High strength/high modulus polyethylene: synthesis and processing of ultra-high molecular weight virgin powders

Bruno P. Rotzinger
Ciba-Geigy AG, Zentrales Forschungslaboratorium, CH-4002 Basel, Switzerland

Henri D. Chanzy
CERMAV, CNRS, BP 68-38402, Saint Martin d'Heres Cedex, France

and Paul Smith*
Materials Department and Department of Chemical and Nuclear Engineering, University of California, Santa Barbara, CA 93106 USA
(*Received 7 November 1988; revised 20 January 1989; accepted 24 January 1989*)

High strength/high modulus tapes and filaments were prepared directly from virgin ultra-high molecular weight (UHMW) polyethylene powders, by low temperature compression moulding and subsequent tensile drawing. We report in detail on the effects of various polymerization and compression moulding variables on the drawability of virgin UHMW polyethylene powders.

(Keywords: polyethylene; synthesis; drawing; virgin polymers; high strength; high modulus; UHMW PE)

INTRODUCTION

In previous papers[1,2] we introduced a technique for the production of high strength/high modulus polyethylene films, fibres and tapes that is based on tensile drawing of virgin (i.e. as-polymerized) ultra-high molecular weight polyethylene films. The films were produced by depositing a vanadium catalyst system on glass slides, followed by polymerization of ethylene at relatively low temperatures. The method thus dispenses with the solution processing that constitutes the now commercial gel spinning technology[3,4], hitherto employed as the major route to untangle long chains prior to tensile drawing. It is obvious that the virgin film method lacks industrial significance and, therefore, we continued the search for solvent-free routes to high strength/high modulus polyethylene products. It is the purpose of this paper to describe a technique to manufacture high strength/high modulus materials directly from certain virgin polyethylene powders. This process was first disclosed in ref. 5.

Processing of powders of ultra-high molecular weight polyethylene (UHMW PE) has attracted attention because of the unique properties of this polymer, including extraordinary abrasion resistance and excellent wear and friction characteristics. Major difficulties have been met in attempts to process these interesting materials using conventional techniques. This is due primarily to the extremely high viscosity of molten UHMW PE which virtually prevents flow and motion of long chains across the boundaries of the original polymer particles. As a matter of fact, UHMW PE is commercially shaped into useful articles mostly at temperatures exceeding 200°C (see, for example, ref. 6) and at relatively high pressures, up to 5000 kg/cm^2.

In earlier studies on cold compacting of UHMW PE[7,8], it was concluded that this polymer required processing at temperatures exceeding its melting point, in order to yield mechanically coherent films. It was recognized, however, that not all powders studied performed identically. These differences were attributed to variations in the gross structure of the virgin particles, such as porosity, shape, size and morphology[7–9].

Over the last ten years, independently of the present work, Kanamoto, Zachariades, Porter and their co-workers[10–12] have made considerable advances in processing a certain UHMW PE 'reactor powders' below the melting temperature. In their most recent paper on this topic[13], Kanamoto *et al.* reported on a two-stage solid-state extrusion and tensile drawing process in which Hercules HiFax 1900 reactor powder was consolidated and drawn into tapes below the melting point of polyethylene, yielding uniaxially oriented specimens having a Young's modulus up to 107 GPa and tensile strength of 1.4 GPa.

The above, seemingly conflicting, results, in our view[1,2], are readily understood in terms of differences in entanglement densities in the various as-polymerized powders, which control their solid-state flow behaviour[14]. One of the most remarkable properties of low-entanglement density solid polyethylenes (such as single crystals, gels derived from (semi-)dilute solutions, low molecular weight samples and, as will be demonstrated in this paper, certain virgin polymer materials) is their ability to flow below their melting point. This characteristic not only underlies the techniques to produce ultra-oriented structures (e.g. refs. 1, 2, 14, 15) from such materials, but also permits the formation of

---

* To whom correspondence should be addressed

0032-3861/89/101814-06$03.00

coherent parts and films below the melting temperature. Remarkably, such low-entanglement density solids flow more readily below, than above the melting temperature! The latter, of course, is due to the fact that above the melting temperature the macromolecules rapidly entangle[16], and display the poor flow characteristics accompanying the high viscosity (see also refs. 10, 11). It is noteworthy to point out that this interesting phenomenon is not uniquely restricted to polyethylene. For example, commercial as-polymerized poly(tetrafluoroethylene) (PTFE) displays a very similar behaviour (the reader is referred in particular to ref. 17). As a matter of fact, some of the processing techniques for this polymer,such as paste extrusion, and many sealant applications of PTFE are based on this unusual solid-state flow behaviour of the virgin (untangled) polymer; a property that is lost upon melting. In addition, Leenslag and Pennings[18] elegantly demonstrated that virgin, as-polymerized poly(L-lactide) contained few chain entanglements, and could be drawn directly into high strength/high modulus fibres.

Employing the knowledge gathered in our previous studies on virgin polyethylene films[1], we set out to produce under well controlled physico-chemical conditions a series of UHMW PE powders, and to systematically examine their flow and tensile drawing characteristics. For illustrative purposes only, we concerned ourselves with one supported and one homogeneous, vanadium-based (Ziegler) catalyst system. The results obtained in this work are thought to be at least qualitatively relevant to other catalysts and, conceptually, to other polymer systems.

EXPERIMENTAL

Polymerizations

Supported catalyst. In a dry box, 200 mg of dried (4 h at 400°C under nitrogen) fused Silicagel (SiO_2, surface area of 400 m^2/g) was suspended in 40 ml dry heptane. Subsequently, 10 ml of a solution of freshly distilled vanadium (IV) chloride (VCl_4) in heptane was added. The vanadium (IV) was converted to vanadium (III) following the procedure of Chanzy *et al.*[19] by boiling the solution for 10 min, cooling and decanting. The catalyst residue was washed three times with 50 ml of heptane and then suspended in 150 ml of heptane. In an atmosphere of argon gas, a dry pressure bottle was charged with 200 ml of a 1 mM solution of triisobutyl aluminium (Tiba) in heptane. The solution was heated (or cooled) to a pre-selected polymerization temperature and 50 ml of the suspension was added. The bottle was sealed and charged to 10 psig ethylene, unless indicated otherwise. After 2 h the polymerization was terminated, the bottle was vented and the polymer formed therein recovered by filtration. This virgin polyethylene was washed in methanol/hydrochloric acid, then with pure methanol and, finally, dried.

Soluble catalyst. In an atmosphere of argon gas, a dry pressure bottle was charged with 150 ml of heptane and 50 ml of a 20 mM solution of diisobutyl aluminium chloride (Dibac) in heptane. The contents were heated/cooled to the preselected polymerization temperature and 50 ml of a 0.2 mM solution of vanadium (III) acetyl acetonate in heptane/toluene [90/10 v/v] was added. The bottle was sealed and pressurized with 10 psig of ethylene. After the polymerization was terminated the bottle was vented and the polymer recovered by filtration. The polyethylene was washed with methanol/hydrochloric acid, then with pure methanol, and dried.

Characterization

Molecular weight. Molecular weights of the various samples were estimated from their inherent viscosities in tetralin at 135°C; the polymer concentration was 0.1 g/l. The inherent viscosities of all samples, independent of the polymerization conditions, was in the range from 22–30 dl/g, which corresponds to average molecular weights ($\bar{M}_w$) of $\sim 3\text{–}5 \times 10^6$ (ref. 20).

Thermal properties. Thermal characteristics of the polymers were examined by differential scanning calorimetry using a Mettler TA 3000 instrument. The sample weight was approximately 2 mg, and the scan speed was 10°C/min. The melting points quoted in this paper invariably refer to the peak temperatures in the thermograms.

Mechanical properties. The mechanical properties of the various virgin polymers were examined at elevated temperatures using an Instron Tensile Tester, Model 1122, that was equipped with a temperature regulated environmental chamber. The details of the specimen preparation and testing conditions are presented in the appropriate sections.

RESULTS

Compression moulding

One of the most remarkable properties of the majority of the virgin polymer powders described in this paper is their flow behaviour at low temperatures. All virgin UHMW PE powders synthesized in this work were readily compressed into mechanically coherent sheets at temperatures that were several tens of degrees below their melting point. This extraordinary property is illustrated in *Figure 1A*. This figure shows a photograph of a nearly transparent sheet of ultra-high molecular weight ($\bar{M}_w \sim 5.10^6$) polyethylene powder, polymerized at −20°C employing the SiO_2-supported VCl_3 catalyst system (experiment 2, *Table 1* see below), compression moulded at 500 kg/cm^2 and 100°C. For comparison, a 'sheet' manufactured from the commercial product Hostalen GUR 415 (of similar molecular weight, Hoechst AG) is shown in *Figure 1B*. The latter material required a temperature as high as 140°C, at 500 kg/cm^2, to yield any mechanical coherence at all.

A separate study was devoted to the effect of the moulding temperature on the room temperature mechanical coherence of the resulting sheets. An optimum temperature window was found to exist between 80–120°C for compression moulding of most polymers described below. At lower temperatures, premature failure of the material was observed in subsequent drawing experiments. At temperatures exceeding 120°C reduced drawability was observed due to incipient melting of the virgin polymers accompanied by the formation of chain entanglements (see e.g. refs. 1,2).

Thus, the virgin polyethylene powders produced in this

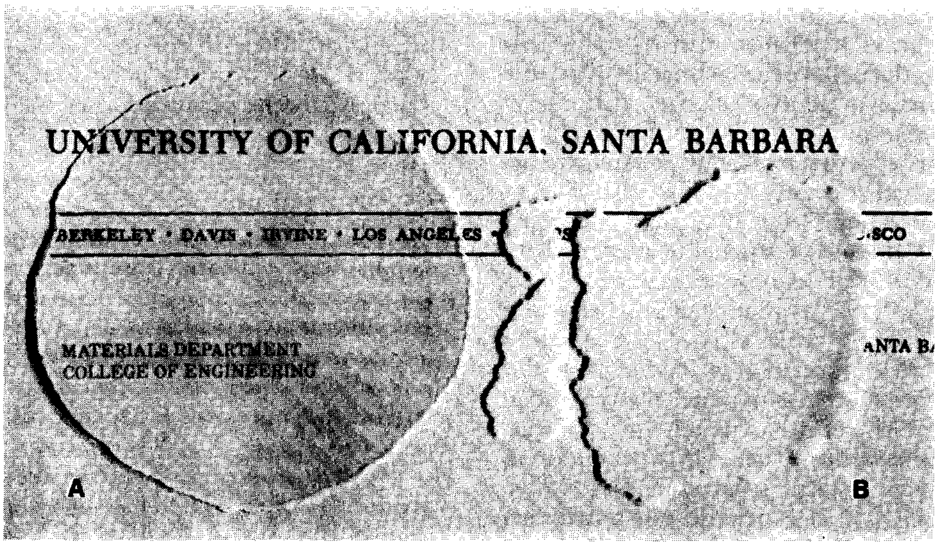

Figure 1 (A) Coherent film of virgin ultra-high molecular weight polyethylene (produced at −20°C employing a SiO_2-supported VCl_4 catalyst system, experiment 2, *Table 1*), compression moulded at 500 kg/cm^2 and 100°C. (B) Commercial (Hostalen GUR 415) UHMW PE powder compressed at 500 kg/cm^2 and 140°C; at lower temperatures even less coherence was produced

Table 1 Polymerization data for supported vanadium catalyst

	$[VCl_4]$ (mmol/l)	[Tiba] (mmol/l)	T_{pol} (°C)	t (h)	p (psig)	Y (g)	T_m (°C)	ΔH_f (J/g)	η_{inh} (dl/g)
1	0.8	3.0	25	2	10	10.5	141.3	199	24.6
2	0.8	3.0	−20	2	10	3.4	140.1	208	24.3
3	0.8	3.0	−40	16	10	1.5	139.9	193	–
4	0.8	1.0	5	2	10	5.7	142.5	187	25.5
5	0.8	1.0	5	2	30	5.4	143.5	190	28.9
6	0.8	1.0	5	2	60	7.5	143.0	199	28.7
7	5.0	1.0	5	2	10	24.8	142.3	194	–
8	2.0	1.0	5	2	10	11.7	142.2	203	–
9	1.0	1.0	5	2	10	3.5	141.1	205	22.4
10	0.5	1.0	5	2	10	2.7	141.0	198	–

$[VCl_4]$ = concentration VCl_4 in catalyst preparation; [Tiba] = concentration triisobutyl aluminium; T_{pol} = polymerization temperature; t = polymerization time; p = ethylene pressure; Y = UHMW PE yield; T_m = melting point; d.s.c., 10°C/min heating rate; ΔH_f = enthalpy of fusion; η_{inh} = inherent viscosity (0.1 g/l, tetralin, 135°C)

work were compression moulded under standard conditions of 500 kg/cm^2 pressure and a temperature of 100°C, during 3 min to yield sheets having a thickness in the range of 200–600 μm.

Supported catalyst

Polymerization. The VCl_3/Tiba/SiO_2 catalyst, an analogue to the one successfully employed in the polymerization of ethylene on glass slides[1,2], was utilized to produce a series of UHMW polyethylenes. Polymerizations were carried out over a range of temperatures, ethylene pressures and catalyst activity. Pertinent polymerization data are collected in *Table 1*. Catalyst residues were <4% w/w in all cases. This supported catalyst system under all polymerization conditions yielded a fine UHMW polyethylene powder. The molecular weights $\bar{M}_w$ invariably were in the range of 3-5 million. The melting temperatures and enthalpies of fusion displayed no strong dependence on the polymerization variables and were found to be, respectively, between 141–143°C and about 200 J/g for most virgin PE samples.

The virgin polyethylene powders were compression moulded into sheets at 100°C. Strips having a width of 0.5 mm and a gauge length of 10 mm were cut from the films. The deformation behaviour of these specimens was tested at 120°C; the rate of elongation was 100 mm/min.

Effect of polymerization temperature. Experiments 1–3 represent a series of polymerizations that were carried out to investigate the influence of the polymerization temperature on the tensile deformation behaviour. *Figure 2* displays stress–strain curves for these materials recorded at 120°C. The maximum draw ratio was found to drastically increase from 19 to more than 40 times upon decreasing the polymerization temperature from 25 to −40°C (cf. *Table 2*). (Due to instrument size limitations, the maximum measured draw ratio for single stage tensile drawing was 40. No results will be presented in this paper on two stage drawing.) This finding is in

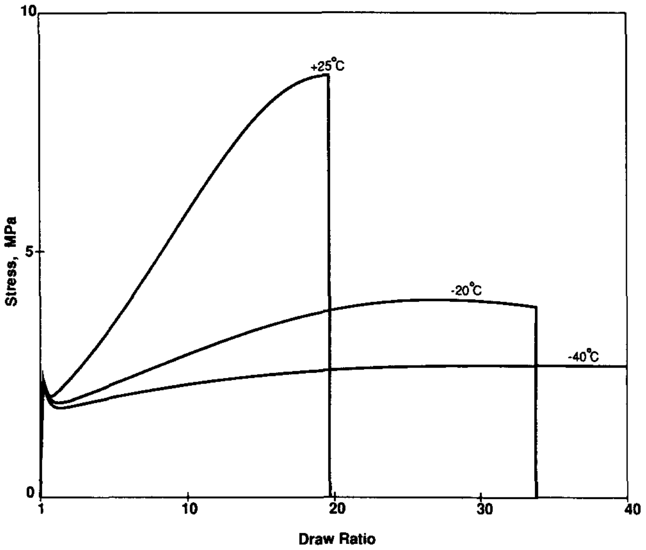

Figure 2 Stress–strain curves recorded at 120°C of films of compression moulded virgin PE powders ($T_{\text{moulding}} = 100$°C) polymerized at +25, −20 and −40°C. Note the remarkable difference in post yield slope (strain hardening) of the curves

Table 2 Effect of polymerization temperature on maximum draw ratio

Experiment number	Temperature (°C)	Draw ratio at 120°C
1	+25	19
2	−20	34
3	−40	>40

Table 3 Effect of ethylene pressure on maximum draw ratio

Experiment number	Pressure (psig)	Draw ratio at 120°C
4	10	35
5	30	17
6	60	12

excellent agreement with earlier results obtained in the study on deformation of virgin UHMW PE films (refs. 1, 2). Note that the post-yield slope, i.e. the 'rate' of strain hardening, was sensitively dependent on the polymerization temperature of the virgin materials. At decreasing temperature, a strong decrease in the post-yield slope of the stress–strain curve was observed. A similar dependence was previously reported for UHMW PE films precipitated from exceedingly dilute solutions[14].

Effect of ethylene pressure. Polymerizations 4–6 were carried out at different ethylene pressures. The powders produced were compression moulded under standard conditions, and their tensile drawing behaviour examined. The results are summarized in *Table 3*. This table reveals that increasing ethylene pressure resulted in a decreased maximum draw ratio of the virgin UHMW PE powders.

Effect of catalyst concentration. The effect of the catalyst activity was investigated in experiments 7–10, by altering the vanadium (IV) chloride concentration in the preparation of the catalyst. The productivity of the catalyst was found to drastically increase with increasing vanadium concentration (see *Table 1*), whereas the maximum draw ratio of the virgin polyethylenes decreased (*Table 4*).

Mechanical properties. The various virgin UMHW PE powders produced in experiments 1–3 were compression moulded into sheets at 110°C, and strips with a width of about 0.5 mm and a gauge length of approximately 10 mm were cut from the films. These strips were drawn at 130°C to various draw ratios up to the instrument imposed maximum of 40 x , yielding oriented polyethylene filaments of 50–350 denier. The mechanical properties of the drawn, tape-like filaments were tested at room temperature. The gauge length was 25 mm, and the rate of elongation was 25 mm/min. The results of these investigations are presented in *Figures 3* and *4*. It was assumed that the density of the samples was 1 g/cm^3. *Figure 3* displays the familiar Young's modulus/draw ratio plot. This graph shows that the polymerization conditions did not affect the efficiency of the tensile drawing process (represented by the E/λ slope), but limited only the maximum achievable draw ratio and, therewith, modulus. It was found that the modulus/draw ratio slope was comparable to that previously observed for melt and solution spun/drawn polyethylenes (cf. refs. 3, 20). *Figure 4* shows a plot of the tensile strength *versus*

Table 4 Effect of catalyst concentration on maximum draw ratio

Experiment number	[VCl$_4$] (mmol/l)	Draw ratio at 120°C
7	5.0	18
8	2.0	29
9	1.0	33
10	0.5	>40

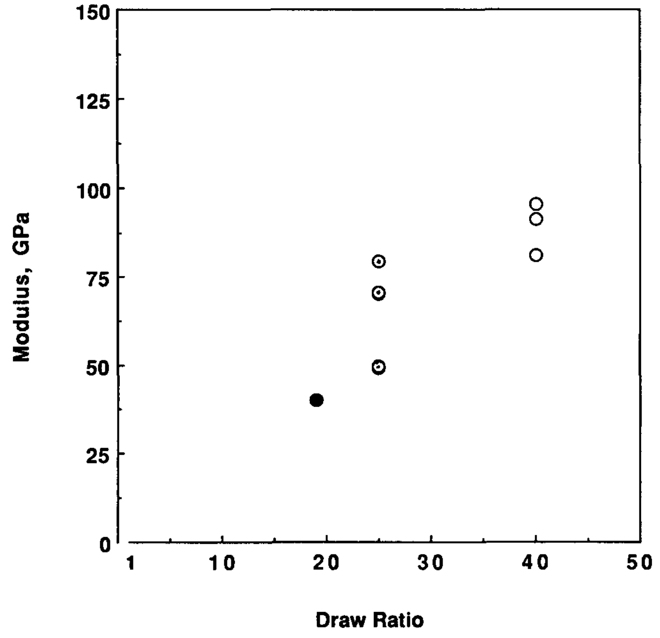

Figure 3 Room temperature Young's modulus vs. draw ratio of compressed virgin UHMW PE powders produced with the supported vanadium catalyst system. Polymerization conditions: ●, experiment 1; ⊙, experiment 2; O, experiment 3 (*Table 1*)

the Young's modulus. This graph shows that the simple compression moulding/drawing technique described in this paper, yields oriented high-modulus polyethylenes with tensile strengths that are comparable to those obtained with the gel spinning technology[3]. This finding is of interest, particularly in view of the relatively large cross-sectional areas, or linear densities of the present filaments (50–350 denier, as opposed to 1–10 denier for most solution-spun filaments), which are commonly assumed to be associated with reduced strengths.

Soluble catalyst

Polymerization. This section describes a series of polymerizations that were carried out with the soluble vanadium (III) acetyl acetonate/diisobutyl aluminium chloride catalyst. Pertinent polymerization data are given in *Table 5*. Fine powders were obtained in experiments 11 and 12. At a polymerization temperature of −20°C (experiment 13), the initially powdrous particles agglomerated. The agglomerates were recovered, and cut into smaller pieces.

Effect of polymerization temperature. The effect of the polymerization temperature on the maximum draw ratio of the cold-compression moulded films is shown in *Table 6*. Once again, we observed a strong influence on λ_{max}. It increased from 13 to >40 upon reduction of the polymerization temperature from +60 to −20°C.

Mechanical properties. The room temperature mechanical properties of compressed powders, drawn at 130°C to various draw ratios, are presented in *Figures 5* and *6*. *Figure 5* shows a plot of the Young's modulus *versus* draw ratio. The slope of this curve, which represents the efficiency of the tensile orientation temperature, appeared to be independent of the polymerization of the virgin powders and comparable to that for UHMW PE polymerized with the supported catalyst system (*Figure 3*).

The tensile strengths of the various samples are plotted against their Young's modulus in *Figure 6*. The values of the tenacities, at constant modulus, of these oriented virgin UHMW PE materials appeared to be comparable to those of the specimens prepared from powders produced with the supported catalyst (cf. *Figure 4*), despite the presence of the supporting silica particles in the latter material, which could have created stress concentrations normally causing reduced strength.

Table 6 Effect of polymerization temperature on maximum draw ratio

Experiment number	Temperature (°C)	Draw ratio at 120°C
11	+60	13
12	+25	18
13	−20	>40

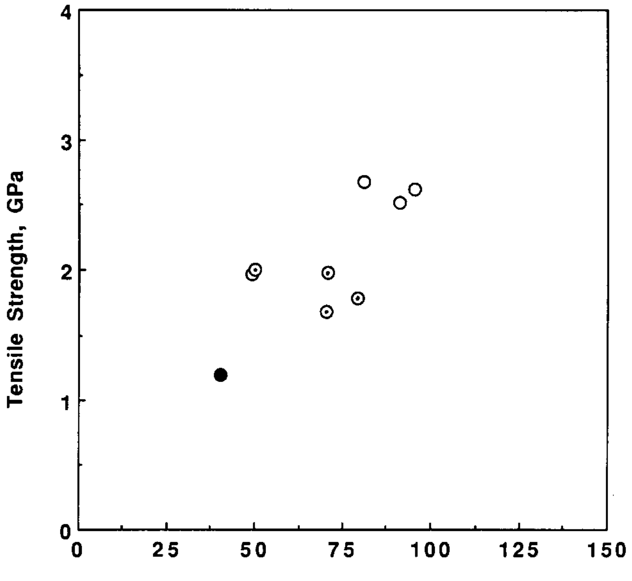

Figure 4 Tensile strength/Young's modulus plot of samples in *Figure 3*

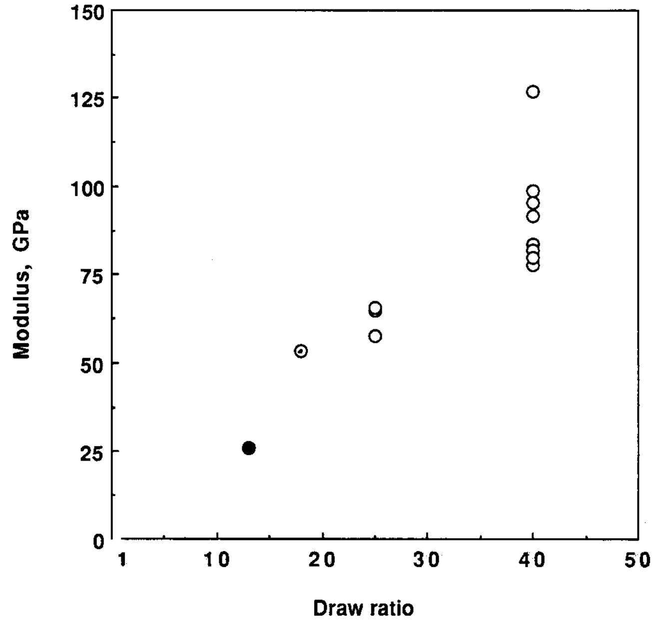

Figure 5 Young's modulus vs. draw ratio of compressed UHMW PE powders produced with the soluble vanadium catalyst system. Polymerization conditions; ●, experiment 11; ⊙, experiment 12; O, experiment 13 (*Table 6*)

Table 5 Polymerization data for soluble vanadium catalyst

Sample	[Vaa] (mmol/l)	[Dibac] (mmol/l)	T_{pol} (°C)	t (h)	p (psig)	Y (g)	T_m (°C)	ΔH_f (J/g)	η_{inh} (dl/g)
11	0.2	20	60	1	10	0.6	138	203	20.4
12	0.2	20	25	1	10	11.1	142	212	24.3
13	0.2	20	−20	16	10	53.2	142	223	26.7

[Vaa] = concentration vanadium acetyl acetonate in catalyst preparation; [Dibac] = concentration diisobutyl aluminium chloride

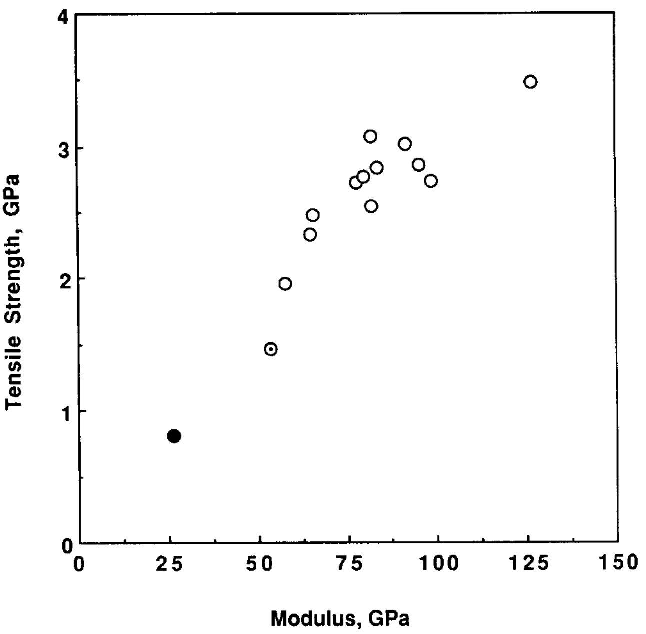

Figure 6 Tensile strength/Young's modulus plot of drawn tapes cut from compressed, virgin UHMW PE powders, polymerized at various temperatures (see *Figure 5*) with the soluble vanadium catalyst system

DISCUSSION

In this work a number of general guidelines have been established for the synthesis of UHMW PE powders that exhibit a high inherent deformability in their virgin, i.e. never molten, state. The maximum draw ratio of low temperature compacted films of these materials was found to systematically depend on synthesis variables as follows: reduced polymerization temperature, reduced catalyst activity and reduced monomer pressure resulted in drastically enhanced maximum draw ratio. Ironically, the development of modern catalysts mostly has been towards more active (high yield, relatively high temperature) systems, which result in materials with poor processing and drawing characteristics, as is shown in the present work.

The above effects and trends are readily understood in terms of the previously proposed[1,2] schematic for the formation of chain entanglements during polymerization of ethylene, and their supposed effect on the tensile behaviour[14]. In this pictorial model it was suggested that at increased (local) polymerization temperature a longer part of the growing chain is in the liquid state, leading to an increased entanglement density in the virgin, as-polymerized polyethylenes. Bearing in mind that the polymerization of ethylene is exothermic, it is to be expected that increased monomer pressure and catalyst concentration result in raised local polymerization temperatures and accompanying reduced drawability.

It is clear that the results obtained for the present (relatively low yield) vanadium Ziegler catalyst systems cannot be employed to quantitatively predict the deformation behaviour of UHMW PE materials produced with other catalysts. However, it appears highly plausible that the general guidelines unveiled in this work are applicable to many other systems.

CONCLUSION

Virgin ultra-high molecular weight polyethylene powders with intrinsic excellent deformability can be directly synthesized under moderate polymerization conditions. These powders exhibit a most remarkable solid-state flow behaviour. They can be consolidated well below their melting temperature into mechanically coherent, semi-transparent films, which can be directly drawn into high strength/high modulus films, tapes and fibres.

ACKNOWLEDGEMENTS

Most of the experimental data presented in this paper were gathered during the authors' stay in the Central Research and Development Department at the Experimental Station of E. I. du Pont de Nemours and Company, Inc. at Wilmington, DE, USA.

REFERENCES

1 Smith, P., Chanzy, H. D. and Rotzinger, B. *Polym. Commun.* 1985, **26**, 258

2 Smith, P., Chanzy, H. D. and Rotzinger, B. *J. Mater. Sci.* 1987, **22**, 523

3 Smith, P., Lemstra, P. J., Kalb, B. and Pennings, A. J. *Polym. Bull.* 1979, **1**, 733

4 Smith, P. and Lemstra, P. J. *et al.* US Patents 4344908 (1982), 4411854 (1983), 4422993 (1983), 4430383 (1984), 4436689 (1984)

5 Chanzy, H. D., Rotzinger, B. and Smith, P. US Patent 4769433 (1988; filed 1985)

6 Prout, E. O. 'Modern Plastics Encyclopedia.' McGraw-Hill, New York, 1988, p. 54

7 Haldin, G. W. and Kamel, I. L. *Polym. Eng. Sci.* 1977, **17**, 21

8 Truss, R. W., Han, K. S., Wallace, J. F. and Geil, P. H. *Polym. Eng. Sci.* 1980, **20**, 747

9 Zachariades, A. E. and Kanamoto, T. *Polym. Eng. Sci.* 1986, **26**, 658

10 Kanamoto, T., Sherman, E. S. and Porter, R. S. *Polym. J.* 1979, **11**, 497

11 Zachariades, A. E., Watts, M. P. C. and Porter, R. S. *Polym. Eng. Sci.* 1980, **20**, 555

12 Kanamoto, T., Tsuruta, A., Tanaka, K. and Takeda, M. *Polym. J.* 1984, **16**, 87

13 Kanamoto, T., Ohama, T., Tanaka, K., Takeda, M. and Porter, R. S. *Polymer* 1987, **28**, 1517

14 Smith, P., Lemstra, P. J. and Booij, H. C. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 877

15 Ciferri, A. and Ward, I. M., Eds. 'Ultra-High Modulus Polymers', Applied Science, London, 1979

16 Smith, P. and Lemstra, P. J. *Colloid and Polym. Sci.* 1980, **258**, 891

17 Starkweather, H. W. Jr. *J. Polym. Sci. Polym. Phys. Edn.* 1979, **17**, 73

18 Leenslag, J. W. and Pennings, A. J. *Polym. Commun.* 1987, **28**, 92

19 Chanzy, H. D., Day, A. and Marchessault, R. H. *Polymer* 1967, **8**, 567

20 Francis, P. S., Cooke, R. Jr. and Elliott, J. H. *J. Polym. Sci.* 1957, **31**, 453

21 Capaccio, G., Gibson, A. G. and Ward, I. M. in 'Ultra-high Modulus Polymers' (Eds. A. Ciferri and I. M. Ward), Applied Science, London, 1979, p. 1