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Hydrostatic extrusion of composites based on linear polyethylene

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Blends of linear polyethylene with carbon black (1 and 10 wt %) and two low-molecular weight substances, camphor (10 wt %) and dimethylerephthalate (DMTP) (10 wt %), have been hydrostatically extruded under different conditions. Both camphor and DMTP were partly compatible with the polyethylene. Compared to an unfilled linear polyethylene, hydrostatically extruded under similar conditions, an increase in tensile strength is noted in some cases. This increase in strength may be accompanied by a decrease in stiffness. The composites containing the compatible substances could be processed at a significantly lower pressure level compared to the unfilled polyethylene.

1. Introduction

Hydrostatic extrusion is one of the available techniques used for producing high modulus linear polyethylene. The properties and the structure of the resulting polyethylene extrudate have been studied extensively by Ward and co-workers [1–3]. Normally, an increase in extrusion ratio (area reduction) results in a substantially improved stiffness. Using this technique, samples having a tensile modulus of 60 to 70 GPa can be obtained. It has been proposed that the polyethylene, extruded in this way, consists of oriented crystallites (lamellae), with the *c*-axis in the extrusion direction, which are connected by oriented tie-molecules. The stiffness and strength of the specimens are related to the number and state of such molecules.

In most cases, hydrostatic extrusion techniques have been applied only to pure polymers. In an earlier work [4], we reported on hydrostatic extrusion of a two-phase material; one phase being linear polyethylene (LPE), 50 wt %, and the other a water-soluble material consisting mainly of sodium lignosulphate (Wanin S). It was found that the polyethylene fraction formed thin, rather long fibres, which were easily isolated by dissolving the Wanin S matrix in water. The properties of the thin fibres and the pure LPE, extruded under similar conditions, were found to be largely identical.

In this work, hydrostatic extrusion is applied to other two-phase systems, one of the phases still being the linear polyethylene grade. As the second component three different materials were employed, one incompatible with polyethylene (carbon black) and two others, which at least partly formed a solution with polyethylene at an elevated temperature (camphor and dimethylterephthalate). The amount of non-polyethylene material was 10 wt %; in one case (carbon black) a lower concentration, 1 wt %, was also studied.

For the carbon black-containing composites a monotonic increase in tensile modulus and strength with the extrusion ratio was observed. The influence of the extrusion ratio on the mechanical behaviour of the composites was in general rather similar to that of the unmodified material. However, addition of carbon black (10 wt %) resulted in a reduced stiffness compared to the pure material (at the same extrusion ratio and rate), while the tensile strength was more or less unaffected. If however only 1 wt % of carbon black was added to the polyethylene, the tensile strength increased compared to the pure polymer, whereas the modulus did not change markedly. The melting points of the composite extrudates increased, as for the unfilled polyethylene, with increasing extrusion ratio.

Hydrostatically extruded polyethylene contain-

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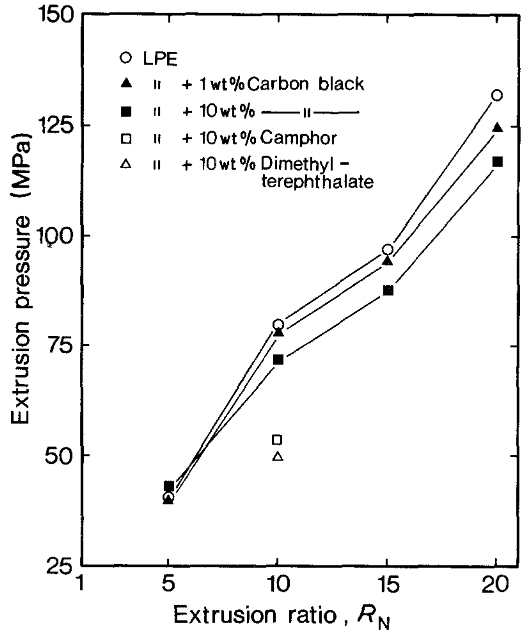

Figure 1 Extrusion pressure plotted against extrusion ratio for LPE with different fillers at an extension temperature of 125° C.

ing 10 wt% camphor or dimethylterephthalate (DMTP) showed a reduction in the tensile modulus while there was an increase in the tensile strength. This investigation, however limited with regard to the number of substances studied and the range of experimental conditions, is intended to show that techniques like alloying, dispersion hardening etc., may prove useful also in the polymer area [5].

2. Experimental procedure

2.1. Materials

The linear polyethylene (LPE) grade, Rigidex 50, supplied by BP Chemicals Int. Ltd., had a melt index of 6.0 g per 10 min. (BS 2782 Method 10S C) and a density of 0.962 g cm^{-3}. According to Gibson and Ward [2] the average molecular weights are $\bar{M}_w = 101\,450$ and $\bar{M}_n = 6180$.

The carbon black used was Ketjenblack EC (supplied by Akzo Chemie). The camphor and dimethylterephthalate were laboratory chemicals (analytical grades). The melting points of the camphor and DMTP, were 176° C and 140° C, respectively.

2.2. Preparation of the billets (pre-extrudates)

After homogenization of the polymer and the filler in a mixing extruder (a Co-Kneter, made by Buss AG, with $L/D = 11, D = 46$ mm) at 160° C the granulated blends were injection moulded. Homogenization of the camphor-containing material had however to be performed at 185° C due to the high melting point of this substance. The injection-moulding machine used was an Arburg Allrounder 221E/170R. The melt temperature was 160° C (185° C for the camphor-containing material), the mould temperature was 20° C, and the holding pressure was 60 to 70 MPa.

The billets intended for the hydrostatic extrusion had a length of 110 mm; billets with four different diameters were produced in order to obtain different extrusion ratios.

2.3. Hydrostatic extrusion

The hydrostatic extrusion technique has been described in detail earlier [4]. Four extrusion ratios, R_N, (the ratio between the area of the billet and that of the extrudate) were studied: 5, 10, 15 and 20. The hydrostatic extrusion was performed at 125(± 2)° C, with billets containing camphor or DMTP also at 112(± 2)° C. In Fig. 1 the required extrusion pressure at 125° C is shown for the pure LPE and for the composites at an extrusion rate of about 35 mm min^{-1} and $R_N = 10$. Compared to the unfilled material, addition of carbon black does not have any significant influence on the extrusion pressure, while a substantial reduction is noted with camphor or DMTP as the second phase. A similar effect has been observed when Wanin S (lignosulphonate, technical grade) was used as a filler [4]. The behaviour observed at an extrusion temperature of 112° C was largely similar.

2.4. Tensile testing

Stress–strain measurements were performed at room temperature (20 ± 0.5° C) with a conventional tensile tester (Instron model 1193) equipped with an extensiometer with a gauge length of 25 mm. The strain rate was 3.3×10^{-4} sec^{-1}. The tensile modulus (E) was evaluated at 0.1% strain (secant modulus).

The tensile strength at rupture, σ_B, was difficult to determine due to slippage in the clamps. To circumvent this problem, the diameter of the extrudate was reduced somewhat. This reduction was confined to a small region (2 mm) located approximately on the central portion of the extrudate. Obviously the values obtained in this way provide no absolute value of the tensile

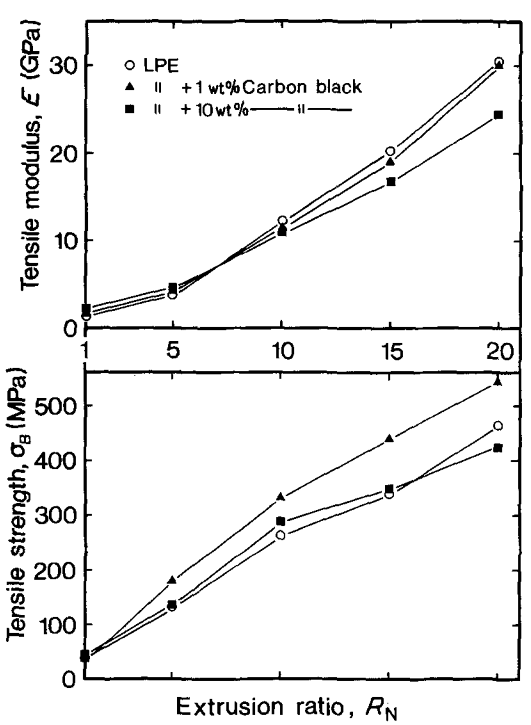

Figure 2 Tensile modulus and strength as functions of extrusion ratio for carbon black filled LPE. Extrusion temperature 125° C.

strength, but can be used when comparing the different composites and the pure LPE. The strength values are probably too low, since no correction for stress concentrations was made.

2.5. Differential thermal analysis

The melting points, T_m, of the materials were determined using differential thermal analysis (using a Mettler TC 2000 machine). The T_m values were compensated for the influence of the heating rate (5° C min^{-1}).

3. Results

3.1. Carbon black-containing composites

The influence of the extrusion ratio, R_N, on the tensile modulus, E, in the extrusion direction is shown in Fig. 2 for the unfilled polyethylene and the LPE containing 1 wt% and 10 wt% carbon black. The extrusion temperature was 125° C. As Fig. 2 shows, the tensile modulus increases with the extrusion ratio of all three materials. Addition of 1 wt% carbon black does not significantly affect E compared to the unfilled LPE, while for the 10 wt% extrudate a marked decrease is observed, especially at higher extrusion ratios. At an extrusion ratio of 20, the tensile modulus for the unmodified LPE is ~ 30 GPa, while it decreases to ~ 24 GPa if 10 wt% carbon black is added.

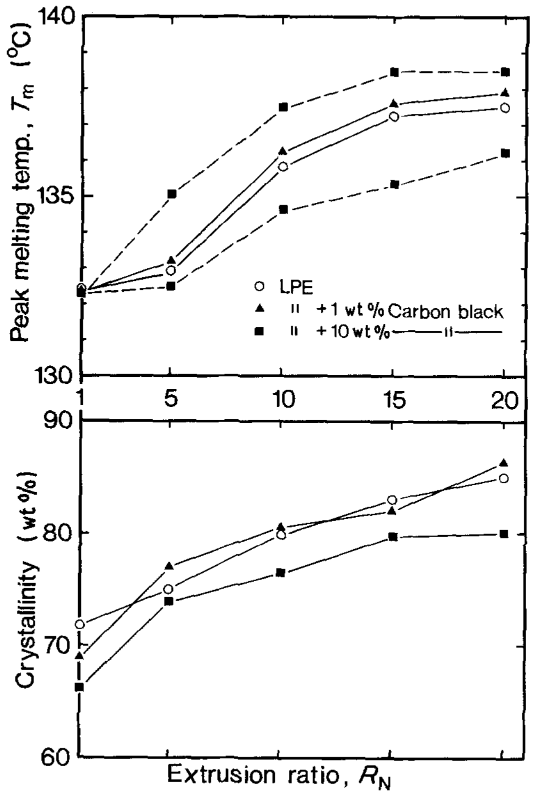

Figure 3 Peak melting temperature and crystallinity against extrusion ratio for carbon black filled LPE. LPE containing 10 wt% carbon black exhibits two melting peaks; both the corresponding peak melting temperatures are shown in the upper figure.

The influence of carbon black on the tensile strength, σ_B, in the extension direction exhibits an interesting feature (Fig. 2.). While the strength of the pure LPE and the LPE containing 10 wt% carbon-black is more or less the same for all extrusion ratios, the specimens containing 1 wt% carbon-black display an increase in σ_B. The tensile strength of the unfilled materials is ~460 MPa, R_N = 20; addition of 1 wt% carbon black results in an increase up to 535 MPa.

As can be seen from Fig. 3, the melting points of the materials shift to higher temperatures with increasing extrusion ratios. This is in agreement with earlier results [4, 6]. In this respect the pure LPE and the polymer containing 1 wt% carbon black behave rather similarly. The melting point increases from 132 to 133° C up to 137 to 138° C (extrusion ratio 20). The increase in T_m with increasing R_N levels off at higher values, [4, 6]. The specimen containing 10 wt% carbon black

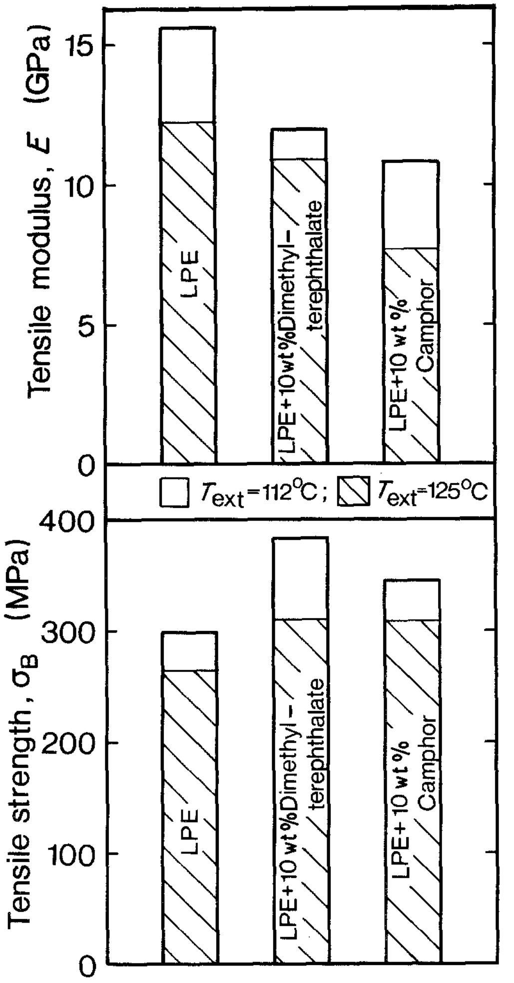

Figure 4 Tensile modulus and strength of LPE with camphor and dimethylterephthalate extruded with $R_N = 10$.

exhibits a more complex behaviour. Two melting peaks are evident in the endotherms for all four extrusion ratios. The corresponding T_m values are shown in Fig. 3. The lower melting point of the 10 wt% sample is significantly lower than the T_m values of the pure material and the other composite, while the upper is clearly higher.

In Fig. 3 the degree of crystallinity, calculated from the heat of fusion for a completely crystalline polyethylene ($\Delta H_f = 290$ J g^{-1} [7]), is also given as a function of R_N. Obviously the crystallinity increases with increasing extrusion ratio. For unfilled LPE and LPE–1 wt% carbon black the crystallinity level is approximately the same at comparable extrusion ratios, while the crystallinity of the 10 wt% extrudate is lower, especially at R_N = 15 to 20.

3.2. LPE with camphor and dimethylterephtalate

In Fig, 4 the influence of 10 wt% camphor and 10 wt% DMTP on the tensile modulus of linear polyethylene is shown. The extrusion ratio was 10 and the two extrusion temperatures were used, 112 and 125° C. It is evident that addition of these materials, which are compatible with polyethylene, reduces the stiffness. For example, with an extrusion temperature of 112° C the modulus decreases from ~ 16 GPa to ~ 11 GPa due to the presence of camphor, see Fig. 4. As expected, the tensile modulus also decreases with increasing extrusion temperature.

The σ_B-values of the composites are compared with σ_B of the pure material in Fig. 4. As with the polyethylene containing 1 wt% carbon black, σ_B of the composites is higher. This is true at both extrusion temperatures.

The melting points of pure LPE and the two modified ones, prior to and after the hydrostatic extrusion, are given in Table I. It is noted that addition of camphor or DMTP reduces the T_m value of the LPE phase, indicating that a solution is formed when mixing the two components. Thus, both prior to and after the hydrostatic extrusion, the modified materials have a lower melting point compared to the unfilled LPE. It should be pointed out that there were no melting peaks corresponding to the pure additives (camphor 176° C and DMTP 140° C) in the endotherms for the filled materials.

TABLE I Peak melting temperature of LPE and LPE filled with DMTP and camphor, before and after the hydrostatic extrusion ($R_N = 10$).

Sample	Peak melting temperature (° C)		
	Billet	Hydrostatic extrudate	
		T_{ext} = 112° C	T_{ext} = 125° C
LPE	132.3	137.4	135.8
LPE + 10 wt% Dimethylterephthalate	129.4	133.7	133.7
LPE + 10 wt% Camphor	129.1	132.6	132.6

The hydrostatic extrusion results, as for the pure material, in an increase in T_m ($\approx 4^\circ$ C at a R_N of 10) of the filled materials. In contrast to what is observed for the unmodified material, the extrusion temperature does not appear to play a major role in this context.

4. Discussion

The primary aim of this communication is to point out that filled or otherwise modified polymers can be processed using hydrostatic extrusion and that the resulting material may have a somewhat improved property profile. This has also been shown in an earlier work concerning hydrostatic extrusion of blends of polyethylene and a water soluble material containing mainly sodium lignosulphonate [4]. Furthermore, the results indicate that techniques used in metallurgy (e.g. alloying, dispersion hardening) to control and modify the structure and properties of the materials may possibly also be applied to polymers, though in a modified way. The improvement in tensile strength due to addition of, for example, small amounts of carbon black may illustrate this point.

The increase in tensile strength and the accompanying decrease in stiffness reported above for some of the investigated systems, e.g. LPE containing 1 wt% carbon black, may be difficult to explain. If the tensile modulus is related to the density of stretched tie-molecules between the oriented crystalline lamellae (or degree of stretching of the tie-molecules), then incorporation of small amounts of carbon black could probably reduce the size of the crystallites (perpendicular to the chain extension direction), which would lead to an increase in the number of tie-molecules. These are not necessarily stretched to the same extent as observed in the pure extrudate, which could result in stiffness. The tensile strength would, however, be expected to be related to the number of tie-molecules, irrespective of whether they are fully extended or not. The increase in the number of such molecules due to the presence of small amounts of carbon black would then result in a higher tensile strength. Preliminary results, relating to measurements of the die-swell after hydrostatic extrusion, revealed that LPE containing 1 wt% carbon black exhibited a lower die-swell than the unfilled material at extrusion ratios greater then 5. This indicates that the density of tie-molecules is higher in the composite [2].

Addition of 10 wt% carbon black probably partly destroys the high modulus structure produced by the hydrostatic extrusion, and no improvement in properties would be obtained. This is to some extent supported by the appearance of a lower melting temperature peak (which may be more related to the structure of normally melt-crystallized LPE) in the endotherms together with the high temperature peak as reported above for LPE containing 10 wt % carbon black. Furthermore, the die-swell of LPE-10 wt% carbon black extrudates was higher than for unfilled LPE and LPE-1 wt % carbon black.

The changes in mechanical properties of polyethylene found in the presence of partly compatible substances (camphor and DMTP) are more difficult to interpret in terms of a simple molecular model, because the structure of a solidified system of this type is not known. It may be added that the interaction between LPE and camphor or DMTP, as revealed in the DTA-peaks, is further confirmed by mutual solubility of the two phases when in the molten state. Furthermore, there were no melting peaks corresponding to the pure additives (camphor 176° C and DMTP 140° C) in the endotherms for the filled materials.

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