Crosslinking of polyethylene fibres using trans-1,4-polybutadiene as a macromolecular prorad

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A new route for the production of high modulus and strength, crosslinked ultra-high molecular weight polyethylene (UHMW-PE) structures was explored. trans-1,4-Polybutadiene (t-1,4-PB) is added to UHMW-PE, prior to dissolution and ultra-drawing, to enhance the crosslinking efficiency of drawn tapes upon electron-beam irradiation. It was found that undrawn solution-cast films exhibit a two-phase structure consisting of a continuous UHMW-PE phase and dispersed t-1,4-PB domains. Upon drawing, the t-1,4-PB phase is deformed to elongated domains with a width of a few nanometres, and both the UHMW-PE and t-1,4-PB phase are highly oriented. The addition of t-1,4-PB indeed enhances the crosslinking efficiency of drawn, oriented UHMW-PE tapes. Tapes with a high gel fraction (>95%) and improved high-temperature resistance could be produced.

(Keywords: polyethylene; trans-1,4-polybutadiene; blends)

INTRODUCTION

With the so-called 'gel-spinning process', ultra-high molecular weight polyethylene (UHMW-PE, $M_w > 10^3$ kg mol^{-1}) fibres can be produced, possessing impressive mechanical properties such as high modulus (> 100 GPa), high strength (> 3 GPa) and high strain at break (3–5%)[1–3]. This combination of properties makes these fibres very suitable for a variety of applications such as ropes, sails, bullet-proof vests and helmets[4,5]. However, applications of these fibres in structural composites are limited due to some less favourable properties, such as a low melting temperature, creep under static loading conditions[6] and poor off-axis properties (low shear modulus and strength)[7,8].

Both the positive and less favourable properties of UHMW-PE fibres originate from their highly anisotropic nature. The fibres consist of oriented and more or less chain-extended PE chains. The PE covalent bonds are predominantly aligned in the fibre direction and provide the high stiffness and strength of the fibres. The poor off-axis and creep properties originate from the relatively weak intermolecular interactions (van der Waals forces) in these oriented fibres.

The poor off-axis properties of UHMW-PE fibres can potentially be improved by enhancing intermolecular interaction. Previously, electron-beam (EB) irradiation was studied with the aim of introducing chemical crosslinks in UHMW-PE fibres[9,10]. EB irradiation was performed both prior to and after solid-state drawing. It was found that crosslinking prior to drawing reduces the maximum attainable draw ratio and consequently the

attainable Young's modulus and tensile strength[11], whereas EB irradiation after solid-state drawing mainly causes chain scission, thereby reducing the tensile strength and creep resistance of the fibres[9,10].

An elegant method for crosslinking melt-crystallized, drawn PE fibres was developed by Ward and co-workers[12,13]. EB irradiation of melt-spun, drawn fibres in the presence of acetylene gas resulted in crosslinked fibres with enhanced high-temperature properties and reduced creep. However, no significant improvement of the crosslinking efficiency was found upon irradiation of solution-spun, ultra-drawn UHMW-PE fibres in the presence of acetylene gas[12,13]. It is likely that diffusion of acetylene into oriented UHMW-PE fibres is restricted, due to the high crystallinity of the fibres, and consequently the rather poor balance between chain scission and crosslinking upon radiation is hardly improved.

In this study, a new route for the crosslinking of UHMW-PE fibres was explored. As for the acetylene route, described above, an attempt was made to increase the crosslinking efficiency by introducing 'unsaturation' in oriented UHMW-PE fibres. To circumvent the restricted diffusion of gases into oriented UHMW-PE fibres, a macromolecular crosslinking agent (prorad) was blended with UHMW-PE prior to solution spinning and ultra-drawing. In this preliminary study, the use of trans-1,4-polybutadiene (t-1,4-PB) as a macromolecular prorad was investigated. t-1,4-PB is a linear, semicrystalline polymer containing one C=C bond per four carbon atoms and possessing a high tendency to crosslink[14]. t-1,4-PB has a conformationally disordered crystalline phase between 70 and 140°C, in which molecular segments are relatively mobile[15]. This mobility is

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expected to further enhance the crosslinking efficiency of this polymer[16].

EXPERIMENTAL

The UHMW-PE grade used was Hostalen Gur-412 (Hoechst Ruhrchemie, $M_w = 1500 \, \text{kg mol}^{-1}$). t-1,4-PB was polymerized at room temperature using a $\text{VCl}_3/\text{Al}(\text{C}_2\text{H}_5)_3$ catalyst system[17] ($M_v = 75 \, \text{kg mol}^{-1}$, vinyl content 0.9–1.2%).

UHMW-PE and t-1,4-PB were mixed in several ratios and 0.5% (w/w) di-t-butyl-p-cresol (DBPC) was added. The materials were suspended in xylene at a UHMW-PE concentration of 1.5% (w/v). The suspension was degassed and the mixtures were subsequently heated in an oil bath to 120°C. The suspension was stirred until the 'Weissenberg effect' occurred. After complete dissolution, the solution was poured into an aluminium tray. Dry films were obtained after solvent evaporation at ambient conditions. The films were then extracted with n-hexane to remove the stabilizer.

D.s.c. thermograms of films were recorded using a Perkin–Elmer DSC-7 differential scanning calorimeter. A standard heating rate of $10°\text{C min}^{-1}$ was adopted. Indium was used for temperature and heat-of-fusion calibration.

Transmission electron microscopy (TEM) was performed using a Jeol JEM 2000 FX microscope, operated at 80 kV. Samples were treated with a 2% OsO_4 solution at room temperature for 24 h, then embedded in an epoxy matrix. The specimens were then trimmed and treated for 16 h with RuO_4 solution. Finally, thin sections were obtained by ultramicrotomy at room temperature using a Reichert Ultracut E microtome.

Wide-angle X-ray scattering (WAXS) patterns were obtained using a Statton camera. Ni-filtered Cu $\text{K}\alpha$ radiation was generated at 50 kV and 30 mA.

EB irradiation was performed with a 3 MeV Van de Graaff accelerator at the Interuniversitair Reactor Instituut (Delft, The Netherlands). The tapes were mounted on aluminium plates and irradiated at 30°C with doses ranging between 20 and 150 kGy. Irradiation was performed in a nitrogen atmosphere.

Gel fractions were determined via Soxhlet extraction of the tapes in xylene for at least 72 h. The swelling ratios were determined from samples that had been swollen for 5 h in xylene at 120°C.

RESULTS AND DISCUSSION

Figure 1 shows TEM micrographs of solution-crystallized, dried films prepared by casting mixtures of UHMW-PE and t-1,4-PB from solution. The t-1,4-PB and UHMW-PE lamellae can be distinguished in the undrawn films, and both types of lamellae exhibit a preferred orientation parallel to the film surface. D.s.c. thermograms of solution-cast films are shown in *Figure 2*. The melting peaks of UHMW-PE and t-1,4-PB are both at about 130°C and partly coincide in the thermograms. However, a shoulder on the left-hand side of the peak due to the melting of t-1,4-PB can still be discerned. The thermograms also exhibit some endothermic peaks around 60–70°C, which are related to the solid–solid phase transition of t-1,4-PB from a monoclinic crystal structure to a hexagonal condis phase. The occurrence of more than one peak at this transition has been observed
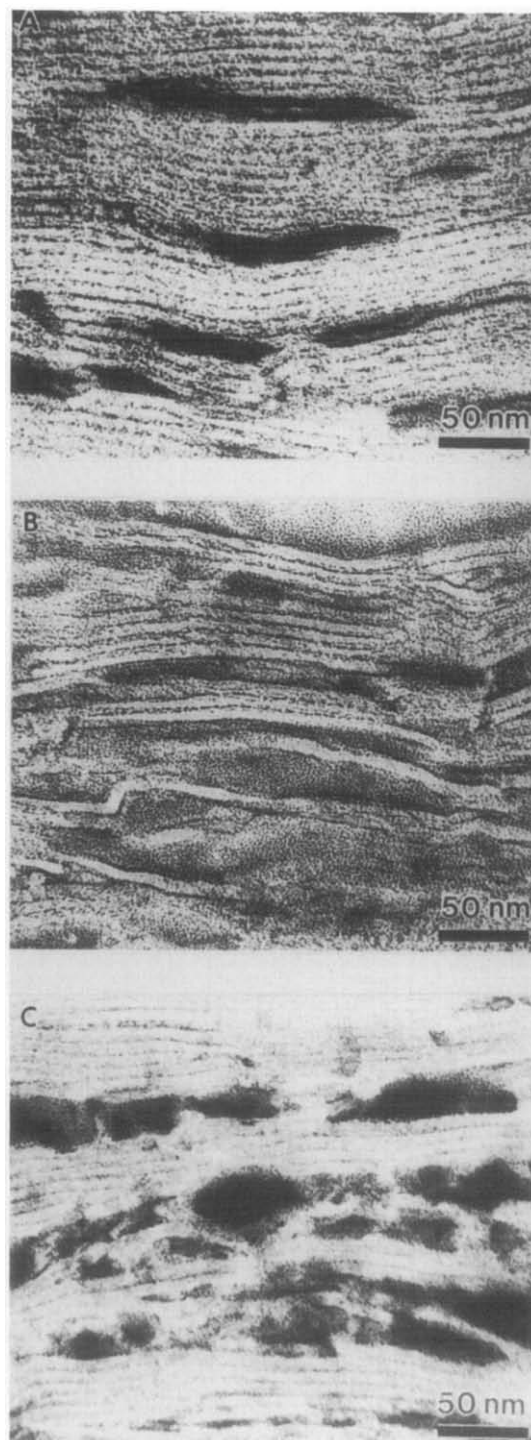

Figure 1 Transmission electron micrographs of solution-crystallized UHMW-PE/t-1,4-PB films. t-1,4-PB content (wt%): (A) 10; (B) 20; (C) 50

before and was attributed to the presence of monoclinic crystals with different thermal stabilities[18]. In *Figure 3a*, a WAXS pattern of a solution-cast film is shown. Reflections due to both PE (the intense inner and outer reflection) and t-1,4-PB crystals are observed in the blends. The TEM, d.s.c. and WAXS experiments indicate that a two-phase morphology is present in the undrawn, solution-cast films. Apparently, phase separation occurs upon casting/quenching of the (homogeneous) solutions. This phase separation is induced by the separate crystallization of UHMW-PE and t-1,4-PB[19] upon cooling the solution in xylene. After casting, UHMW-PE
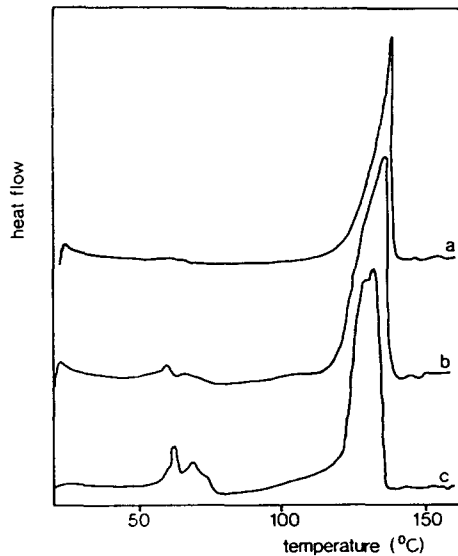
Figure 2 D.s.c. thermograms of solution-cast UHMW-PE/*t*-1,4-PB films containing (a) 10, (b) 25 and (c) 50 wt% *t*-1,4-PB
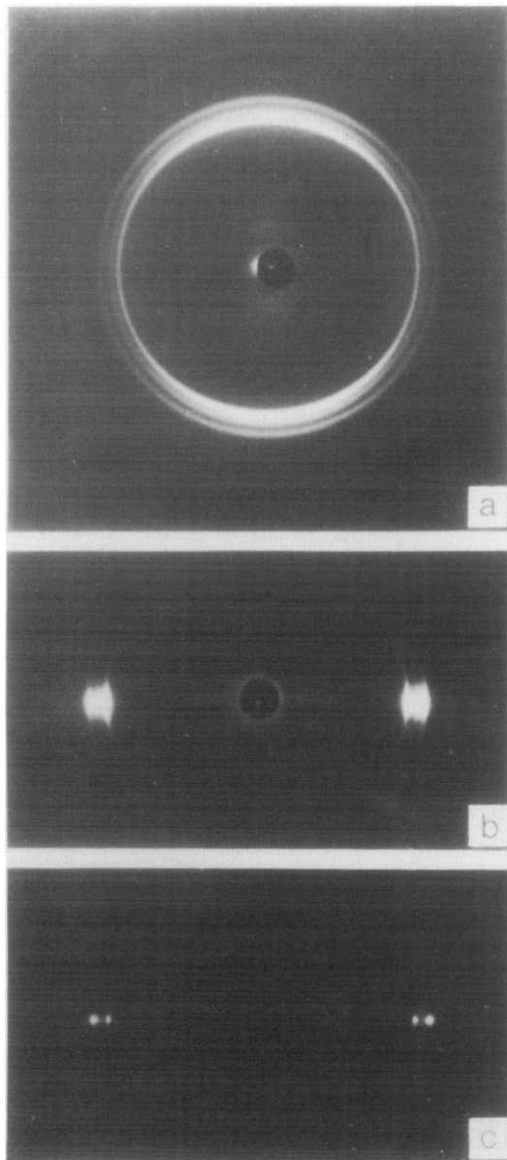

Figure 3 WAXS patterns of an UHMW-PE/*t*-1,4-PB blend containing 33 wt% *t*-1,4-PB at several draw ratios: (a) $\lambda = 1$, (b) $\lambda = 11$ and (c) $\lambda = 40$. X-ray beam is parallel to film surface; drawing direction is vertical

forms a continuous phase which provides coherence to the films. Within this continuous UHMW-PE phase, *t*,1-4-PB domains are dispersed, their dimensions depending on the *t*-1,4-PB fraction and quenching conditions.

In *Figure 4*, d.s.c. thermograms of drawn, solution-cast tapes containing 20 wt% *t*-1,4-PB are shown. The *t*-1,4-PB shoulder of the melting peak decreases with increasing draw ratio and finally disappears or coincides completely with the UHMW-PE peak. Also, the solid–solid phase transition of *t*-1,4-PB disappears. The WAXS patterns of solution-cast films with different draw ratios (*Figure 3*) show that both the UHMW-PE and the *t*-1,4-PB chains are oriented in the drawing direction. Moreover, the reflections due to *t*-1,4-PB can no longer be distinguished at high draw ratios. *Figure 5* shows TEM micrographs of drawn tapes. The micrographs indicate that *t*-1,4-PB is finely dispersed in elongated domains with a thickness in the order of a few nanometres. Apparently, the large-scale two-phase morphology of the undrawn, solution-cast films is largely destroyed during solid-state drawing. Based on these experimental data, one might be tempted to conclude that an almost molecular dispersion of oriented *t*-1,4-PB is obtained. However, [13]C n.m.r. studies indicated that the phenomena observed in the d.s.c. and WAXS experiments are related to a gradual transition of the monoclinic *t*-1,4-PB crystal structure to the hexagonal crystal structure upon solid-state drawing[20].

In *Figure 6*, experimental results for the EB irradiation of drawn blends are presented. It is shown that the gel fraction increases with increasing irradiation dose and *t*-1,4-PB content (*Figure 6a*). A maximum gel fraction of approximately 95% is observed. In *Figure 6b*, swelling ratio measurements of drawn tapes are shown. As expected, the swelling ratio decreases with increasing irradiation dose. The influence of the *t*-1,4-PB content on the swelling ratio is less clear, i.e. a systematic trend
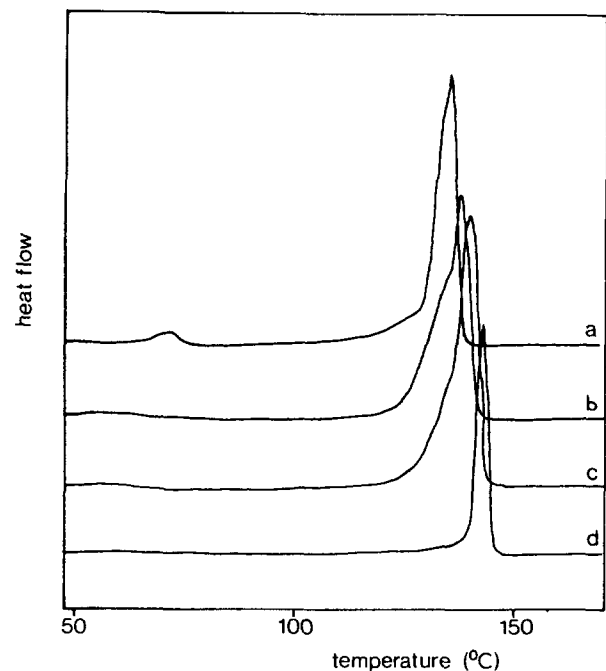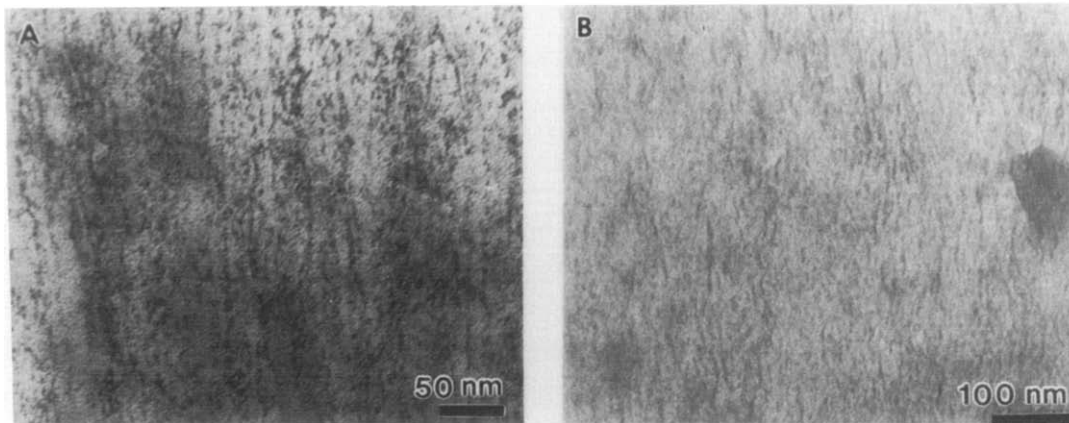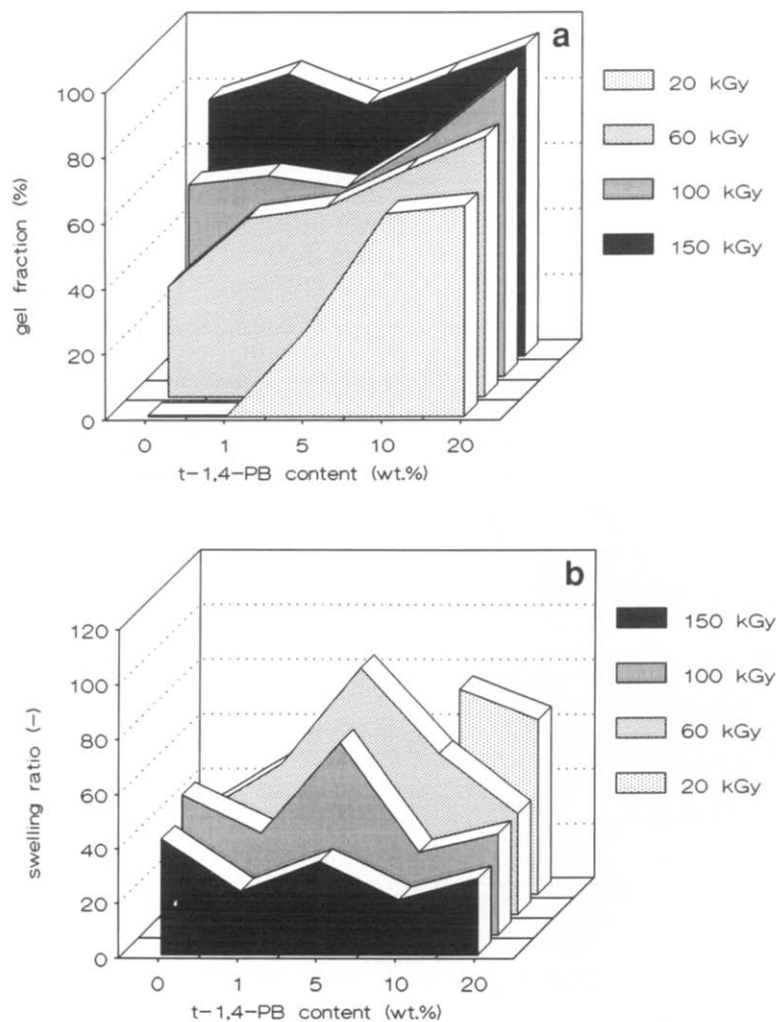

Figure 4 D.s.c. thermograms of an UHMW-PE/*t*-1,4-PB blend containing 20 wt% *t*-1,4-PB: (a) $\lambda = 1$, (b) $\lambda = 10$, (c) $\lambda = 30$ and (d) $\lambda = 65$

Figure 5 Transmission electron micrographs of drawn UHMW-PE/*t*-1,4-PB blends containing 50 wt% *t*-1,4-PB: (A) $\lambda=10$ and (B) $\lambda=25$. Drawing direction is vertical


Figure 6 (a) Gel content and (b) swelling ratio of UHMW-PE/*t*-1,4-PB tapes ($\lambda=40$) as a function of *t*-1,4-PB content and irradiation dose

is not observed. Apparently, a higher *t*-1,4-PB content in the tapes causes more material to be incorporated in the network (a higher gel fraction) without resulting in a systematic increase in crosslink density (lower swelling ratio).

Upon constrained heating at 200°C, EB-irradiated UHMW-PE tapes fracture and melt. EB-irradiated tapes containing 1 wt% or more *t*-1,4-PB remain intact upon constrained heating. After constrained heating, the modulus of the tapes is approximately 30% of the original value, regardless of the amount of *t*-1,4-PB present in the blends, and a shish-kebab morphology is observed (*Figure 7*). These results indicate that a rather inhomogeneous network is formed, containing a
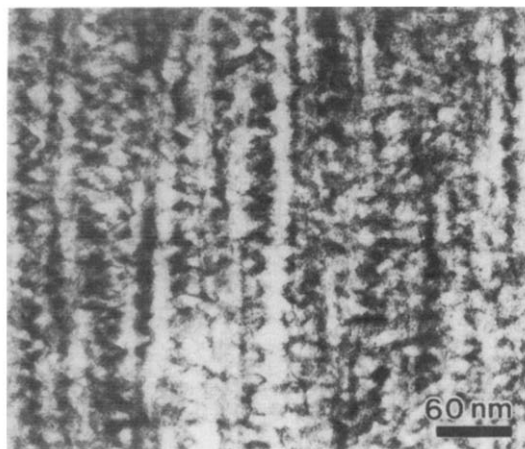
Figure 7 Transmission electron micrograph of an irradiated UHMW-PE/*t*-1,4-PB tape after constrained heating at 200°C

considerable portion of, for instance, loose loops and dangling ends. Upon constrained heating, relaxation of these chain segments occurs, resulting in a loss in orientation and Young's modulus.

It was shown that a continuous chemical network can be introduced in drawn UHMW-PE fibres if *t*-1,4-PB is added as a macromolecular prorad. The enhanced crosslink efficiency results in high gel fractions and an improved temperature stability. However, the maximum attainable Young's modulus and tensile strength decrease with increasing *t*-1,4-PB content[19] and the plateau creep rate of the crosslinked, drawn tapes is hardly reduced[19]. Apparently, the obtained network structure is not homogeneous. The drawn blends consist of elongated *t*-1,4-PB domains finely dispersed in a matrix consisting of PE fibrils. These PE fibrils contain disordered domains (defect zones) in which some *t*-1,4-PB chains are probably trapped and mixed on a molecular scale. The crosslinks situated in these disordered domains provide the continuity of the network but are not sufficient to improve the creep resistance[19].

After drawing, the *t*-1,4-PB phase is dispersed on a nanometre scale and is highly oriented. Apparently, solid-state drawing of UHMW-PE is extremely effective in orientating and dispersing guest molecules, such as *t*-1,4-PB. The combination of an excellent dispersion and

orientation can potentially be used to generate a variety of other desirable properties within drawn UHMW-PE films. For instance, it was shown recently that polarizers with excellent optical characteristics can be produced by incorporating and orienting dichroic dyes in solution-cast, drawn UHMW-PE films[21,22].

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