Polymer Bulletin 13, 209–214 (1985)

Polymer Bulletin

Additives

Effects of Additives on Gel-Spinning of Ultra-High Molecular Weight Polyethylene

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INTRODUCTION

In recent years, additives have played a continuously increasing role in polymer processing (1-3). They frequently affect the flow behaviour quite markedly and often improve the mechanical properties and product stability in a rather unpredictable way.

In studying gel-spinning of ultra-high molecular weight polyethylene (UHMWPE) we came across an interesting effect due to adding 1 wt % of Aluminium-stearate to the spinning solution (4). Whereas without this additive, drawing of the gel directly after leaving the die, resulted in a rapid decrease in tensile strength of the ultimate fibre, the additive enabled us to pull the extrudate with speeds exceeding 300 m/min while the strength of level was still maintained at about 3 GPa.

This unexpected phenomenon induced some further investigations into the influence of additives on the spinnability of polyethylene solutions.

It is the purpose of this communication to present some experimental data on the effect of carbon black and EPDM rubber. Rather surprisingly we found that mixing carbon black with the polyethylene solution yielded, after extrusion and hot-drawing, a fibre with a tensile strength of 3.2 GPa despite the fact that it contained 7 wt % of carbon black.

EXPERIMENTAL

The linear polyethylene (UHMWPE) used throughout this study was Hifax 1900 with $\bar{M}_w = 4 \times 10^6$ and $\bar{M}_n = 2 \times 10^5$. Oxidative degradation of the polyethylene was prevented by mixing all solutions with 0.5 wt % of the anti-oxidant 2,6-di-t-butyl, 4-methylcresol. The EPDM (ethylene, propylene, dicyclopentadiene) rubber sample was supplied by DSM (Geleen, The Netherlands). The Carbon black (Degussa FW1) had an average particle size of 13 mm and a BET surface area of 320 m^2/g. It was purchased from Degussa (Antwerp, Belgium).

For the gel-spinning experiments (4), the UHMWPE was dissolved in paraffin oil at a concentration of 5 wt %. The solutions were stored at 150°C for 48 hours and subsequently cooled slowly to room temperature. Gelation was observed to begin at about 90°C. The solid gel was cut into small pieces of approximately 5 mm in diameter and fed into the extruder, which was operated at a temperature of 170°C. In all experiments the free extrusion rate was 1 m/min. The extrudate was quenched in ambient air leading to the formation of a gel-filament. A take-up drum was placed at a distance of 1.5 m from the die-exit. This allowed us to collect the extrudate at different winding speeds. After spinning, the paraffin oil was extracted from the gel with n-hexane and the remaining porous as-spun fibre was dried in vacuum at 50°C. Hot-drawing of these fibres was carried out at 148°C always to the maximum draw ratio. Freely extruded gels could be drawn

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to ratios of about 100 while the ones taken-up at speeds of about 75 m/min were drawable tc ratios of 10 at the most.

For the suspension spinning experiments, UHMWPE suspensions were prepared by mixing the powder with solutions of 1 wt % EPDM, 1 wt % of Al-stearate and 0.5 wt % of anti-oxidant in paraffin oil at 100°C. The suspension was cooled down to room temperature while being moderately stirred, and poured into the extruder.

This apparatus was a Reifenhauser S013-25 extruder equipped with two different dies.

Most of the experiments were performed using a die with an entrance angle of 6°, a length of 14.5 cm and an exit diameter of 1.8 mm. The second die was a cylindrical one, ending in a cone with an entrance angle of 74° and an exit diameter of 2mm.

Tensile testing was carried out using a Zwick Z1.3B tensile tester operated at a cross-head speeds of 12 mm/min and at a temperature of 20°C. The original sample length was 25 mm. The cross-sectional areas of the fibres were determined from the fibre weight and length.

RESULTS AND DISCUSSION

Recent investigations have indicated that the mechanism of the formation of ultra-strong polyethylene fibres is rather complicated because it involves the streaming of an entanglement network through an orifice and morphological and topological transformations in the hot-drawing step. The shear stresses at the wall of the orifice and the elongational velocity gradients in this converging flow tend to split up the entanglement network into fibrillar units. At a certain flow rate elastic turbulences occur which give rise to filament irregularities resulting in weaker fibres. These elastic turbulences, also referred to as "melt fracture" show up in particular in the case of very long chain molecules. They may be avoided by choosing low shear rates, using dies with small entrance angles and high length to diameter, L/D,capillaries and applying of high temperatures and good solvents in order to get rid of adsorption and crystallization. Moreover, it has been found that additives are capable of reducing these flow instabilities and also drawing of the extrudate has a favourable effect. These observations stipulated our experimental conditions of an extrusion rate of 1 m/min, a temperature of 170°C and drawing the extrudate at various rates. The as-spun filaments always had a smooth appearance. The paraffin oil was removed by extraction with hexane and the dried porous fibre was subsequently hot-drawn at 148°C. The number of "flow-defects" in the fibre were supposed to be reflected in the stress-strain behaviour.

Drawing the gel-filament composed of only 5 wt % UHMPE in paraffin oil gave rise to a lowering in the tensile strength from 3 GPa at 1 m/min to 0.5 GPa at 25 m/min (Fig. 1, curve A). Adding 1 wt % of Aluminium-stearate showed no decrease in tensile strength far beyond drawing rates of 70 m/min (Fig. 1, curve B). This may be accounted for by a possible prevention of the large polyethylene molecules from being adsorbed onto the die wall. Furthermore, the Al-stearate increases the solvent viscosity which increases the lifetime of entanglements and thereby promoting the formation of fibrillar flow clusters. These flow units will undoubtedly crystallize in an oriented manner by the action of the elongational flow field. The presence of the Al-stearate also makes the solvent poorer which in turn cause a contraction of the coils and increase in lifetime of the entanglements. It may also inhibit crystallization.

Carbon black

Carbon black (7) is known to decrease the extrudate swell of rubbers and to diminish the severity of extrudate irregularities (1). As a result of adsorption of portions of chains on the surface of the carbon particles the disentangling of the molecules seems to be retarded and the strength

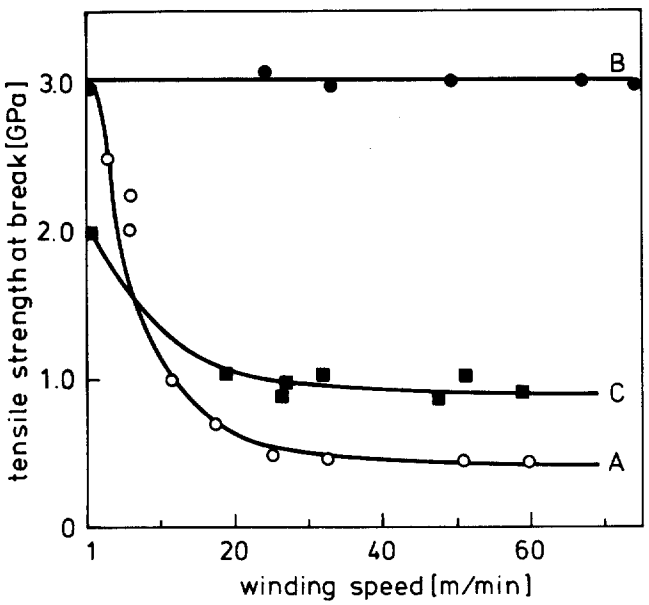

Fig. 1: The tensile strength of UHMWPE fibres versus the winding speed at which the extrudate was collected on a bobbin. Curve A represents the data for a gel consisting of 5 wt % UHMWPE in paraffin oil. Curve B illustrates the effect of adding 1 wt % of Aluminium-stearate to the gel. Curve C refers to gels that also contained 1 wt % of Carbon black.

of polymer melts is found to be increased (8). One may therefore expect that this additive will influence gel-spinning. Adding 0.35 wt % of carbon black with a fine particle size to the 5 wt % polyethylene solution resulted in 7 wt % carbon black in the fibre. The tensile strength after extraction with hexane and hot-drawing was 3.2 GPa and the Young's modulus was 78 GPa. This strength level (9) was not expected in view of this high percentage of foreign particles that tend to cause stress concentrations although they could possibly improve the structure by epitaxial crystallization (10). Higher concentrations of carbon black in the gel, 1 wt % for instance, corresponding to 20 % in the final fibre diminishes the tensile strength to 1.5 GPa. But drawing of the extrudate up to 60 m/min appeared to have no influence on the fibre strength confirming the idea that the entanglements cannot slip so easily and thus induce early elastic turbulences (14). When we added 1 wt % of carbon black to the gel already containing 1 wt % of Al-stearate and stretched the extrudate, the strength decreased from 2 GPa to 1 GPa in the winding speed range of 1 to 20 m/min. The as-spun fibre was found to be composed of fibrillar aggregates of globules as revealed by the scanning electron micrograph of fig. 2. This particular morphology always yields, after hot-drawing a fibre with a low tensile strength. It is conceivable that the Al-stearate has been adsorbed on the carbon black, having a large surface area, thereby lowering the viscosity of the solvent and stimulating the adsortpion of large polyethylene molecules on the die wall.

EPDM rubbers

There was some hope that further understanding could be gained by

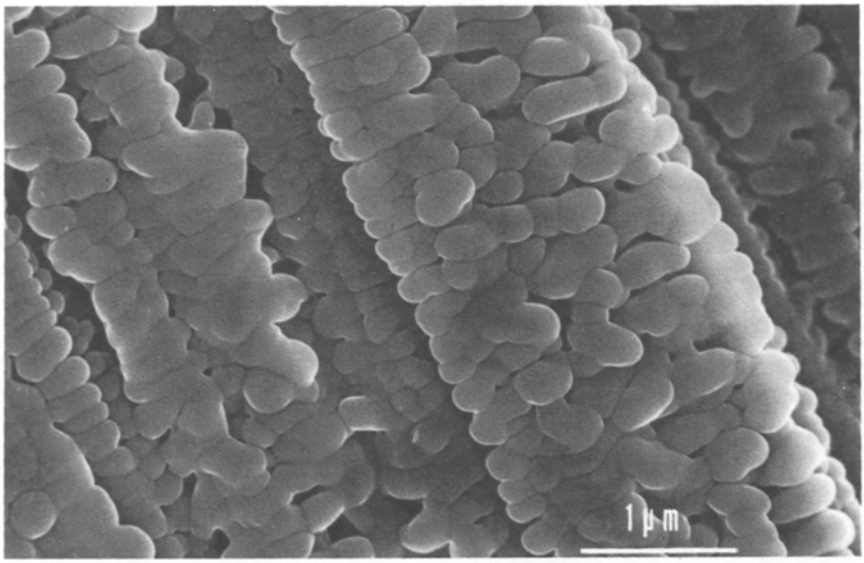

Fig. 2: Scanning electron micrograph of an extracted as-spun fibre produced by spinning a 5 wt % UHMWPE solution in paraffin oil which also contained 1 wt % of Al-stearate and 1 wt % of carbon black the winding speed was 16 m/min.

exploring the effect of EPDM rubber which increases the solution viscosity but does not interfere with the Al-stearate. Fig. 3 shows that for the

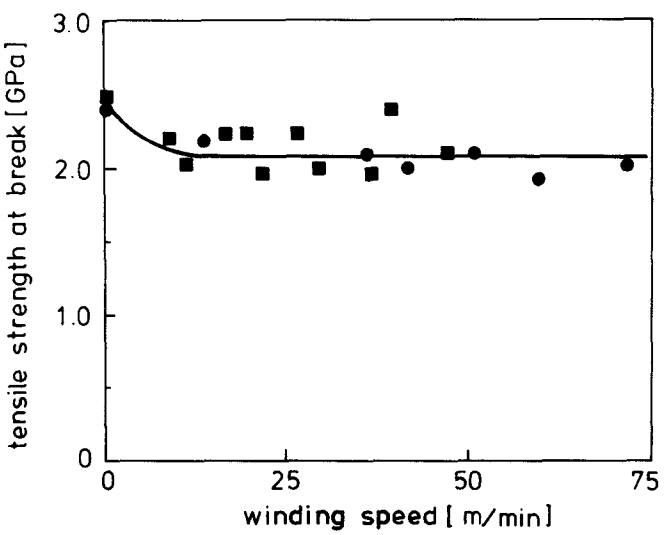

Fig. 3: The tensile strength of UHMWPE fibres versus the winding speed for gels of UHMWPE in paraffin oil containing 1 wt % Al-stearate and 1 wt % EPDM rubbers and for suspension of UHMWPE powder in the paraffin oil system (● = gel-spinning, ■ = suspension-spinning).

gels containing also 1 wt % of EPDM rubber,the winding speeds up to 75 m/min have no influence on the tensile strength. The latter remains constant at a somewhat lower level of 2 GPa which is to be attributed to the fact that not all rubber molecules could be removed by extraction of the gel-filament at room temperature. Residual rubber particles and voids in the hot-drawn fibre can be clearly discerned in the scanning electron-micrograph of fig. 4.

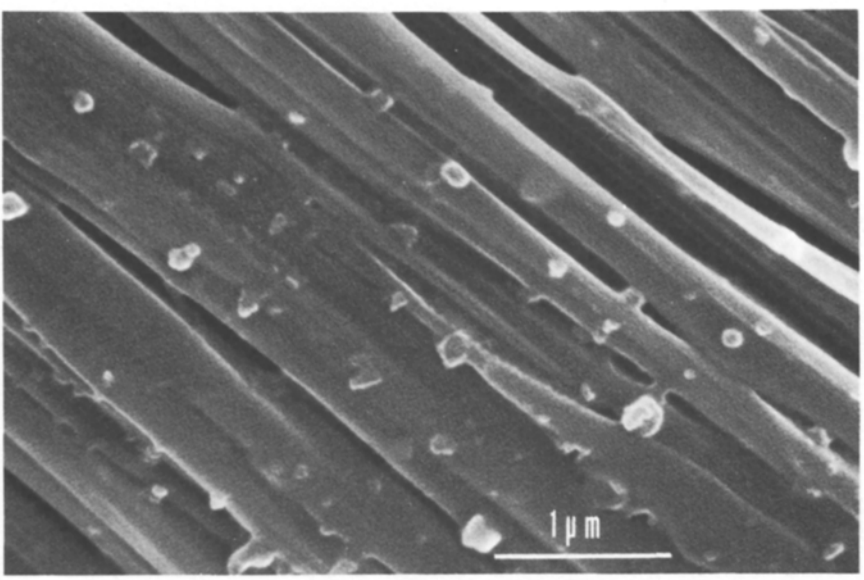

Fig. 4: Scanning electron-micrograph of an UHMWPE fibre produced by suspension spinning using 1 wt % of EPDM rubber in the solvent. It reveals the presence of EPDM particles and voids.

We have also included in fig. 3 the data points for fibres that were produced by suspension-spinning. They fall on the same curve implying that dissolving UHMWPE powder in oil within the residence time of only 20 minutes in the extruder leads to the same entanglement structure as acquired in the usual method which lasts 48 hours.

Die geometry

The elastic flow instabilities could also be initiated by the flow field in the orifice instead of exclusively by stretching the extrudate. In order to get some impressions of the effect of the flow field in the extruder exit,the conically shaped die was replaced by a cylindrical one having an entry angle of 74°. This led to a marked decrease in tensile strength as is demonstrated by the curves in fig. 5. In case of the conical die with entry angle of 6° the strength is 3 GPa up to a winding speed of 100 m/min and then drops to 2.5 GPa up to 300 m/min (curve A). The cylindrical die produces a fibre of 2 GPa at 1 m/min and beyond a transition at 60 m/min it generates only 0.7 GPa (curve B). The spinline also fractured at 130 m/min. These results suggest that indeed the increased shear stresses

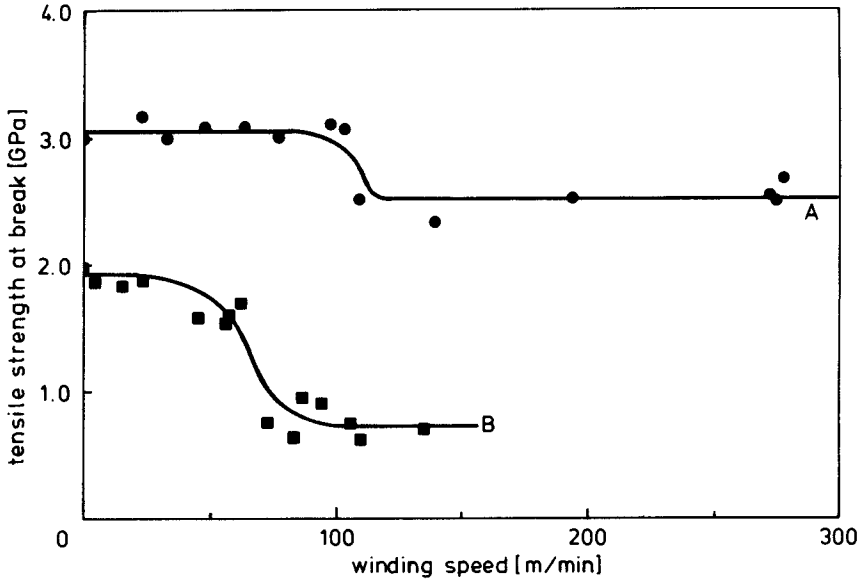

Fig. 5: The tensile strength of UHMWPE fibres versus the extrudate winding speed. The extruder was filled with a conical die (entry angle 6°) (Curve A) and a cylindrical die (entry angle 74°) (Curve B).

at the wall and elongational velocity gradient in the cylindrical die enhances flow instabilities. The transition between the strength levels as exhibited by both curves of fig. 5 may be associated with oscillating flow (5,6) which has been observed for melt extrusion of high density polyethylene.

Conclusions

As judged from the fibre tensile strength-extrudate draw speed relationship for UHMWPE solutions in paraffin oil, carbon black particles diminish flow instabilities and extrudate irregularities as does EPDM rubber. Reductions in fibre tensile strength by both additives is caused by their weakening the fibre structure.

Increasing the shear rate at the wall by using a more abrupt die geometry lowers drastically the mechanical properties of the fibres.

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Accepted March 14, 1985