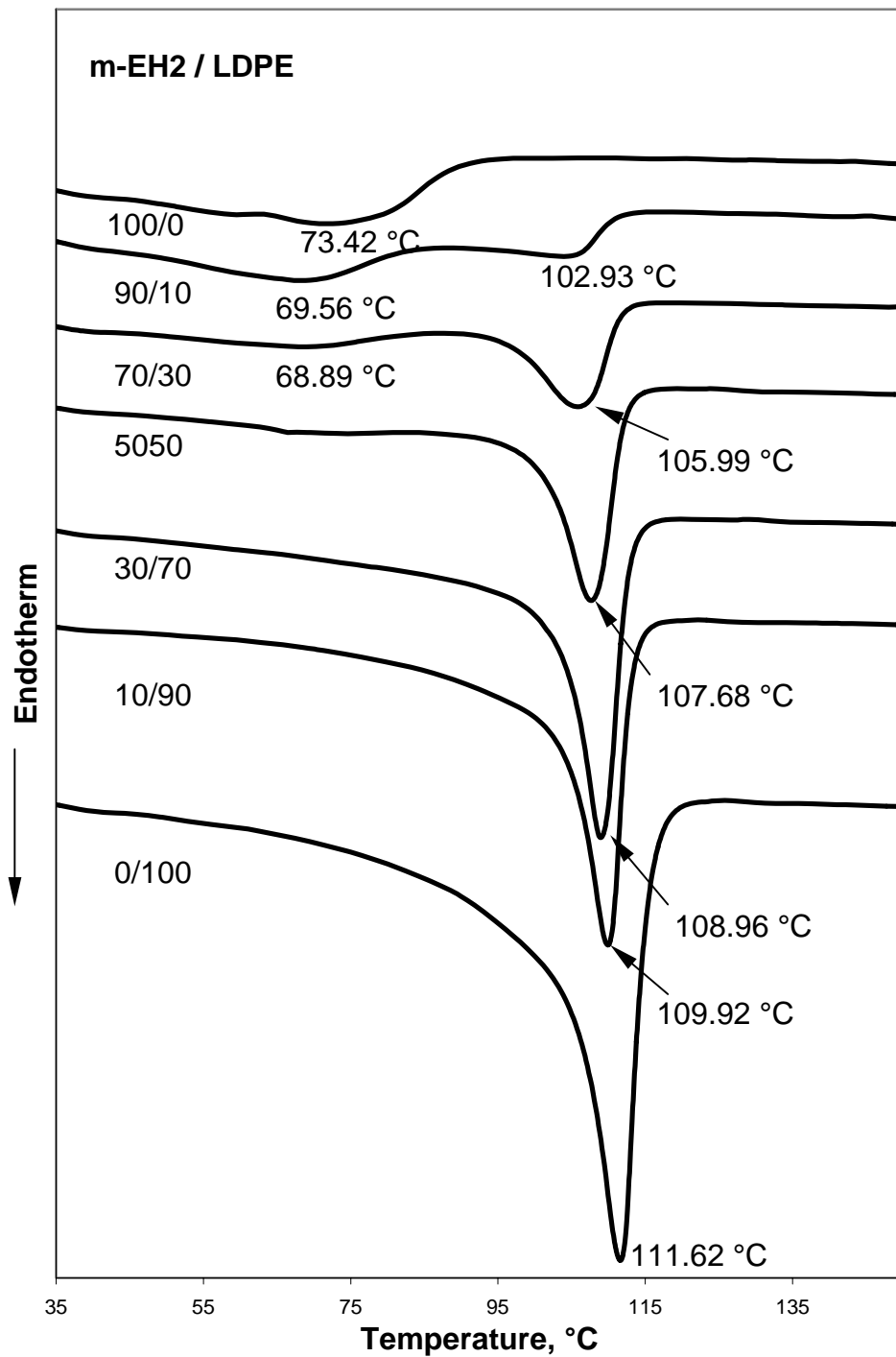


Figure 3b. DSC Cooling scans for m-EH2/LDPE blends

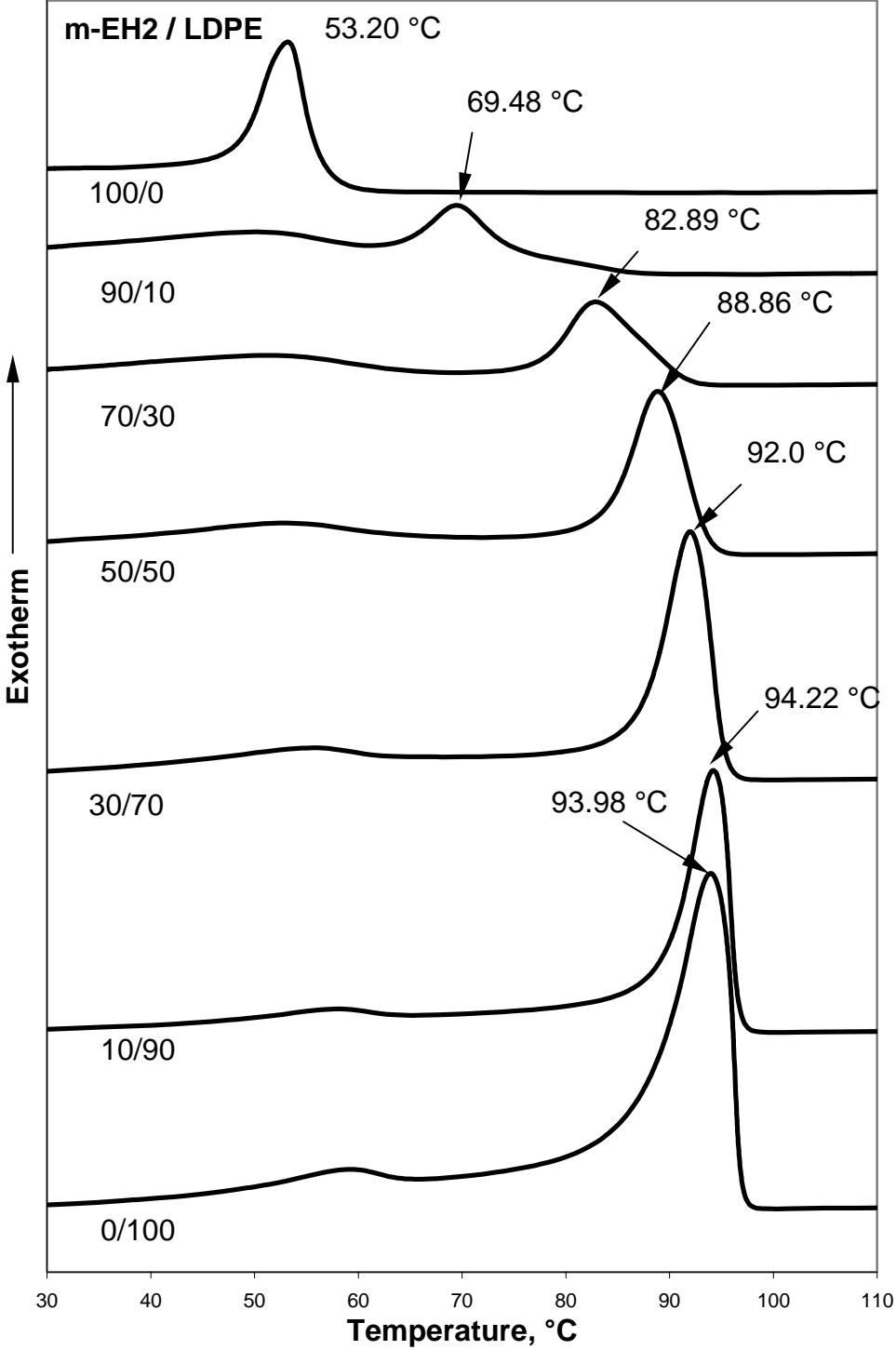


Figure 4a. DSC Heating scans for ZN-EH/LDPE blends

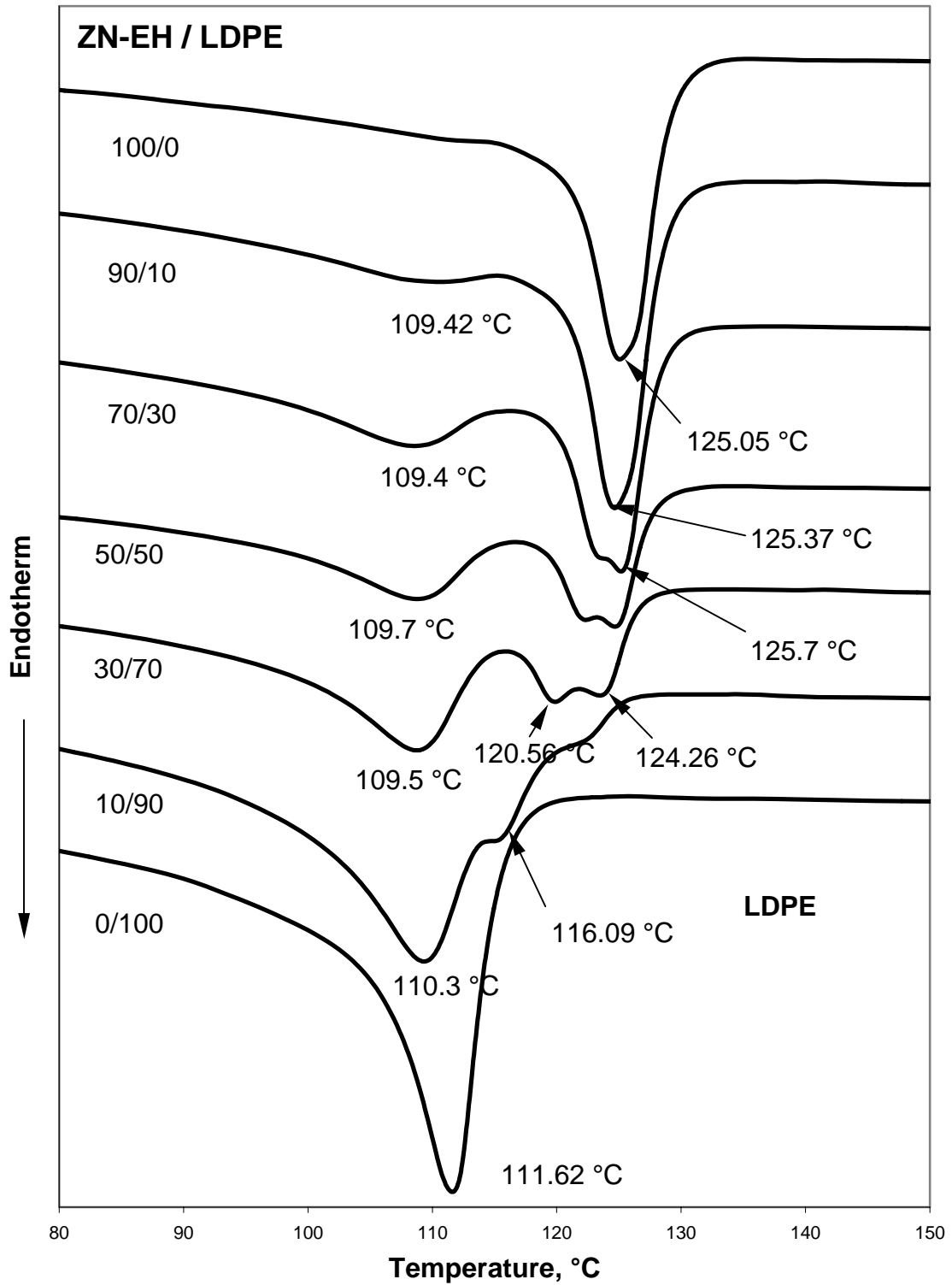


Figure 4b. DSC Cooling scans for ZN-EH/LDPE blends

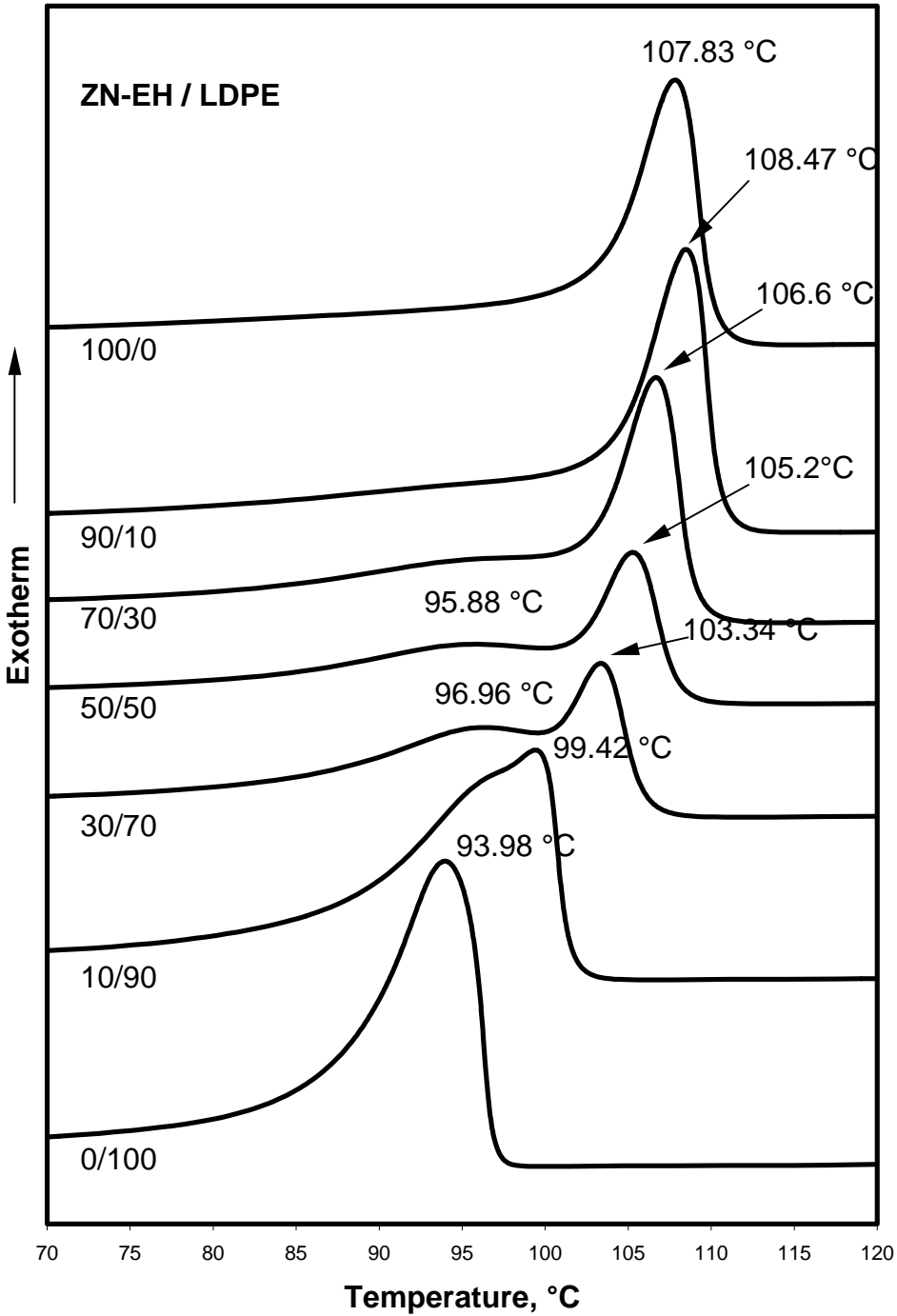


Figure 5. Tensile modulus as a function of composition

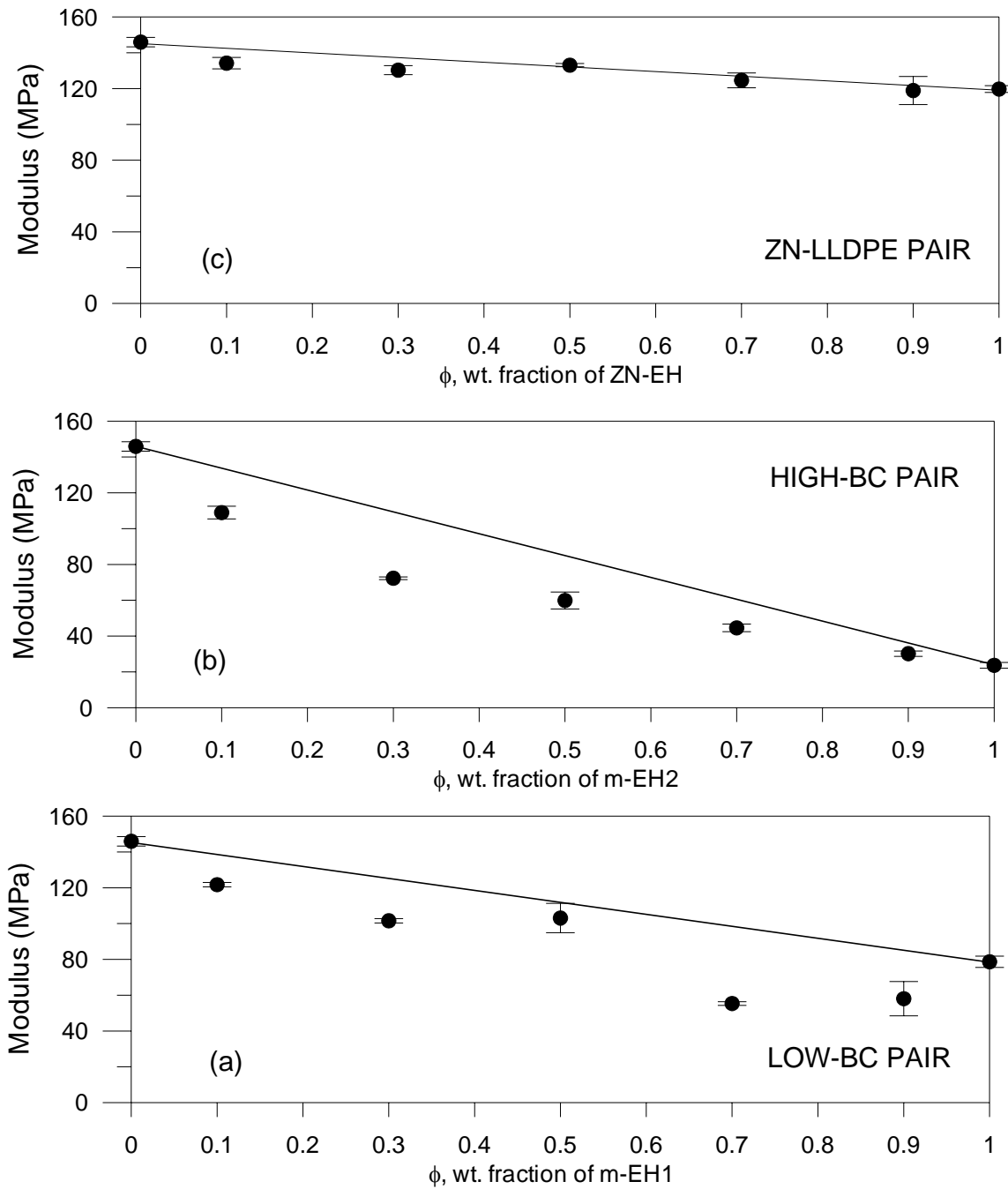


Figure 6. Strength at yield as a function of composition

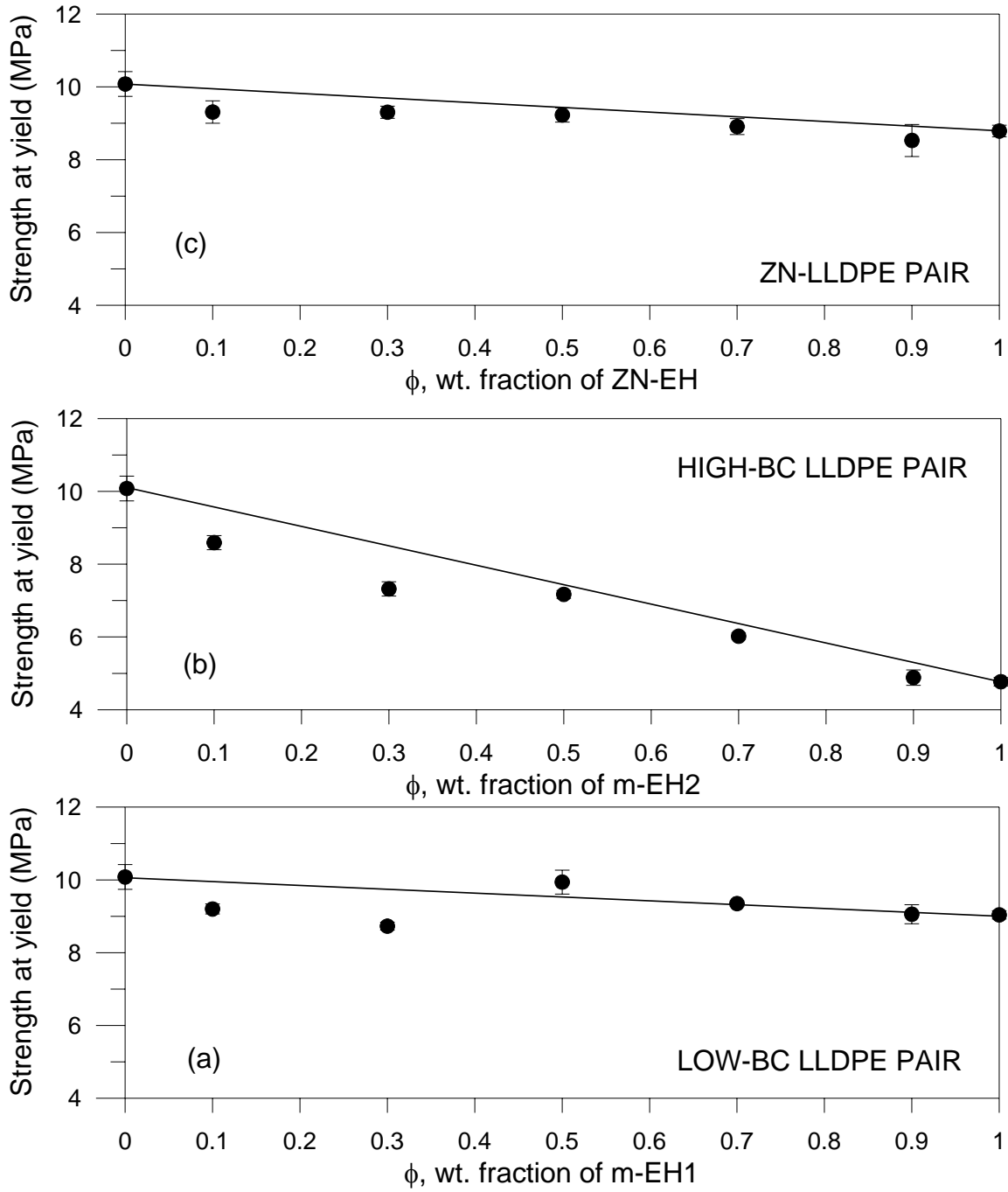


Figure 7. Ultimate tensile strength as a function of composition

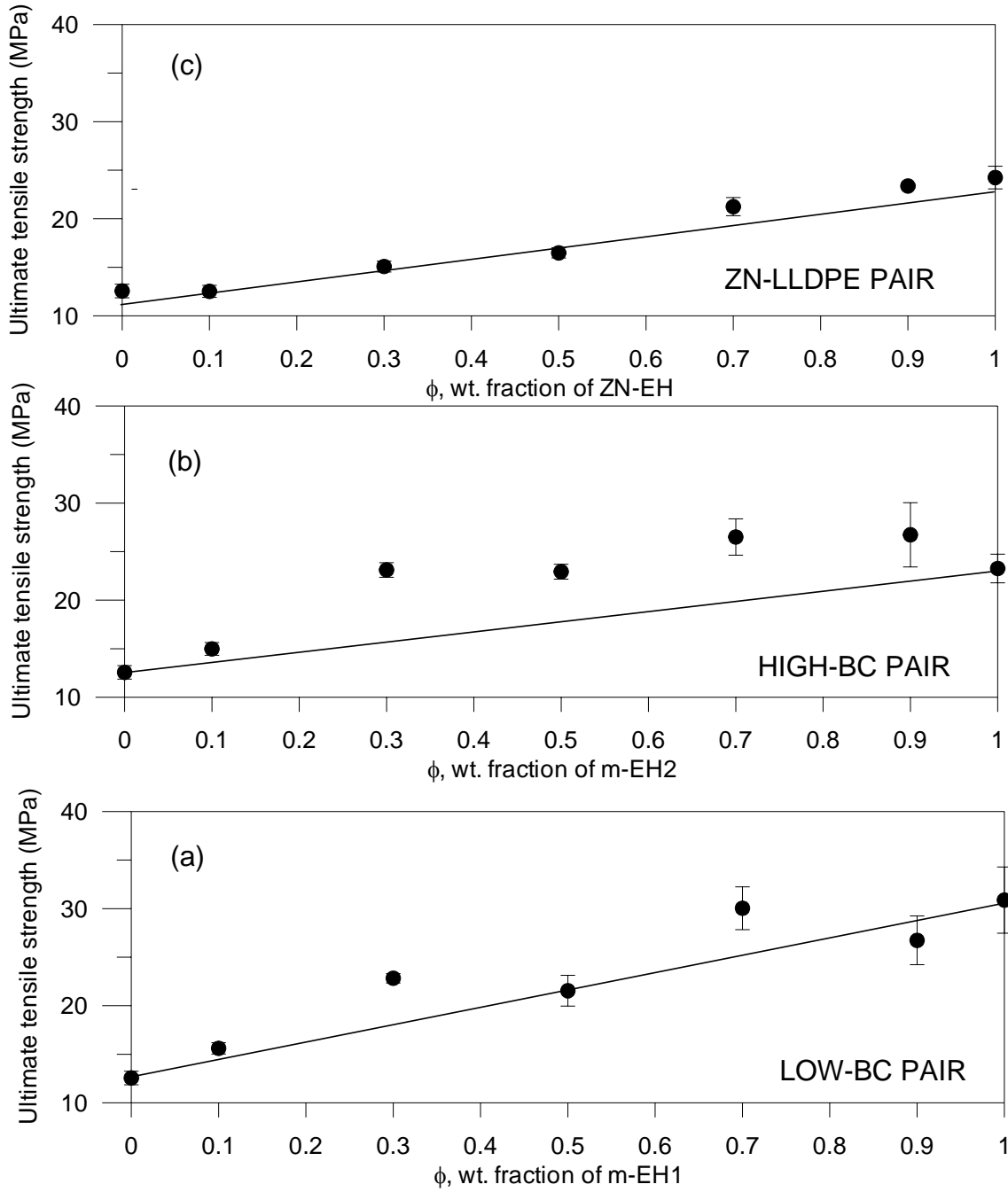


Figure 8. Elongation at break as a function of composition

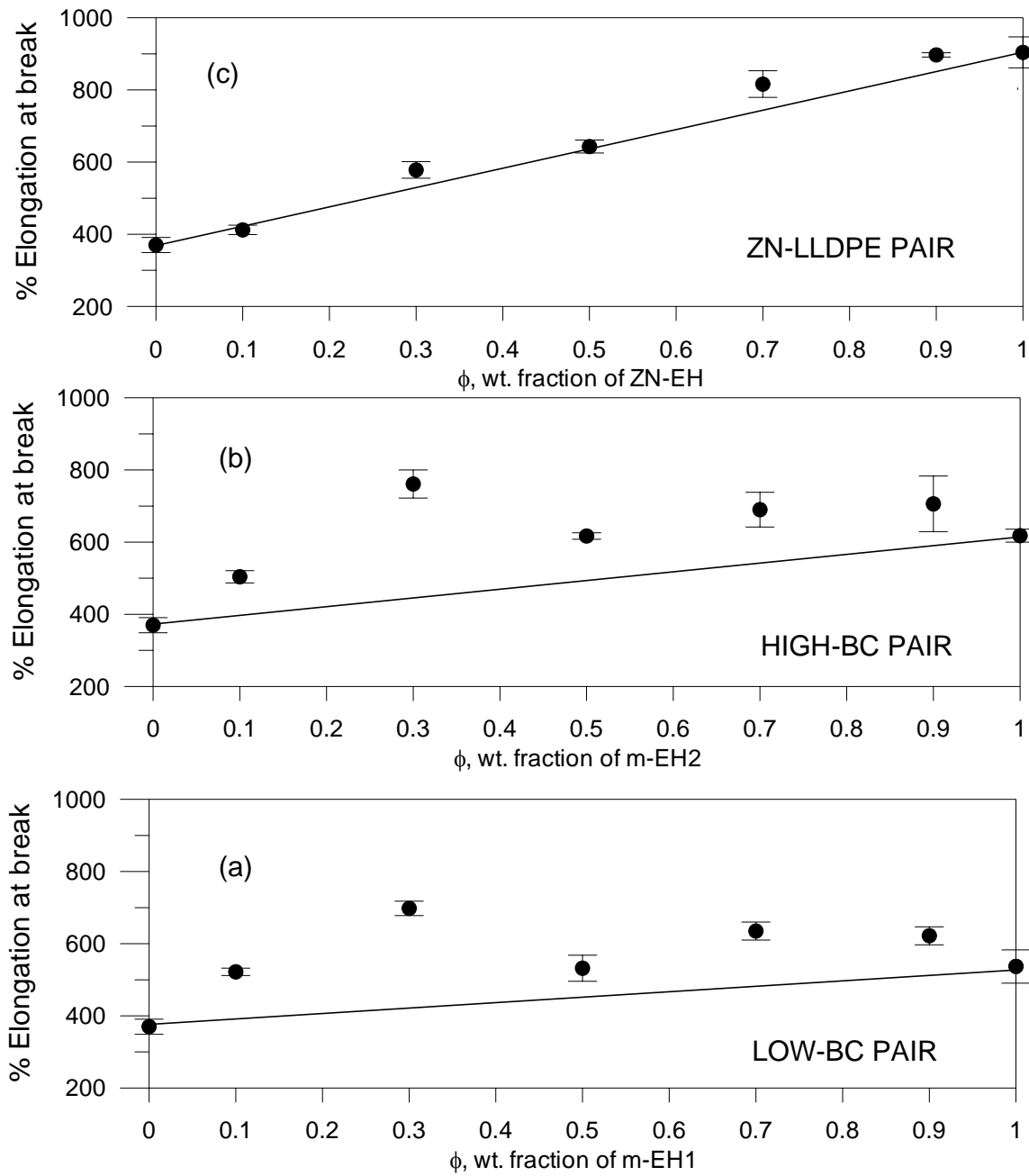


Figure 9. Work of rupture as a function of composition

