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Effects of temperature and load on the melt index of LDPE/LLDPE blends of different blend ratios

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The temperature, load and blend ratio effects on the melt index of low density polyethylene (LDPE) /linear low density polyethylene (LLDPE) blends were studied. The experimental results suggested that the correlation between overall melt index and blend ratio of LDPE/LLDPE blends was governed by a log–linear relationship. This relationship, in turn, offered a simple method for the estimation of the melt index of LDPE/LLDPE blends with minimum experimental work. The results of the temperature effect indicated that if blending was for improving processability, the sensitivity of the melt index of LDPE should then be less than that of LLDPE; whereas, the reverse sensitivity of melt index to temperature was for improving properties of end products. It was shown that melt index increased with increasing applied load. The compressibility characteristics of the polymer melt was thought to account for the susceptibility of melt index to the applied load. Two distinct melting peaks were obtained from the differential scanning calorimetry (DSC) thermograms. This suggested that compatibility was not responsible for the effects shown by the factors studied in this work.

1. Introduction

One of the main objectives of launching linear low density polyethylene (LLDPE) into the market in the late 1970s after the introduction of the UNIPOL gas phase polymerization process was to substitute it for high pressure type low density polyethylene (LDPE). Although the penetration of LLDPE into the industry has had some successes over the years, it has been proved that complete substitution of LLDPE for LDPE in practice is difficult. The reason for such hindrance mainly lies upon the differences in the intrinsic material properties and processing characteristics between the two types of polyethylene (PE). While LLDPE does offer certain superior mechanical behaviours over those of LDPE, its shear insensitivity, weaker melt strength, higher processing temperature and pressure etc. than those of LDPE have restricted it from being used in its pure form unless machine modifications are carried out. However, investment costs will be incurred in machine modifications. Nonetheless, the less expensive LLDPE resin, on the other hand, forms an obvious attraction, of which, processors have to balance it against the mentioned "disadvantages" exhibited by LLDPE.

As a "mid-way" measure in this respect, the general practice in the industry is therefore to blend together the two types of PE. In fact, blending of different plastic resins is not uncommon in the plastics industry. The purposes of this practice are basically to avoid machine modifications, to fill the gaps of applications left by the pure components, and to decrease material costs etc.

Polymer blending has been a study of interest. However, most of the investigations have been concentrated on the microrheological as well as morphological aspects of the blends. For the more recent studies, Shi, Utracki and co-workers [1–3] have conducted a series of investigations on the morphological properties of polymer blends prepared in a twin-screw extruder. Based on their considerations of the microrheological characteristics of immiscible polymer blends, a procedure was proposed to predict the morphology evolution during twin-screw compounding. They further developed a quenching barrel of the twin-screw extruder which was capable of providing rapid quenching for ease of the subsequent morphological analysis to be carried out. Abtal and Prud'homme [4] conducted a detailed study on the orientation of miscible and immiscible polymer blends which involved blends prepared from polystyrene and poly(vinylmethylether). Measurements of orientation in their study were made possible by the application of Fourier transform infrared spectroscopy and birefringence. It was discovered that the orientation of the two types of polymer blends was different, and that the overall orientation of the blend was increased by phase separation. Another piece of work on the morphology development in polymer blends again using a twin-screw extruder was performed by Sundararaj and Macosko [5], who noticed that there was a sheet formation in polymer blends during twin-screw extrusion. They claimed that this sheeting and the breakup mechanisms were the important nature of polymer melt blends.

Processing and end-use products' behaviors of polymer blends can be considered as a reflection of the compatibility of the blend components. Wetton and Corish [6] demonstrated that compatibility could be characterized by the results obtained from a dynamic mechanical thermal analysis apparatus. The subject of compatibility of polymer blend was also studied by Deanin [7]. Both of the above studies offer a useful basis of practical significance if compatibility of polymer blends is of concern.

LLDPE and their blends were extensively studied by Schlund and Utracki [8–12]. Their investigations were mainly concentrated on the shear and extensional flow behaviours exhibited by the LLDPE and their blends. They have related their findings to the molecular structure of the LLDPE. More recent work on the similar subject was reported by Baker *et al.* [13] and, Tincer and Coskun [14]. While all these studies and others have enhanced our understanding of the fundamental aspects of polymer blending, and in particular, blends involving polyethylene, they are too academic, and thus, the results cannot be directly applied to and benefited by the processors in the industry. Furthermore, only a few of the previous studies had discussed melt index (MI), which is an important parameter in the polyethylene processing industrial sector.

In the polyethylene processing industry, processors normally require the data of melt index and resin density for their product design and determining the operation conditions. MI gives an indication of the flowability of the polymer melt, whereas density offers information on the crystallinity of the polymer. The current report concentrates on the former with the objective to provide the industry with some guidelines of practical significance. The values of MI are known to be susceptible to load and temperature. To what extent MI of a given blend ratio of LDPE/LLDPE is affected by load and temperature forms the primary purpose of the current study. It will be seen that the results of this investigation have not only broadened our understanding of this effect, but MI of different blend ratios of LDPE/LLDPE under difficult loads and temperatures can also be predicted with minimum experimental work.

2. Experimental methods

One low density and three linear low density polyethylenes were chosen for the study. The LDPE was selected as the base resin whereas the LLDPEs were the blend partners. The basic properties of the resins as supplied and the values of their melt index tested in this study are reported in Table I.

Melt index was determined by a CEAST melt flow indexer. The test method conformed to the ASTM standard. The melt index of each sample was tested at least ten times before an arithmetic mean was taken. Three temperatures (170, 190 and 210 °C) were chosen to study the temperature effect, whereas load effect was investigated with 1, 2.16 and 3.8 kg weights.

LDPE/LLDPE blends were prepared in a small laboratory size single-screw extruder having a 19.05 mm diameter screw. The screw has a design of square pitch, a 20 length-to-diameter ratio and a compression ratio of 3 : 1. The extrudate was extruded through a 2 mm diameter circular pin die to form a monofilament which was subsequently fed into the melt flow indexer for the determination of the melt index. The pre-specified weight of the basic resin (i.e. LDPE) and the LLDPE with which it was to be blended were first measured separately in their pure form. They were then thoroughly mixed in a container before being poured into the hopper of the extruder. As soon as the extrudate was extruded from the pin die, it was immediately cooled in a water bath which had water circulation and was kept at 20 °C. The temperature profile and screw speed of the extruder were carefully controlled in such a way that no melt fracture was observed on the extrudate. For each pair of resins chosen, three blend ratios (20 : 80, 50 : 50 and 80 : 20 w/w %) were prepared. The sample coding used in this study is described in Table I.

A Du Pont 990 differential scanning calorimeter was used to reveal the basic thermal characteristic of the blends. The thermograms were obtained by heating the sample from 30 to 250 °C at a gradient of $10\,^{\circ}\mathrm{C\,min^{-1}}$.

3. Results and discussions

3.1. Blend ratio effects

In the previous study on the blend ratio effect of binary polyethylene blends, Wong [15] noticed that the melt index of a blend could not be described by the weighted mean expression. He noticed that there was in fact an exponential decaying characteristic between melt index of the blend and blend ratio. He then modified the Arrhenius equation to the form shown in Equation 1 to correlate his experimental data

$$MI_{\mathrm{EST}} = R\,MI_1^{x_1}, MI_2^{x_2}) + S \qquad (1)$$

where MI_{EST} was the estimated melt index of a blend, R and S were constants, x was weight fraction, and

TABLE I Sample coding and physical properties of the selected resins

Sample coding	Resin type	Melt index[a] from supplier (g 10 min^{-1})	Melt index[a] (g 10 min^{-1})	Density (kg m^{-3})	Remarks
A	LDPE	4.0	3.97	921	Base resin
B	LLDPE	20.0	18.90	924	Blend partner
C	LLDPE	52.0	51.02	926	Blend partner
D	LLDPR	2.0	1.90	918	Blend partner

[a] Melt index measured at 190 °C and 2.16 kg.

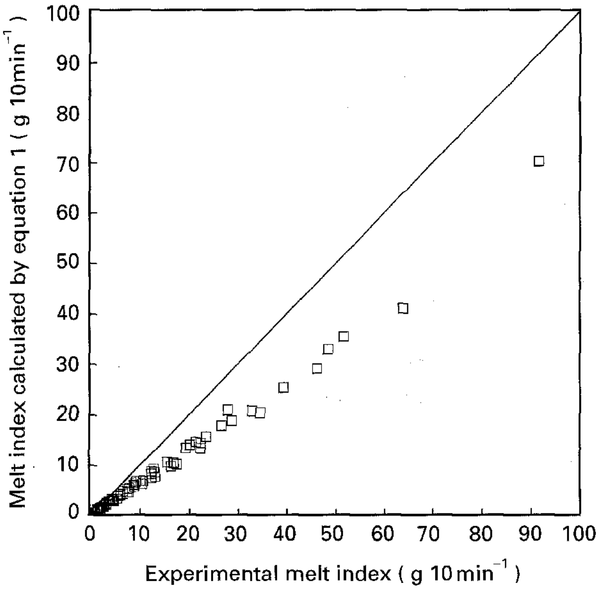

Figure 1 Comparison of melt index (all data).

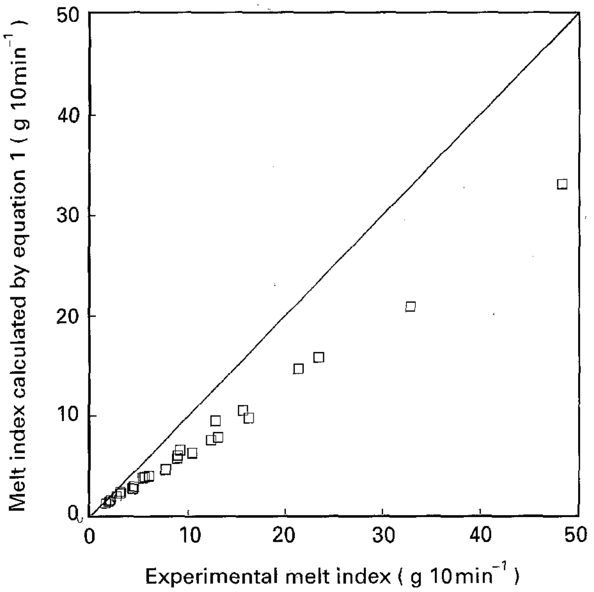

Figure 2 Comparison of melt index (190 °C and 2.16 kg).

subscripts 1 and 2 represented components 1 and 2 respectively. Equation 1 was claimed to produce melt index estimation of a binary polyethylene blend with good accuracy. His work was, however, only applied to the melt index measured at 190 °C and 2.16 kg, which is the usual condition for determining melt index of polyethylene, and thus his findings have somewhat limited application.

An attempt was made to study whether or not the above modified Arrhenius equation could cover the experimental data obtained in this work. Fig. 1 is a plot of melt indices calculated by Equation 1 against those obtained experimentally in this current investigation. It has to be emphasized that Fig. 1 consists of all the experimental data obtained in this study, including those determined at test conditions other than 190 °C and 2.16 kg. It can be seen from the figure that all the melt indices were under-estimated by Equation 1. Apparently, this deviation between the estimated and experimental melt index was bigger as melt index got larger. This trend of difference appeared to be the same when even only the melt indices obtained at 190 °C and 2.16 kg were investigated as shown in Fig. 2.

The exponential decaying characteristic noticed by Wong for the melt index measured at 190 °C and 2.16 kg was supported by the results obtained in this study. In fact, this characteristic was found to be equally true for the melt indices measured at other temperatures and pressures. Upon analysing the experimental results, it was found that a linear–linear plot of the melt index against blend ratio of the base component A was able to produce a reasonably good straight line relationship. However, a semilog plot yielded an even better linear relationship than the linear–linear plot as reflected by the values of the regression coefficients obtained. Thus, it is believed that the melt index of a binary LDPE/LLDPE blend has a log–linear relationship with its blend ratio as depicted in the following form

$$\mathrm{MI}_{\mathrm{EST}} = A \exp (Bx_1) \qquad (2)$$

where MI_{EST} is the estimated melt index, A and B are the constants, x is the weight fraction and subscript 1 refers to the base resin of the blend. All the results of the current work are shown in Figs 3 to 11. Excellent regression coefficients in the range of 0.980 to 0.995 were obtained for all the experimental data.

Linear–linear plots of the raw data of blends A/B and A/C revealed that the overall melt indices of those blends were more susceptible to the first 25 to 30 wt% of the base resin A (i.e. LDPE). A proportion of LDPE of more than 30% appeared to have less effect on the overall melt index. This finding is illustrated in Figs 12 and 13. A similar graphical presentation of blend A/D, however, showed a different characteristic. It was noticed that the overall melt index of this blend was more affected by the introduction of linear low density polyethylene rather than by the low density polyethylene (Fig. 14). In other words, the

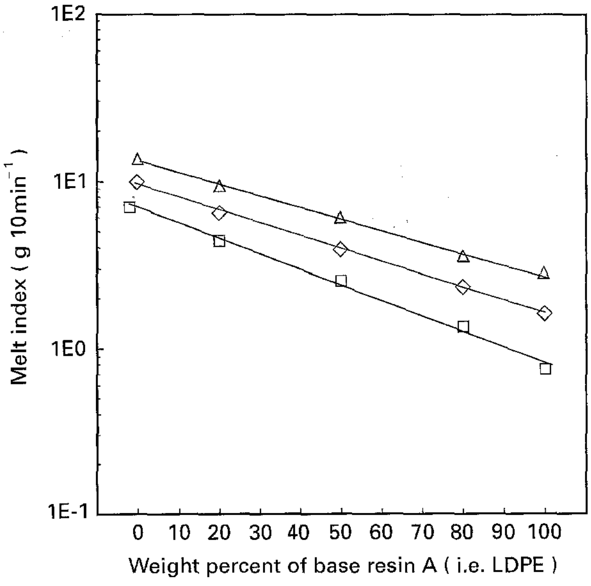

Figure 3 Melt index versus blend ratio of the base resin A (blend A/B 1 kg load). □ 170 °C; ◇ 190 °C; Δ 210 °C.

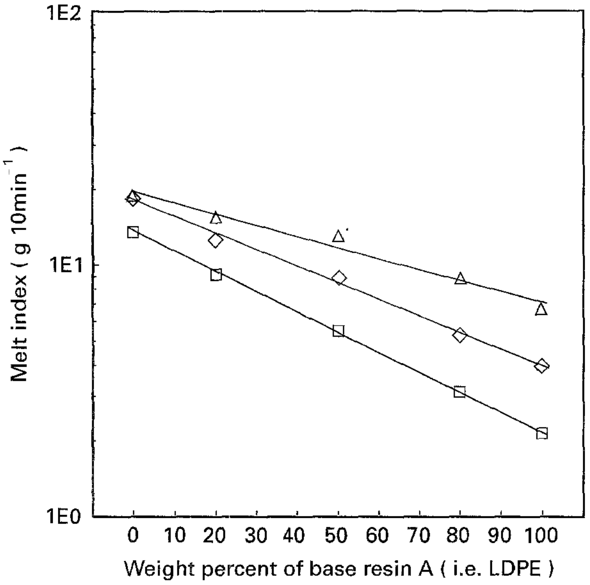

Figure 4 Melt index versus blend ratio of the base resin A (blend A/B 2.16 kg load). □ 170 °C; ◇ 190 °C; Δ 210 °C.

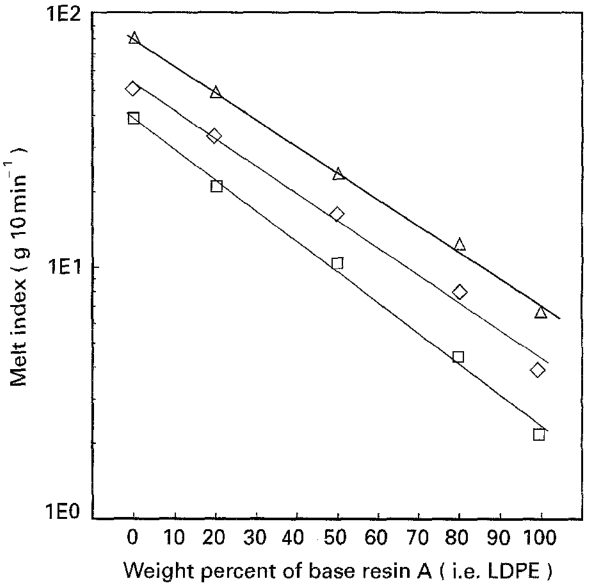

Figure 7 Melt index versus blend ratio of the base resin A (blend A/C 2.16 kg load). □ 170 °C; ◇ 190 °C; Δ 210 °C.

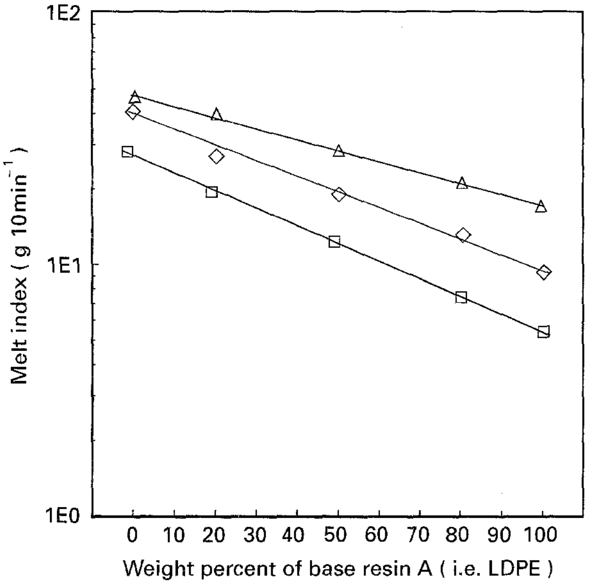

Figure 5 Melt index versus blend ratio of the base resin A (blend A/B 3.8 kg load). □ 170 °C; ◇ 190 °C; Δ 210 °C.

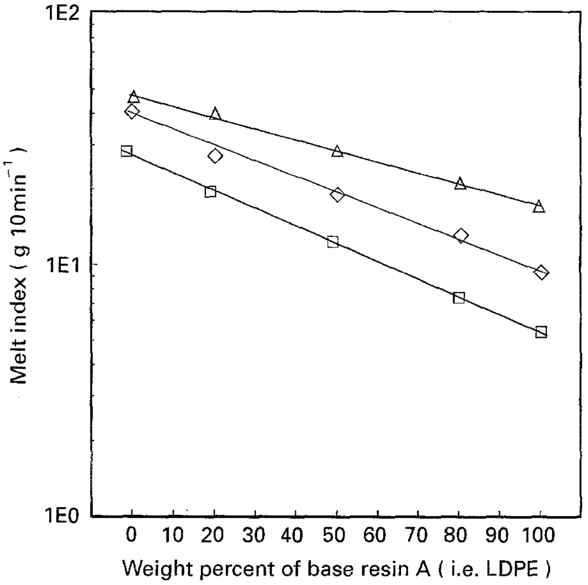

Figure 8 Melt index versus blend ratio of the base resin A (blend A/C 3.8 kg load). □ 170 °C; ◇ 190 °C; Δ 210 °C.

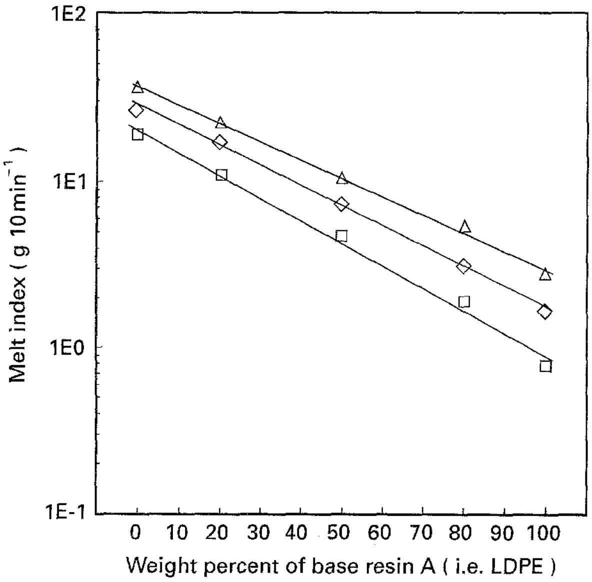

Figure 6 Melt index versus blend ratio of the base resin A (blend A/C 1 kg load). □ 170 °C; ◇ 190 °C; Δ 210 °C.

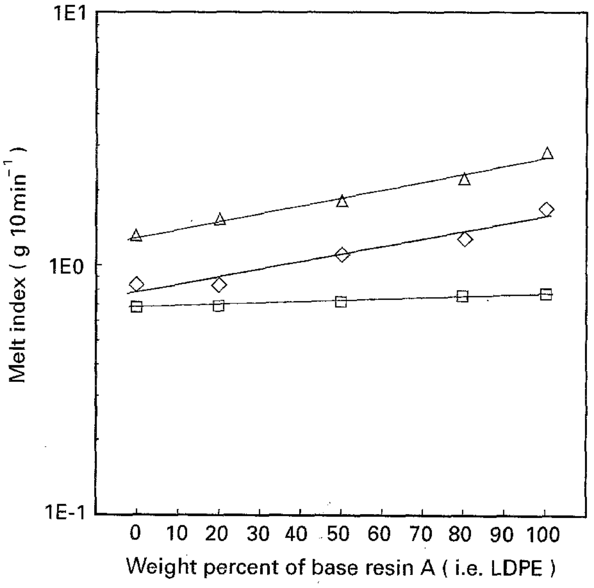

Figure 9 Melt index versus blend ratio of the base resin A (blend A/D 1 kg load). □ 170 °C; ◇ 190 °C; Δ 210 °C.

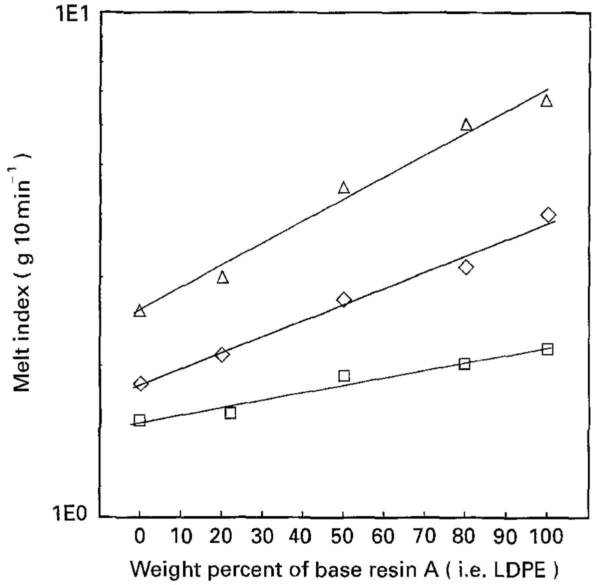

Figure 10 Melt index versus blend ratio of the base resin A (blend A/B 2.16 kg load). □ 170 °C; ◇ 190 °C; Δ 210 °C.

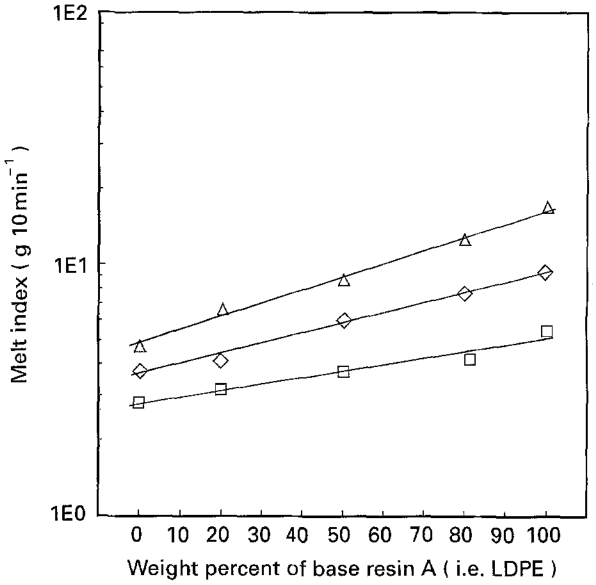

Figure 11 Melt index versus blend ratio of the base resin A (blend A/B 3.8 kg load). □ 170 °C; ◇ 190 °C; Δ 210 °C.

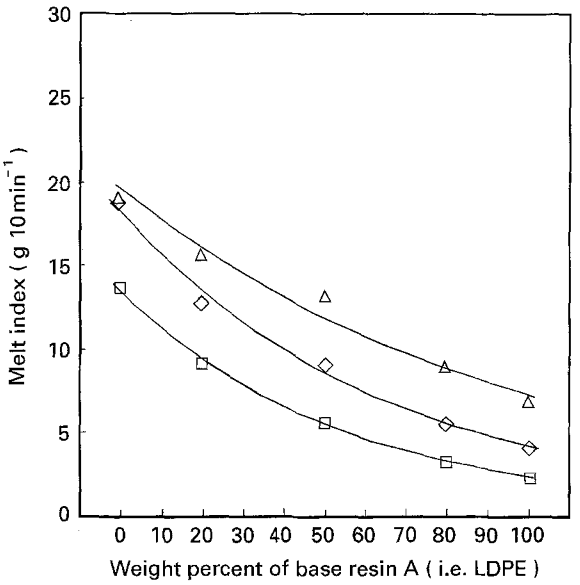

Figure 12 Illustration of the sensitivity of the first 30% of the base resin A on melt index (blend A/B 2.16 kg load). □ 170 °C; ◇ 190 °C; Δ 210 °C.

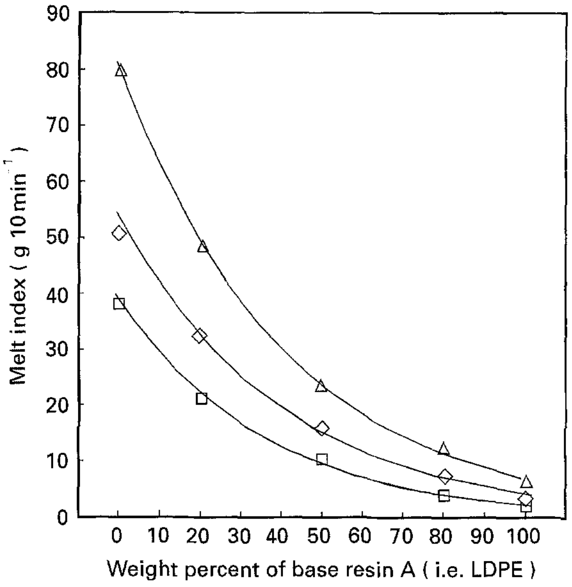

Figure 13 Illustration of the sensitivity of the first 30% of the base resin A on melt index (blend A/C 2.16 kg load). □ 170 °C; ◇ 190 °C; Δ 210 °C.

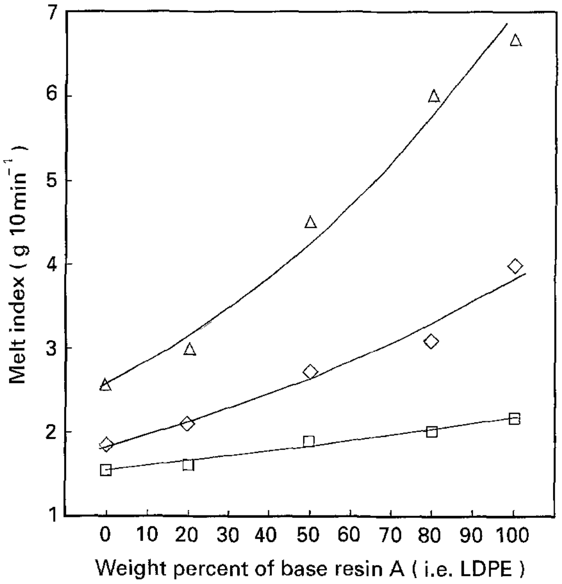

Figure 14 Illustration of the sensitivity of LLDPE (< 30 %) on melt index (blend A/D 2.16 kg load). □ 170 °C; ◇ 190 °C; Δ 210 °C.

melt index of this blend is more sensitive to LLDPE than to LDPE. This finding can be related to the experience gained in the industry which is to be discussed below.

Many product specifications are known to be best satisfied by employing LLDPE. However, as already mentioned, the intrinsic properties of LLDPE have restricted it to be processed in its pure form on conventional manufacturing machinery, so that blending a small percentage (usually not more than 30%) of LDPE has been found to be able to overcome the problem, without losing the superior end-product properties offered by LLDPE. In this situation, blending is involved because of processing difficulties; but blending is also involved for reasons other than processing aspects. For product specifications (especially toughness) that cannot be satisfied by pure LDPE, the general practice in the industry in this respect is to blend a small amount (again, not more than 30%) of LLDPE into the main bulk for improvement in the properties of end-products. Too much LLDPE blended will yield processing instability such as melt fracture.

In both of the above situations, blending of LLDPE and LDPE is involved but for different purposes. Whether or not the objective of either the situations to be reached depends on the characteristics of the blending partners chosen. Among the major characteristics, melt index is one of them. The results of this study discussed in the next section will provide some facts and suggestions as how to consider choosing the correct blending partners.

3.2. Temperature effects

Viscosity of polymer melt has been an important property to both polymer scientists and processors. Numerous work had been carried out in the past on the different aspects of the subject. Most of the investigations used different types of rheometers/viscometers. Although these measuring instruments may provide valuable facts and data on polymer melt viscosity, they are expensive instruments. Melt indexers, on the other hand, offer a much cheaper method than rheometers to obtain similar indications on the flowability of polymer melt. Furthermore, investigations on the temperature and load effects can be easily carried out.

Since melt index reflects flowability of a polymer melt, it is, therefore, envisaged that melt index will increase with increasing temperature regardless of whether the melt is a pure polymer or a blend. For a given blend ratio, Figs 3 to 11 show that melt index of all blends tested in this study increased as temperature increased . The constant B, as described in Equation 2, is the gradient of the curve which was calculated by the mathematical regression method. The values of B are summarized in Table II. It can be noticed from the table that there were two trends between constant B and temperature. While for blends A/B and A/C, the gradient decreased with increasing temperature, it increased with increasing temperature for blend A/D. Although the actual values of B appeared to be small, its relationship with temperature was found, however, to be definite and reproducible.

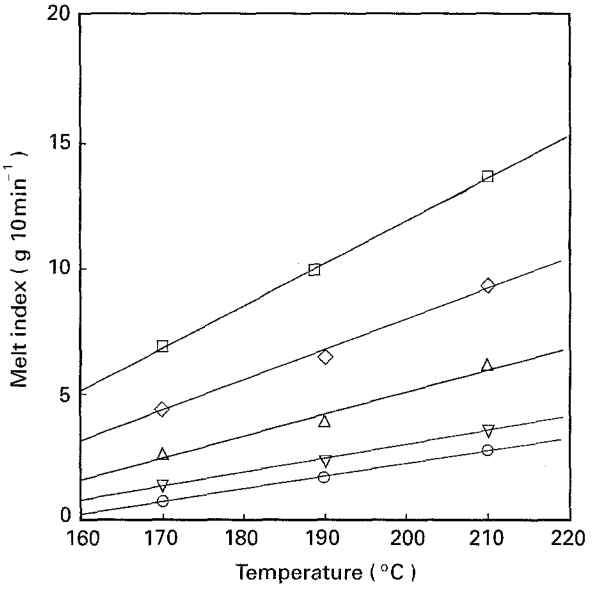

Figure 15 Temperature effect on melt index (blend A/B 1 kg load). □ 0% A; ◇ 20%*A*; Δ 50% A; ∇ 80% A; ○ 100% A.

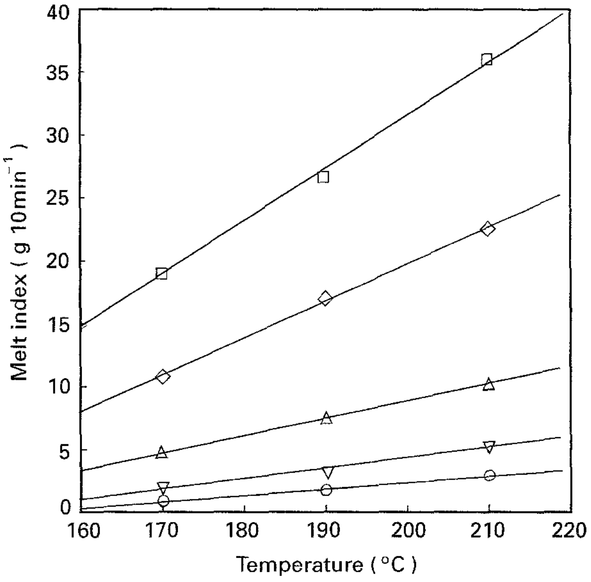

Figure 16 Temperature effect on melt index (blend A/C 1 kg load). □ 0% A; ◇ 20%*A*; Δ 50% A; ∇ 80% A; ○ 100% A.

The decreasing values of constant B for A/B and A/C blends as temperature increased indicated that the melt index of these two blends were less sensitive as temperature increased. Careful study of the data revealed that the decrease in gradient as temperature increased was most likely attributed to the smaller increase of the melt index at the low blend ratio (< 30%) of the base resin than those at blend ratios of more than 30%. A cross linear–linear plot of melt index against temperature of these two blends (Figs 15 and 16) resulted a good straight line relationship and can be represented by a simple equation as follows

$$MI_{\mathrm{EST}} = PT + Q \tag{3}$$

where P and Q are constants, and T is temperature. It can be seen from the figures that the sensitivity of the

TABLE II Values of constant B of Equation 2

Blend	1 kg			2.16 kg			3.8 kg		
	170 °C	190 °C	210 °C	170 °C	190 °C	210 °C	170 °C	190 °C	210 °C
A/B	− 0.021	− 0.018	− 0.016	− 0.018	− 0.015	− 0.010	− 0.016	− 0.014	− 0.010
A/C	− 0.031	− 0.028	− 0.025	− 0.028	− 0.025	− 0.024	− 0.026	− 0.023	− 0.022
A/D	0.001	0.007	0.007	0.003	0.007	0.010	0.006	0.009	0.012

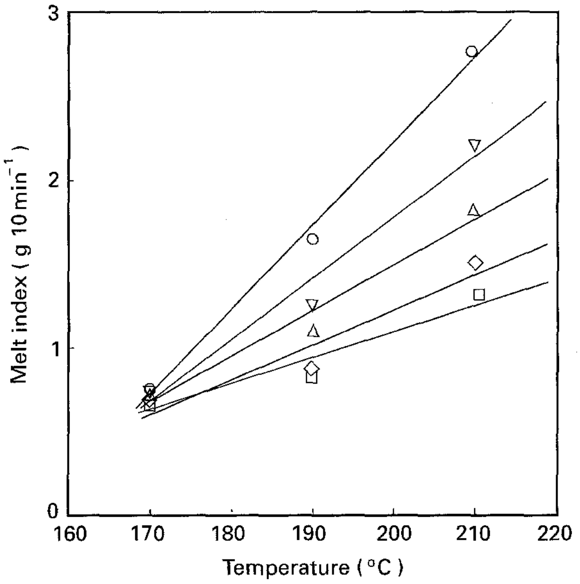

Figure 17 Temperature effect on melt index (blend A/D 1 kg load). □ 0% A; ◇ 20%*A*; Δ 50% A; ∇ 80% A; ○ 100% A.

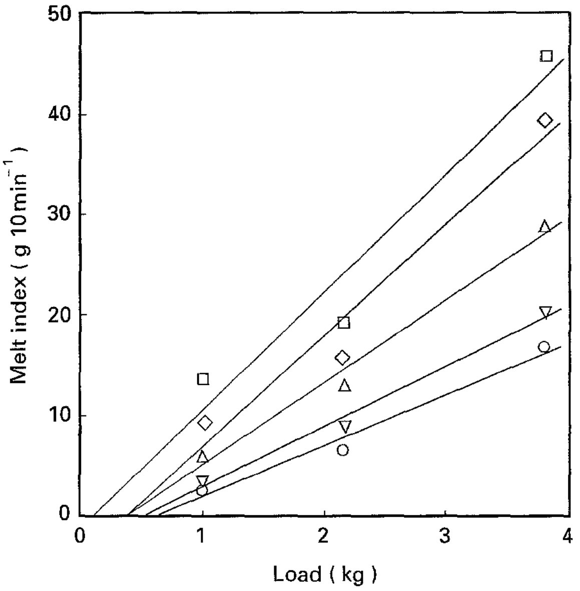

Figure 18 Load effect on melt index (blend A/B 210 °C). □ 0% A; ◇ 20%*A*; Δ 50% A; ∇ 80% A; ○ 100% A.

melt index of the blends to temperature increased from the pure base resin A to its blending partner in its pure form, as reflected by the slope of the graph. This means that the melt index of the chosen blending partner LLDPE was more affected by temperature than that of the chosen base resin (LDPE). Similar analysis carried out on the data of blend A/D showed an opposite trend (Fig. 17). This time, the base resin was more susceptible to temperature than its blending partner.

It was discussed in the above section that the blending of polyethylene was usually for different reasons. To improve processing difficulties exhibited by pure LLDPE without machine modifications on a conventional manufacturing line means, in a broad sense, to improve the flowability of the polymer melt during processing. Improving flowability can refer to either improving the melt strength or reducing melt viscosity. For this objective, the blended resin (e.g. LDPE) should have no or minimal effect on other characteristics of the process and products. The current study demonstrated that to achieve this, the flowability of the blending LDPE partner in terms of melt index should be less sensitive to temperature than the LLDPE because a small proportion of LDPE would have made a big change on the overall melt index of the blend already. If blending LLDPE is primarily for improving the properties of end products made of LDPE, the sensitivity of the polymer melt to temperature should be the reverse as shown in this study, i.e. the melt index of LDPE (the base resin) should be more susceptible to temperature than that of the LLDPE. The main key in both situations is that the proportion of the blending partner should be kept as low as possible, and yet the effects that it brings should be as large as possible.

3.3. Load effects

Three loads (1, 2.16 and 3.8 kg) were tested to investigate the load effect on the melt index of the LDPE/ LLDPE blends. The selection of these loads were based on the ASTM recommendation for the determination of melt index. As expected, it was shown that larger load has induced higher flowrate (i.e. higher melt index) than smaller load. However, for a given temperature, it can be seen from Figs 3 to 11 and Table II that the gradient (i.e. constant B) decreased with increasing load for A/B and A/C blends; and increased with increasing load for A/D blend. Although no explanation to this finding can be offered at this stage, it is believed that compressibility and induced crystallinity behaviour of the polymer melts have a significant part to play in this respect.

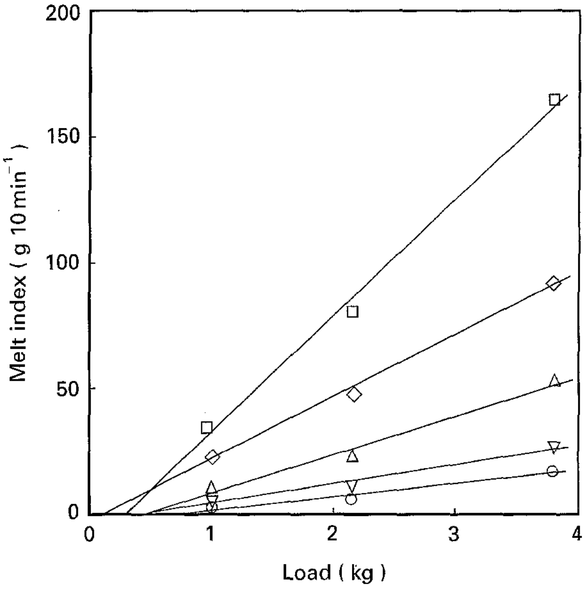

Figure 19 Load effect on melt index (blend A/C 210 °C). □ 0% A; ◇ 20%*A*; Δ 50% A; ∇ 80% A; ○ 100% A.

Correlating melt index of the blends and loads was attempted in this work. A linear–linear relationship was found to best represent the two parameters. To illustrate this characteristic, some experimental results were selected and are shown in Figs 18–20.

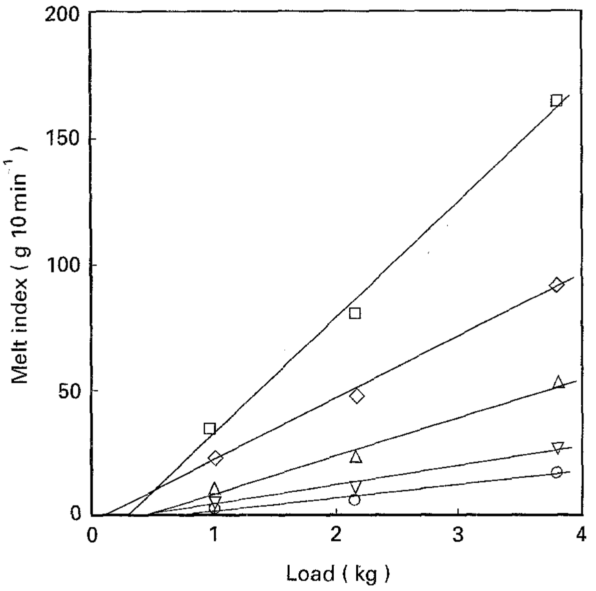

Figure 20 Load effect on melt index (blend A/D 210 °C). □ 0% A; ◇ 20%*A*; Δ 50% A; ∇ 80% A; ○ 100% A.

3.4. Differential scanning calorimetry (DSC) analysis

Compatibility of a blend always presents some attractions to polymer scientists and engineers. Indeed, the processability and physical properties of a blend largely depend on the degree of compatibility of the constituent blending components. Haghighat and Birley [16] were able to demonstrate, using a DSC, that compatibility of LDPE/LLDPE blends highly depended upon the thermal history of the blends. Their experimental technique involved quenching the extrudate in water prior to performing the thermal analysis.

Similar preparation work to that of Haghighat and Birley were carried out in this study. Two water temperatures, 10 and 20 °C, were used to cool the extrudate from the single-screw extruder. Small samples of the extrudate were then placed and sealed in an aluminium pan. Heating of the DSC was set at a gradient of 10 °C min^{-1} from 30 to 250 °C. The thermograms indicated that there was no difference between the two cooling temperatures, and that no single peak as described by Haghighat and Birley was obtained. Apparently, two distinct peaks were shown in all the thermograms. Whilst the lower peak corresponded to the melting point of LDPE, the higher peak was attributed to the melting point of LLDPE (Fig. 21). Based on this DSC analysis, it would then be more convincing that the results of the melt index were independent of the compatibility of the blends.

3.5. Estimation of melt index

Values of melt index are often required for either setting processing conditions or for mould design consideration. If a blend of certain blend ratio is employed, it has been shown that the overall melt index of the blend is to be different from the simple weighted mean of the blend components. Hence, from a practical point of view, it would be useful if an overall melt index could be estimated without performing the actual index measurement. Such requirement might be difficult. However, estimation of melt index of a LDPE/LLDPE blend with minimum experimental work has been shown in this study to be relatively simple. The procedure of estimation only involves the determination of the melt index of the two polyethylenes in their pure form at specific test conditions. The two values are then plotted on log–linear graph of melt index against blend ratio. Since it has been demonstrated that the melt index of such blends have an exponential decaying relationship with the blend ratio as described by Equation 2, the two points can then be connected by a straight line, and the melt index of different blend ratios can be interpolated from the straight line. Based on the results presented in this work, this simple approach will yield estimated melt index of good accuracy.

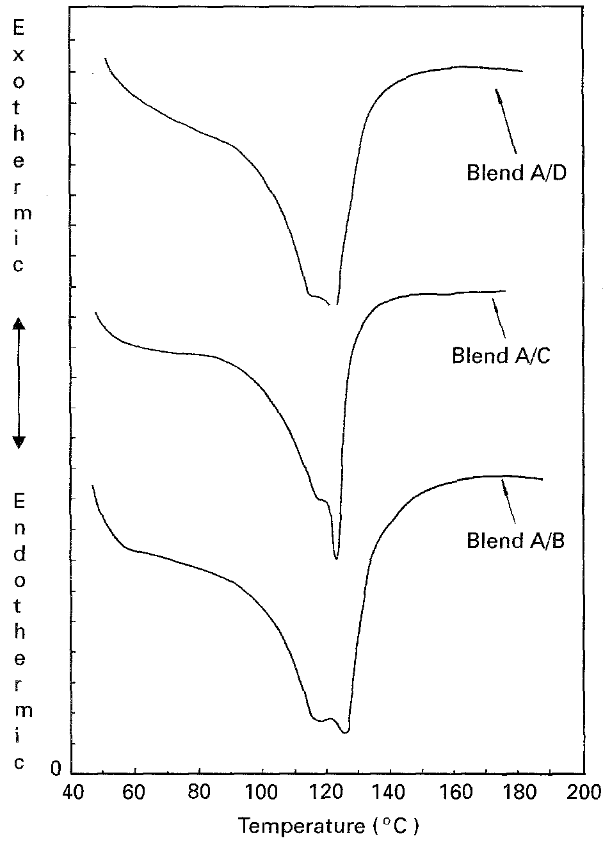

Figure 21 Thermograms of LDPE/LLDPE blends (blend ratio: 50/50).

4. Conclusions

It was demonstrated that melt indices of LDPE/LLDPE blends had a characteristic exponential decaying relationship with blend ratio at test conditions other than 190 °C and 2.16 kg. This relationship was best described by Equation 2, which, subsequently, provided a simple approach to estimate melt index of such blends with minimum experimental work involved. The effect of a small amount (< 30%) of a blend partner on the overall melt index was shown to depend on the sensitivity of melt index to temperature of the two blend components. Compressibility of polymer melt was thought to be responsible for the load effect on melt index. The DSC analysis suggested that the temperature, pressure and blend ratio effects on the overall melt index of LDPE/LLDPE blends were independent of the compatibility of the two components.

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