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SOLICITUD
PATENTE DE INVENCION
PCT

EXPEDIENTE N°

10-2342

TITULO: PELÍCULA DE POLIETILENO CON ALTA RESISTENCIA A LA TENSION Y CON ALTA ENERGÍA DE TENSION PARA ROMPERSE

CLASIFICACION INTERNACIONAL: _____

SOLICITANTE: TEIJIN ARAMID B.V.

DOMICILIO: HOLANDA

APODERADO: JULY GALINDO QUINTERO

BOGOTÁ, D.C. _____

09-02-2010

PETITORIO



SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



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FORMULARIO UNICO DE SOLICITUD DE PATENTE PCT ENTRADA EN FASE NACIONAL

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SOLICITUD DE:

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Patente de Invención

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Patente de Modelo de Utilidad

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Capítulo I

☐

Capítulo II

②

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⑤

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Título(54): PELÍCULA DE POLIETILENO CON ALTA RESISTENCIA A LA TENSIÓN Y CON ALTA ENERGÍA DE TENSIÓN PARA ROMPERSE

⑦

Clasificación Internacional (51):

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Julio 09, 2007

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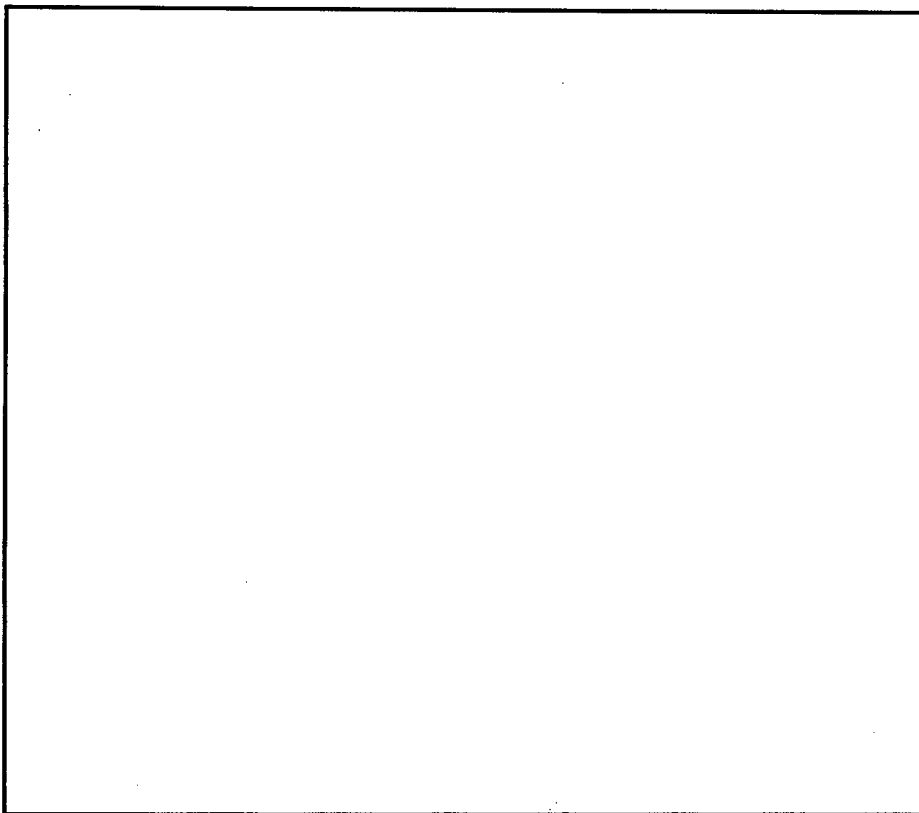
Enero 12, 2010

10

ANEXOS

- ☒ Comprobante de pago de la tasa de presentación de la solicitud.
- ☐ Documento que acredita la existencia y representación legal cuando el solicitante sea persona jurídica.
- ☐ Poderes, si fuere el caso.
- ☐ Documento de cesión del inventor al solicitante o a su causante.
- ☐ Declaraciones
- ☒ Copia de la solicitud internacional. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicaciones, dibujos)
- ☐ Copia del examen preliminar internacional efectuado por la Autoridad Internacional de Examen Preliminar (IPEA).
- ☐ Traducción del examen preliminar internacional efectuado por la IPEA.
- ☐ De ser el caso, copia del contrato de acceso.
- ☐ De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas.
- ☐ De ser el caso, certificado de depósito del material biológico.
- ☐ Arte final 12x12.
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud.
- ☐ De ser el caso, modificaciones efectuadas a la solicitud internacional.
- ☐ Otros.

11 FIGURA CARACTERISTICA



12

Solicito la Concesión de la patente,

NOMBRE: JULY GALINDO QUINTERO

FIRMA:

C.C. 52.996.296 BTA TP 158.806
C.S.J.

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



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FECHA : ENERO 12 DE 2010

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	Nº. PAGO	FECHA PGO	Vr. PAGO
CARDENAS Y CARDENAS P.I. CONSIGNACION		BANCO DE BOGOTA	062754387	44531023	12/01/2010	3.456.000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01 SOLICITUDES	1 TRAMITES DE SOL. DE PATENTE DE IN	554.000.00
TOTAL :			554.000.00

SON: QUINIENTOS CINCUENTA Y CUATRO MIL PESOS

RESPONSABLE :

CARDENAS & CARDENAS

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

ABOGADOS

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 10-002342- -00000-0000

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***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CARDENAS Y CARDENAS P.I.	CONSIGNACION	BANCO DE BOGOTA	062754387	44531023	12/01/2010	3.456,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
2	50005-01-01	SOLICITUDES	*** REIVINDICACION UNITARIA ADICIONAL
			TOTAL : \$ 52,000.00

SON: CINCUENTA Y DOS MIL PESOS

RESPONSABLE :

RECIBO DE CAJA APLICADO AL EXPEDIENTE No.

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Industria y Comercio

INDUSTRIA Y COMERCIO
SUPERINTENDENCIA

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

DIVISION DE NUEVAS CREACIONES

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Clasificación Internacional :

(71) Solicitante(s) **TEIJIN ARAMID B.V.**

(72) Inventor(es) **DE WEIJER, Anton, Peter; VAN DE HEE, Hendrik; PETERS, Martinus, Wilhelms, Maria, Gemma; RASTOGI, Sanjay; WANG, Bing**

(74) Apoderado: **JULY GALINDO QUINERO**

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(54) Título: **PELÍCULA DE POLIETILENO CON ALTA RESISTENCIA A LA TENSION Y CON ALTA ENERGÍA DE TENSION PARA ROMPERSE**

(22) Fecha de solicitud:	
(51) Clasificación Internacional:	
(71) Solicitante(s) TEIJIN ARAMID B.V.	
(72) Inventor(es) DE WEIJER, Anton, Peter; VAN DE HEE, Hendrik; PETERS, Martinus, Wilhelmis, Maria, Gemma; RASTOGI, Sanjay; WANG, Bing	
(74) Apoderado: JULY GALINDO QUINTERO	
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(54) Título: **PELÍCULA DE POLIETILENO CON ALTA RESISTENCIA A LA TENSIÓN Y CON ALTA ENERGÍA DE TENSIÓN PARA ROMPERSE**

(57) Resumen:

La presente invención se refiere a una película de UHMWPE que tiene una resistencia a la tensión de al menos 2.0 GPa, una energía de tensión para romperse de al menos 30 J/g, un PM de al menos 500000 gramos/mol, y una proporción PM/Mn de al menos 6.

La película puede ser manufacturada a través de un proceso que comprende someter un UHMWPE inicial con un peso promedio del peso molecular de al menos 500000 gramos/mol, un módulo elástico de corte determinado directamente después de la fusión a 160°C de a lo más 0.9 MPa, y una proporción PM/Mn de a lo más 6 a una etapa de compactación y una etapa de estiramiento bajo condiciones tales que en ningún punto durante el procesamiento del polímero su temperatura es elevada a un valor por encima de su punto de fusión.

La película puede ser usada como materia prima en cualquier aplicación en donde la alta resistencia a la tensión y la alta energía de tensión para romperse sean importantes. Aplicaciones apropiadas incluyen aplicaciones balísticas, cuerdas, cables, redes, telas, y aplicaciones protectoras.

RESUMEN

La presente invención se refiere a una película de UHMWPE que tiene una resistencia a la tensión de al menos 2.0 GPa, una energía de tensión para romperse de al menos 30 J/g, un PM de al menos 500000 gramos/mol, y una proporción PM/Mn de al menos 6.

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La película puede ser usada como materia prima en cualquier aplicación en donde la alta resistencia a la tensión y la alta energía de tensión para romperse sean importantes. Aplicaciones apropiadas incluyen

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**PELÍCULA DE POLIETILENO CON ALTA RESISTENCIA A LA TENSIÓN Y
CON ALTA ENERGÍA DE TENSIÓN PARA ROMPERSE**

La presente invención se refiere a una película de polietileno con alta resistencia a la tensión y con alta energía de tensión para romperse, y a un método para la manufactura de tal película a partir de un polietileno específico de ultra alto peso molecular. En este documento el polietileno de ultra alto peso molecular será además indicado como UHMWPE.

Los métodos para la manufactura de películas de UHMWPE con alta resistencia y alto módulo son conocidos en el estado del arte.

El documento US 5,756,660 describe la polimerización de UHMWPE sobre un catalizador específico, seguido por moldeo por compresión, enrollado y estiramiento para formar una película de polímero. En el ejemplo 1, un material es obtenido con un módulo de 160 GPa y una resistencia de 2.8 GPa.

El documento US 5,106,555 describe un método para la compresión por moldeo/estiramiento de UHMWPE.

El documento US 5,503,791 describe una película de polietileno manufacturado por medio de extrusión de una solución de la poliolefina en un primer solvente, seguida por enfriamiento, la remoción del solvente y estirado de la película. Una desventaja de la película así obtenida es que esta siempre contiene una cierta cantidad de solvente residual, el cual puede afectar perjudicialmente las propiedades de la película. En general la cantidad de solvente presente en la solución de películas de gel moldeado es de al menos 100 ppm. Además, la recuperación del solvente es altamente poco rentable.

El documento EP 292074 describe una película de UHMWPE que tiene un peso molecular de 4000000 g/mol, una proporción PM/Mn de 4, una resistencia a la tensión de 2.3 GPa, y un módulo de tensión de 92 GPa. Asumiendo una densidad de 0.97 g/ml, puede ser calculada una energía de tensión a la ruptura de 29.6 J/g.

El documento EP 269151 describe un material que tiene una resistencia a la tensión por encima de 2.0 GPa, un módulo por encima de 70 GPa. y un deslizamiento por debajo de $3 \cdot 10^{-7}$ seg⁻¹. Esta referencia no contiene información de la proporción de PM/Mn del producto final.

El documento US 5,106,558 describe un método para la preparación continua de un polietileno que tiene una alta resistencia y un alto módulo que comprende las etapas de mezclar 100 partes en peso de un polvo de polietileno de ultra alto peso molecular que tiene una viscosidad intrínseca de 5-50 dl/g en decalina a 135°C con 2-50 partes de un compuesto orgánico líquido que tiene un punto de ebullición más alto que el punto de fusión del polietileno, alimentar la mezcla resultante entre un par de rodillos, y someter la mezcla a moldeo por compresión y estirado. Esta referencia no contiene información de la proporción PM/Mn del producto final.

El documento US 6,017,480 describe un proceso para la producción de materiales de poliolefina que comprende las etapas de preparar un artículo moldeado de poliolefina UHPM, estirar el artículo en más de 30 dobleces, contactar el artículo, y restirar el artículo. Esta referencia no contiene información de la proporción PM/Mn del producto final.

Se ha encontrado que todavía hay sitio para la mejora en el campo de las películas de UHMWPE de alta resistencia a la tensión. Más particularmente, hay numerosas aplicaciones, que incluyen aplicaciones balísticas, cuerdas, cables, y

redes, telas, y aplicaciones protectoras donde las películas del PE con alta energía de tensión para romperse, una alta resistencia a la tensión, y otras características deseables que encontrarán aplicación. La presente invención proporciona tal película de UHMWPE.

La película de UHMWPE de acuerdo con la presente invención tiene una Resistencia a la tensión de al menos 2.0 GPa, una energía de tensión para romperse de al menos a 30 J/g, un PM de al menos 500000 g/mol, y una proporción PM/Mn de al menos 6.

Se ha encontrado que la selección de un material con una proporción PM/Mn de al menos 6 en combinación con un PM de al menos 500000 es de importancia para permitir que la película final tenga la alta resistencia a la tensión y la alta energía para romperse en combinación con propiedades deseables adicionales, como será discutido más adelante. Los materiales descritos en los documentos US 5,756,660, US 5,106,555, y US 5,503,791 no cumplen todos los criterios anteriores.

Como se indico antes, la película de UHMWPE de acuerdo con la invención tiene una resistencia a la tensión de al menos 2.0 GPa, determinada de acuerdo con la ASTM D882-00.

Dependiendo de la proporción de estirado y la temperatura de estirado, se pueden obtener resistencias a la tensión de al menos 2.5 GPa, particularmente de al menos 3.0 GPa, mas particularmente de al menos 3.5 GPa. Resistencias a la tensión de al menos 4 GPa también pueden ser obtenidas. La energía de tensión para romperse de la película de UHMWPE de acuerdo con la invención es de al menos 30 J/g. La energía de tensión para romperse es determinada de acuerdo con la ASTM D882-00 usando una proporción de tensión de 50%/min. Es calculada integrando la energía por unidad de masa bajo la curva de tensión-deformación.

La energía de tensión para romperse puede ser aproximada por los siguientes métodos. Estos darán una aproximación completa de la energía de tensión para romperse cuando está será determinada de acuerdo con la ASTM D882-00 como se discutió antes.

Una aproximación de la energía de tensión para romperse puede ser obtenida integrando la energía total absorbida y dividiéndola por la masa de la región del espécimen calibrador original. En particular, puesto que la curva de tensión-deformación de las muestras de UHMWPE con una tenacidad sobre 2.0 GPa es aproximadamente una línea recta, la energía de tensión para romperse puede ser calculada por medio de la siguiente fórmula:

$$TEB = \frac{\sigma}{\rho} * \frac{EAB}{2} * 10$$

en la cual sigma es la resistencia a la tensión en GPa de acuerdo con la ASTM D882-00, rho es la densidad en g/cm³, EAB es la elongación para la ruptura, expresada como un porcentaje de acuerdo con la ASTM D882-00, y TEB es la energía de tensión para romperse en J/g.

Otra aproximación de la energía de tensión para romperse TEB puede ser derivada a partir del módulo tensil y la Resistencia a la tensión de acuerdo con la siguiente formula;

$$TEB = \frac{\sigma^2}{2 * \text{Modulo} * \rho} * 10^3$$

Dependiendo de la proporción de estiramiento, las películas que pueden ser obtenidas de acuerdo con la invención que tienen una energía de tensión para romperse de al menos 35 J/g, particularmente de al menos 40 J/g, mas particularmente de al menos 50 J/g.

El peso promedio del peso molecular (PM) del polímero en la película de UHMWPE de la presente invención es de al menos 500000 gramos/mol, particularmente entre $1 \cdot 10^6$

gramos/mol y 1.10^8 gramos/mol. La distribución del peso molecular y los pesos moleculares promedio (PM, Mn, Mz) del polímero son determinados de acuerdo con la ASTM D 6474-99 a una temperatura de 160°C empleando 1,2,4-triclorobenceno (TCB) como solvente. Puede ser empleado un equipo cromatográfico apropiado (PL-GPC220 de Polymer Laboratories Ltd.) que incluye un dispositivo de preparación de la muestra a alta temperatura (PL-SP260). El sistema es calibrado empleando dieciséis estándares de poliestireno ($\text{PM}/\text{Mn} < 1.1$) en un intervalo de peso molecular de $5 \cdot 10^3$ a $8 \cdot 10^6$ gramos/mol.

La distribución de peso molecular del UHMWPE presente en la película de acuerdo con la invención es relativamente estrecha. Esto es expresado por la proporción del PM (peso promedio del peso molecular) sobre Mn (número promedio del peso molecular) de a lo más 6. Mas particularmente la proporción PM/Mn es a lo mas de 4, aun mas particularmente a lo mas de 3, incluso aun más particularmente de a lo más 2.

El módulo de la película de UHMWPE de acuerdo con la invención es generalmente al menos de 80 GPa. El módulo es determinado de acuerdo con la ASTM D822-00. Dependiendo de la proporción de estiramiento, el módulo puede ser obtenido de al menos 100, mas particularmente de al menos 120 GPa.

Es posible obtener un módulo de al menos 140 GPa, o de al menos 150 GPa.

En una realización de la presente invención, la película de acuerdo con la invención está caracterizada por un valor específico para el parámetro de orientación uniplanar Φ . El parámetro de orientación uniplanar Φ es definido como la proporción entre las áreas del pico 200 y 110 del patrón de difracción de rayos X (XRD) de la muestra de película como se determinan en la geometría de reflexión.

La dispersión de rayos X de amplio ángulo (WAXS) es una técnica que proporciona información sobre la estructura cristalina de la materia. La técnica específicamente se refiere al análisis de los picos de Bragg dispersados en ángulos amplios. Los picos Bragg resultan a partir del largo intervalo de orden estructural. Una medida de la WAXS produce un patrón de difracción, esto es, la intensidad como función del ángulo de difracción 2θ (este es el ángulo entre el rayo difractado y el rayo primario).

El parámetro de orientación uniplanar da información sobre el alcance de la orientación de los planos cristalinos 200 y 110 con respecto a la superficie de la

película. Para una muestra de película con una alta orientación uniplanar los planos cristalinos 200 están altamente orientados en paralelo a la superficie de la película. Se ha encontrado que la alta resistencia a la tensión y la alta energía de tensión para romper la película de acuerdo con la invención son acompañadas generalmente por una alta orientación uniplanar. La proporción entre las áreas de los picos 200 y 110 para un espécimen con cristales orientados aleatoriamente es de alrededor de 0.4. Sin embargo, los cristales con índices 200 están preferiblemente orientados paralelos a la superficie de la película de acuerdo con la invención, resultando en un valor más alto de la proporción del área de los picos 200/110 y por lo tanto en un valor más alto del parámetro de orientación uniplanar.

El valor para el parámetro de orientación uniplanar puede ser determinado empleando un difractómetro de rayos X. Un difractómetro Bruker-AXS D8 equipado con un sistema óptico de enfoque de rayos X multicapa (espejos Göbel) que produce la radiación Cu-K α (longitud de onda $\lambda = 1.5418 \text{ \AA}$) es conveniente. Condiciones de medición: ranura anti-dispersión de 2 mm, ranura del detector 0.2 mm y conjunto generador 40kV, 35mA. La muestra de la película se monta en un porta muestras, por ejemplo, con un poco de cinta de montaje de doble cara. Las dimensiones preferidas de la muestra de película son 15 mm x 15 mm (l x w). Se debe

tener cuidado de que la muestra se mantenga perfectamente plana y alineada con el porta muestras. El porta muestras con la muestra de película es colocado posteriormente en el difractómetro D8 en una geometría de reflexión (con la normal de la película perpendicular al goniómetro y perpendicular al porta muestras). El intervalo del barrido para el patrón de difracción es de 5° a 40° (2θ) con un tamaño de paso de 0.02° (2θ) y un tiempo de conteo de 2 segundos por paso. Durante la medida el porta muestras gira a 15 revoluciones por minuto alrededor de la normal de la película, de modo que no hay necesidad de alinear una muestra adicional. Posteriormente, la intensidad es medida en función del ángulo de difracción 2θ . El área del pico de las reflexiones 200 y 110 es determinada empleando un software estándar de ajuste al perfil, por ejemplo, Topas de Bruker-AXS. Cuando las reflexiones 200 y 110 son picos simples, el proceso de ajuste es preciso y esto está dentro del alcance de la persona experta para seleccionar y llevar a cabo un procedimiento de ajuste apropiado. El parámetro de orientación uniplanar es definido como la proporción entre las áreas de los picos 200 y 110. Este parámetro es una medida cuantitativa de la orientación uniplanar.

El parámetro de orientación uniplanar alto también está relacionado con la proporción PM/Mn, en que los polímeros con una proporción PM/Mn dentro del intervalo especificado en la presente invención pueden ser convertidos en

películas con un valor deseable para el parámetro de orientación uniplanar. Según lo indicado antes, en una realización, la película de acuerdo con la invención tiene un parámetro de orientación uniplanar de al menos 3. Puede ser preferido que este valor sea de al menos 4, mas particularmente de al menos 5, o de al menos 7. Altos valores, tales como valores de al menos 10 o incluso de al menos 15 también pueden ser obtenidos. El valor teórico máximo para este parámetro puede ser tan alto como infinito si el área del pico 110 es igual a cero. Altos valores para el parámetro de orientación uniplanar son a menudo acompañados por altos valores para la Resistencia y la energía para romperse.

La película de UHMWPE de acuerdo con la invención puede ser manufacturada por medio de un proceso que comprende: someter un UHMWPE inicial con un peso promedio del peso molecular de al menos 500000 gramos/mol, un módulo elástico de corte G_N^0 , determinado directamente después de la fusión a 160°C, de a lo más 0.9 MPa, y una proporción PM/Mn de a lo más 6, a una etapa de compactado y una etapa de estirado bajo condiciones tales que en ningún punto durante el procesamiento del polímero su temperatura es elevada a un valor por encima de su punto de fusión.

La materia prima del proceso de acuerdo con la invención es un UHMWPE altamente desenredado. Esto puede ser visto a partir de la combinación del peso promedio del peso molecular, la proporción PM/Mn, y el módulo elástico de corte. Para una aclaración adicional y las realizaciones preferidas en lo concerniente al peso molecular y la proporción PM/Mn del UHMWPE de inicio, se hace referencia a que ha sido afirmado antes para la película de acuerdo con la invención.

Según lo indicado antes, el UHMWPE inicial tiene un módulo elástico de corte G_N^0 determinado directamente después de la fusión a 160°C de a lo más 0.9 MPa, en particular a lo mas de 0.8 MPa, mas particularmente a lo más 0.7. El término "directamente después de la fusión" quiere decir que el módulo elástico de corte es determinado tan pronto como el polímero se ha fundido, en particular dentro de los 15 segundos después de que el polímero se ha fundido. Para este polímero fundido el G_N^0 típicamente se incrementa de 0.6 a 2.0 MPa en varias horas. El módulo elástico de corte directamente después de la fusión a 160°C es una de las propiedades características del UHMWPE muy desenredado empleado en la presente invención.

G_N^0 es el módulo elástico de corte en la región de la meseta plástica. Se relaciona con el peso molecular

promedio entre los enredos M_e , que a su vez es inversamente proporcional a la densidad de los enredos. En una fusión termodinámicamente estable que tiene una distribución homogénea de enredos, M_e puede ser calculada a partir de G_N^0 a través de la formula $G_N^0 = g_N \rho R T / M_e$, en donde g_N es un factor numérico fijo en 1, ρ es la densidad en g/cm^3 , R es la constante de los gases y T es la temperatura absoluta en K.

Así, un bajo módulo elástico de corte representa los largos estiramientos del polímero entre los enredos, y los bajos grados de enredamiento.

El UHMWPE empleado en el proceso de acuerdo con la invención preferiblemente tiene una cristalinidad DSC de al menos 74%, más particularmente de al menos 80%. La morfología de las películas puede ser caracterizada empleando calorimetría de barrido diferencial (DSC), por ejemplo en un DSC7 Perkin Elmer. Así, una muestra de peso conocido (2 mg) se calienta desde 30 hasta 180°C a 10°C por minuto, se mantiene a 180°C durante 5 minutos, luego se enfría a 10°C por minuto. Los resultados del barrido por DSC se pueden trazar como un gráfico del flujo de calor (mW o mJ/s; eje y) contra la temperatura (eje x).

La cristalinidad es medida empleando los datos de la porción calentada del barrido. La entalpia de fusión H (en

J/g) para la transición del fundido cristalino es calculada es calculada determinando el área bajo el grafico de la temperatura determinada justo en el comienzo de la transición principal de la fusión (endotérmica) hasta la temperatura justo sobre el punto donde se observa que la fusión se ha completado. La H calculada es luego comparada con la entalpia de fusión teórica (H_c de 293 J/g) determinada para PE 100% cristalino a una temperatura de fusión de aproximadamente 140°C. El índice de cristalinidad de la DSC es expresado como el porcentaje $100(H/H_c)$.

La película de acuerdo con la invención y los productos intermedios del proceso de manufactura de acuerdo con la invención preferiblemente también tienen cristalinidades según lo indicado anteriormente.

El UHMWPE usado en la presente invención puede tener una densidad másica que es significativamente menor que la densidad de los UWPMPEs convencionales. Mas particularmente, el UHMWPE usado en el proceso de acuerdo con la invención puede tener una densidad másica inferior a 0.25 g/cm³, en particular inferior a 0.18 g/cm³, aun mas particularmente inferior a 0.13 g/cm³. La densidad másica es determinada como sigue. Una muestra de UHMWPE en polvo se vierte en un vaso de precipitados de medida de

exactamente 100 ml. Después de retirar el exceso de material, el peso del contenido del vaso de precipitados es determinado y la densidad másica es calculada. El UHMWPE usado en el proceso de acuerdo con la invención puede ser un homopolímero de etileno o un copolímero de etileno con un comonomero que es otra alfa-olefina o una olefina cíclica ambas con generalmente entre 3 y 20 átomos de carbono. Los ejemplos incluyen propeno, 1-buteno, 1-penteno, 1-hexeno, 1-hepteno, 1-octeno, ciclohexeno, etc. El uso de dienos con hasta 20 átomos de carbono también es posible, por ejemplo, butadieno o 1,4-hexadieno. La cantidad de alfa-olefina (no etileno) en el homopolímero o copolímero de etileno usada en el proceso de acuerdo con la invención preferiblemente es a lo más 10 moles%, preferiblemente a lo más 5 moles%, mas preferiblemente a lo más 1 mol%. Sí una alfa-olefina (no etileno) es usada, esta generalmente presente en una cantidad de al menos 0.001 mol%, en particular al menos 0.01 mol%, aun mas particularmente al menos 0.1 mol%. Obviamente, los intervalos dados anteriormente para la materia prima también aplican para la película final de polímero.

El polímero inicial para uso en la presente invención puede ser manufacturado por medio de un proceso de polimerización en donde el etileno, opcionalmente en la presencia de otros monómeros como se discutió antes, es polimerizado en la presencia de un catalizador de

polimerización de un solo sitio a una temperatura inferior a la temperatura de cristalización del polímero, de modo que el polímero cristaliza inmediatamente con la formación. En particular, las condiciones de reacción son seleccionadas de tal forma que la velocidad de polimerización es más baja que la velocidad de cristalización. Estas condiciones de síntesis fuerzan las cadenas moleculares para cristalizar inmediatamente con su formación, llevando a una morfología única que difiere sustancialmente de la obtenida a partir de la solución o la fusión. La morfología cristalina creada en la superficie de un catalizador dependerá en gran medida de la proporción entre la tasa de cristalización y el índice de crecimiento del polímero. Por otra parte, la temperatura de la síntesis, que en este caso en particular es también la temperatura de cristalización, influenciará fuertemente la morfología del UHMWPE obtenido en polvo. En una realización la temperatura de reacción está entre -50 y $+50^{\circ}\text{C}$, mas particularmente entre -15 y $+30^{\circ}\text{C}$. Está bien dentro del alcance de la persona experta determinar a través de ensayo y error rutinario que temperatura de reacción es la apropiada y en combinación con qué tipo de catalizador, concentraciones de polímero y otros parámetros que influyen la reacción.

Para obtener un UHMWPE altamente desenredado es importante que los sitios de polimerización estén lo

suficientemente alejados uno del otro para prevenir que se enreden las cadenas del polímero durante la síntesis. Esto puede ser hecho empleando un catalizador de un solo sitio que es dispersado homogéneamente a través del medio de cristalización en bajas concentraciones. Más particularmente, concentraciones inferiores de 1.10^{-4} moles de catalizador por litro, en particular inferiores de 1.10^{-5} moles de catalizador por litro del medio de reacción pueden ser apropiadas. Un catalizador soportado de un solo sitio también puede ser usado, mientras se tenga el cuidado de que los sitios activos estén lo suficientemente alejados uno del otro para prevenir el enredo sustancial de los polímeros durante la formación.

Métodos apropiados para la manufactura del UHMWPE inicial usado en la presente invención son conocidos en la técnica. Se hace referencia, por ejemplo a los documentos WO01/21668 y US20060142521.

El polímero es proporcionado en forma de particulado, por ejemplo en la forma de un polvo, o en cualquier otra forma de particulado apropiada. Las partículas apropiadas tienen un tamaño de particular de hasta 5000 micrones, preferiblemente de hasta 2000 micrones, mas particularmente de hasta 1000 micrones. Las partículas preferiblemente

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tienen un tamaño de partícula de al menos 1 micrón, mas particularmente de al menos 10 micrones.

La distribución del tamaño de partícula puede ser determinada por medio de difracción laser (PSD, Sympatec Quixel) como sigue. La muestra es dispersada en agua que contiene tensoactivo y tratada con ultrasonido durante 30 segundos para remover aglomerados/enredos. La muestra es bombeada a través de un rayo laser y la luz dispersada es detectada. La cantidad de difracción de la luz es una medida del tamaño de partícula.

La etapa de compactación es llevada a cabo para integrar las partículas de polímero en un solo objeto, por ejemplo, en la forma de una hoja madre. La etapa de estiramiento es llevada a cabo para proporcionar orientación al polímero y manufacturar el producto final. Las dos etapas son llevadas a cabo en dirección perpendicular la una a la otra. Se observa que está dentro del alcance de la presente invención combinar estos elementos en una sola etapa, o llevar a cabo el proceso en diferentes etapas, cada etapa desarrollando uno o más de los elementos de compactación y estirado. Por ejemplo, en una realización del proceso de acuerdo con la invención, el proceso comprende las etapas de compactar el polímero en polvo para formar una hoja madre, enrollar la placa para formar una hoja madre enrollada y someter la hoja madre

enrollada a una etapa de estiramiento para formar una película de polímero.

La fuerza de compactado aplicada en el proceso de acuerdo con la invención generalmente es de 10-10000 N/cm², en particular de 50-5000 N/cm², mas particularmente de 100-2000 N/cm². La densidad del material después compactar esta generalmente entre 0.8 y 1 kg/dm³, en particular entre 0.9 y 1 kg/dm³.

En el proceso de acuerdo con la invención la etapa de compactado y de enrollado es generalmente llevada a cabo a una temperatura de al menos 1°C por debajo del punto de fusión del polímero sin restricción, en particular de al menos 3°C por debajo del punto de fusión del polímero sin restricción, aún mas particularmente de al menos 5°C por debajo del punto de fusión del polímero sin restricción. Generalmente, la etapa de compactación es llevada a cabo a una temperatura de a lo mas 40°C por debajo del punto de fusión del polímero sin restricción, en particular a lo mas de 30°C por debajo del punto de fusión del polímero sin restricción, mas particularmente a lo mas de 10°C.

En el proceso de acuerdo con la invención la etapa de estirado es generalmente llevada a cabo a una temperatura de al menos 1°C por debajo del punto de fusión del polímero

bajo las condiciones del proceso, en particular al menos 3°C por debajo del punto de fusión del polímero bajo las condiciones del proceso, aun mas particularmente al menos 5°C por debajo del punto de fusión del polímero bajo las condiciones del proceso. Como la persona experta es consciente, el punto de fusión de los polímeros puede depender de las restricciones bajo las cuales se ponen. Esto quiere decir, que la temperatura de fusión bajo las condiciones del proceso puede variar de un caso a otro caso. Se puede determinar fácilmente cuando la temperatura a la cual el esfuerzo de tensión cae agudamente. Generalmente, la etapa de estiramiento es llevada a cabo a una temperatura de a lo mas 30°C por debajo del punto de fusión del polímero bajo las condiciones del proceso, en particular a lo mas 20°C por debajo del punto de fusión del polímero bajo las condiciones del proceso, mas particularmente a lo mas 15°C.

La temperatura de fusión sin restricción del polímero inicial está entre 138 y 142°C y puede ser determinada fácilmente por una persona con conocimientos en la técnica. Con los valores indicados antes se permite el cálculo de la temperatura de operación apropiada. El punto de fusión sin restricción puede ser determinado a través de DSC (calorimetría de barrido diferencial) en nitrógeno, sobre un intervalo de temperaturas de +30 hasta +180°C y con una proporción de incremento de la temperatura de 10°C/minuto.

El máximo del pico endotérmico más grande a partir de 80 a 170°C es evaluado aquí como el punto de fusión.

En el procesamiento convencional de UHMWPE es necesario llevar a cabo el proceso a una temperatura muy cercana a la temperatura de fusión del polímero, por ejemplo, a 1 o 3 grados de esta. Se ha encontrado que la selección del UHMWPE inicial específico usado en el proceso de acuerdo con la invención hace posible operar a valores que están mas por debajo de la temperatura de fusión del polímero de lo que ha sido posible en la técnica anterior. Esto hace que una ventana más grande en la temperatura de operación permita un mejor control del proceso.

Aparatos convencionales pueden ser usados para llevar a cabo la etapa de compactación. Los aparatos apropiados incluyen rodillos de calentamiento, correas sin fin, etc.

La etapa de estiramiento en el proceso de acuerdo con la invención es llevada a cabo para la manufactura de la película de polímero. La etapa de estiramiento puede ser llevada a cabo en una o más etapas en una forma convencional en la técnica. Una forma apropiada incluye llevar la película en una o más etapas sobre un conjunto de rodillos, ambos enrollando en la dirección del proceso en

donde el segundo rodillo gira más rápido que el primer rodillo. El estiramiento puede ocurrir sobre una placa caliente o en un horno con circulación de aire. En general es difícil controlar la temperatura de este tipo de equipos dentro de 1 grado, lo que le permite a la persona experta apreciar lo amplio de la ventana de operación proporcionada por el proceso of la presente invención.

Es una de las características de la presente invención que la proporción total del estiramiento de la película puede ser de hecho muy alta. Por ejemplo, la proporción total de estiramiento puede ser al menos de 120, en particular de al menos 140, mas particularmente de al menos 160. La proporción total del estirado es definida como el área de la sección transversal de la hoja madre compactada dividida por la sección transversal de la película estirada producida a partir de esta hoja madre. El proceso de acuerdo con la invención es llevado a cabo en estado sólido. La película final de polímero tiene un contenido de solvente del polímero de menos de 0.05 % en peso, en particular de menos de 0.025 % en peso, mas particularmente de menos de 0.01 % en peso.

La película de acuerdo con la invención es un objeto tridimensional que está caracterizado porque dos de sus dimensiones son sustancialmente más grandes que la tercera.

Mas particularmente, la proporción entre la segunda dimensión más pequeña, el ancho de la película, y la dimensión más pequeña, el grosor de la película, es de al menos 10, en particular de al menos 50.

La película de polímero o los productos convertidos de la misma de acuerdo con la invención pueden ser usados como materia prima para numerosas aplicaciones, incluyendo aplicaciones balísticas, cuerdas, cables, redes, telas, y aplicaciones protectoras.

Las cualidades balísticas, cuerdas, cables, redes, telas, y aplicaciones protectoras derivadas de la forma de la película de UHMWPE de acuerdo con la invención también son parte de la presente invención.

La presente invención será ilustrada a través de los siguientes ejemplos. Se debe entender que la invención no está limitada de ninguna manera a ellos o por ellos.

Experimental

La compactación es ejecutada en un molde con dimensiones de 610x30mm.

Después de que el molde se llena con el polímero, el

polímero es compactado en una prensa caliente durante varios minutos. Después de enfriar bajando la temperatura a $<40^{\circ}\text{C}$ la hoja es removida del molde. Posteriormente, la hoja se alimenta en un par de rodillos superior e inferior calentados. La distancia entre los rodillos es de 150 micrones. Directamente después del enrollado, la película fue estirada sobre la superficie del rodillo superior. Además, el estirado de la película enrollada fue ejecutado en una placa caliente calentada con aceite localizada entre el juego de los dos rodillos que ruedan a velocidades exactamente definidas.

Example 1

Polimerización

Todas actividades sensibles al agua y/o al aire fueron realizadas bajo una atmosfera de argón empleando técnicas de Schlenk o en una cámara de guantes convencional llena de nitrógeno (Braun MB-150 GI). El Metilalumoxano fue comprador de WITCO GmbH como una solución al 10% en peso en tolueno. El etileno fue obtenido como un gas líquido. Se empleo tolueno seco como el solvente de la polimerización. El catalizador $[3\text{-tBu-2-O-C}_8\text{H}_3\text{CH=N(C}_6\text{F}_5)]_2\text{TiCl}_2$ fue sintetizado de acuerdo con Mitani y colaboradores (M. Mitani, T. Nakano, T. Fujita, Chem. Eur. J. 2003, 9, 2396-2403) y EP0874005. El peso molecular y la distribución de peso molecular fueron medidas a 135°C , por medio de cromatografía de permeación en

gel (GPC; GPC220, Polymer Labs) usando 1,2,4-triclorobenceno como solvente. La polimerización fue llevada a cabo bajo presión atmosférica usando un frasco de fondo Redondo de 2000 ml, equipado con un termopar y un agitador mecánico. Se introdujo Tolueno (1000 ml) al reactor purgado con argón después de lo cual el solvente fue saturado por burbujeo de etileno en la solución durante 30 minutos a $+10^{\circ}\text{C}$. La polimerización fue iniciada por la adición de una solución de metilalumoxano en tolueno (20 ml) después de lo cual una solución del catalizador ($1\ \mu\text{mol}$) en tolueno fue introducido en el reactor mientras se agitaba vigorosamente. Después de 30 minutos la alimentación del etileno fue detenida y fue adicionado alcohol isobutílico para terminar la polimerización. HCl y agua fueron adicionados a la mezcla resultante. El UHMWPE solido fue recuperado por filtración, lavado con agua y acetona y secado (en horno de vacío a 60°C , durante toda la noche). El rendimiento fue de 75 gramos. Su peso y número de peso molecular promedio fue 3600000 y 2300000, respectivamente. La proporción PM/Mn fue 1.56. La densidad másica fue de $0.11\ \text{g}/\text{cm}^3$. La temperatura de fusión del polímero sin restricción fue de 141°C . El módulo elástico de corte determinado directamente después de la fusión a 160°C fue de 0.65 MPa.

16 gramos de polietileno de ultra alto peso molecular desenredado (sintetizado como se menciona antes) fueron compactados con una presión promedio de 160 bar (16 MPa) a una temperatura máxima de 115°C mantenida durante 6 minutos.

La hoja resultante tiene un grosor de 0.9 mm, 610 mm de longitud y 30 mm de ancho. Su densidad fue de 0.95 g/cm³. La hoja fue precalentada a 125°C y directamente enrollada y estirada en una película de acuerdo con el procedimiento mencionado anteriormente. Basado en los cambios dimensionales, la proporción del enrollado fue calculada como 4.5, la proporción de elongación del proceso integrado de enrollado/estiramiento fue de 20. La temperatura de la superficie del juego de rodillos fue de 125°C. Un número de experimentos fue llevado a cabo en donde uno, dos o tres etapas de estiramiento fueron realizadas, a diferentes temperaturas y proporciones de estiramiento. La velocidad de estiramiento fue ajustada de tal forma que la temperatura y las proporciones de estiramiento pudieran ser obtenidas. El número de etapas de estiramiento, la temperatura de las etapas de estiramiento y la proporción total del estiramiento, que incluye la etapa de enrollado, son dadas en la tabla 1. Las propiedades mecánicas, Parámetros de Orientación Uniplanar y resultados de DSC de las películas así obtenidos son dados en la Tabla 1.

Como puede ser visto de la Tabla 1, el proceso de acuerdo con la invención permite la manufactura de películas con una alta resistencia en combinación con una alta energía de tensión para romperse. Estas películas también muestran un alto módulo tensil.

Hay una correlación positiva entre la cristalinidad por DSC y las características físicas de la película, en que las películas con una cristalinidad más alta a menudo tienen una resistencia y un TEB más alto. El parámetro de orientación uniplanar es una medida de la alineación de los polímeros en la película, y además está relacionado con la proporción total de estiramiento. En la presente invención, un parámetro de orientación uniplanar de aproximadamente 3 puede ser obtenido en una proporción de estirado del orden de 80. Como será ilustrado en el Ejemplo Comparativo abajo, donde un polímero convencional es usado como materia prima, un parámetro de orientación uniplanar del orden de 3 puede ser obtenido solamente en proporciones de estiramiento muy altas, y allí no será acompañado por la resistencia alta y valores TEB altos que son parte de la presente invención.

Tabla 1.

Muestra Estirada	Etapas de Estirado	Temp. En El segundo (tercer) estirado (°C)	Proporción Total de Estirado	Resistencia a la Tensión (GPa)	Modulo Tensil (GPa)	TEB (J/g)	Calor de Fusión (J/g)	Cristalinidad por DSC (%)	Parámetro de Orientación Uniplanar Φ (°)	Temperatura De Fusión No Restringida (°C)
E1	2	132	79	2.34	94	42.3	259	88.2%	3.7	153
E2	2	132	79	2.40	92	40.4	252	85.8%	3.0	151
E3	2	132	106	2.42	116	37.8	270	92.2%	4.5	154
E4	2	132	139	2.94	142	44.5	251	85.7%	5.7	154
E5	2	132	168	3.06	149	45.8	270	92.0%	10.2	153
E6	2	132	194	3.27	146	51.6	261	88.9%	12.6	151
E7	3	132 (132)	136	2.89	128	50.9	281	95.7%	3.7	154
E8	3	132 (132)	164	2.75	128	45.8	268	91.5%	4.2	153
E9	3	132 (132)	178	3.01	135	55.4	273	93.0%	5.9	153
E10	3	132 (132)	132	2.98	138	43.9	268	91.5%	6.1	152
E11	3	132 (132)	152	3.19	144	46.9	266	90.6%	5.8	155
E12	3	132 (132)	156	2.92	137	49.6	269	91.6%	5.9	154
E13	3	132 (132)	150	3.15	124	54.0	262	89.2%	8.6	153
E14	2	124	119	3.32	142	40.7	n.d.	n.d.	10.4	n.d.
E15	2	124	116	3.38	139	43.2	n.d.	n.d.	8.1	n.d.
E16	2	124	118	3.22	132	41.4	n.d.	n.d.	8.5	n.d.
E17	2	124	114	3.44	140	44.6	n.d.	n.d.	8.6	n.d.
E18	2	124	113	3.73	137	53.4	n.d.	n.d.	14.3	n.d.
E19	2	124	72	3.06	109	45.0	n.d.	n.d.	8.3	n.d.
E20	2	134	88	3.06	118	41.8	n.d.	n.d.	7.4	n.d.

E21	2	134	114	3.48	137	46.5	n.d.	n.d.	8.6	n.d.
E22	2	134	142	3.77	149	50.1	n.d.	n.d.	14.8	n.d.
E23	2	134	174	3.71	158	46.0	n.d.	n.d.	10.4	n.d.
E24	2	134	196	3.81	160	47.6	n.d.	n.d.	17.9	n.d.
E25	2	134	221	3.72	152	48.0	n.d.	n.d.	11.0	n.d.
E26	2	136	67	2.48	92	47.2	n.d.	n.d.	4.3	n.d.
E27	2	136	62	2.31	92	48.6	n.d.	n.d.	3.1	n.d.
E28	2	136	113	2.99	115	51.6	n.d.	n.d.	6.8	n.d.
E29	2	136	155	3.46	135	60.0	n.d.	n.d.	12.7	n.d.
E30	2	136	96	2.35	97	44.6	n.d.	n.d.	3.2	n.d.
E31	2	136	151	3.14	137	53.8	n.d.	n.d.	6.5	n.d.
E32	2	136	132	3.06	120	52.0	n.d.	n.d.	5.5	n.d.
E33	2	136	142	3.60	146	66.2	n.d.	n.d.	12.0	n.d.
E34	2	136	116	2.97	133	42.8	n.d.	n.d.	6.6	n.d.
E35	2	136	243	3.08	156	50.2	n.d.	n.d.	6.7	n.d.
E36	2	136	122	3.16	122	54.9	n.d.	n.d.	7.5	n.d.
E37	2	136	162	3.18	130	52.3	n.d.	n.d.	6.8	n.d.
E38	2	136	131	3.26	129	51.7	n.d.	n.d.	9.2	n.d.
E39	2	136	137	3.16	141	52.7	n.d.	n.d.	7.3	n.d.
E40	2	136	120	2.93	107	51.5	n.d.	n.d.	5.2	n.d.
E41	3	(138)	162	2.96	149	48.6	n.d.	n.d.	5.8	n.d.
E42	3	(138)	235	3.05	168	53.5	n.d.	n.d.	6.5	n.d.

n.d. = No determinado

Ejemplo Comparativo 1

20 gramos de un polvo de polietileno de ultra alto peso molecular Ziegler-Natta convencional (UHMWPE de serie de Ticona GUR) que tiene un PM de aproximadamente 2600000, un Mn de aproximadamente 360000, una proporción PM/Mn de 7.22, una densidad másica de 0.25 g/cm^3 , y un módulo elástico de corte determinado directamente después de la fusión a 160°C de 1.65 MPa fue usado como materia prima. El polímero inicial fue compactado con una presión promedio de 160 bar (16 MPa) a una temperatura máxima de 134°C que se mantiene durante 6 minutos. La hoja resultante tenía 1.15 mm de grosor, 610 mm de longitud y 30 mm de ancho. Su densidad fue de 0.95 g/cm^3 . La hoja fue precalentada a 135°C y directamente enrollada y estirada en forma de película de acuerdo con el procedimiento mencionado antes. De acuerdo con los cambios en las dimensiones la proporción de enrollado fue calculada como 4, la proporción de elongación del proceso integrado enrollado/estiramiento fue de alrededor de 20. La temperatura superficial del juego de rodillos fue de 138°C . Un número de experimentos fueron llevados a cabo en los cuales uno, dos, o tres etapas de estiramiento fueron realizadas, a diferentes temperaturas y proporciones de estiramiento. La velocidad de estiramiento fue ajustada de tal modo que la temperatura y las proporciones de estiramiento pudieran ser obtenidas. El

numero de etapas de estiramiento, la temperatura de las etapas de estiramiento y la proporción total de estiramiento, que incluye la etapa de enrollado, son dadas en la tabla 2. Las propiedades mecánicas, el parámetro de orientación uniplanar y los resultados de la DSC de las películas obtenidas de esta forma son dados en la tabla 2.

Tabla 2.

Muestra Estirada	Etapas de Estirado	Temp. En El segundo estirado (°C)	Temp. En El tercer estirado (°C)	Proporción Total de Estirado	Resistencia a la Tensión (GPa)	Módulo Tensil (GPa)	TEB (J/g)	Calor de Fusión (J/g)	Cristalinidad por DSC	Parámetro de Orientación Uniplanar Φ (°)	Temperatura De Fusión No Restringida (°C)
CE1	2	153	-	53.6	1.43	73.2	16.9	250	85%	1.04	147.0
CE2	2	154	-	52.8	1.37	71.4	16.1	233	80%	1.18	148.8
CE3	2	154	-	51.4	1.40	70.8	18.9	264	90%	1.61	149.2
CE4	2	155	-	53.2	1.25	50.2	17.1	222	76%	1.02	151.2
CE5	2	154	-	52.4	1.45	73.1	18.1	243	83%	2.02	149.0
CE6	2	155	-	51.3	1.27	64.7	15.3	210	72%	2.09	148.9
CE7	3	153	154	101.1	1.81	103.3	19.2	272	93%	1.23	149.6
CE8	3	153	155	101.1	1.86	96.8	22.0	256	87%	1.33	148.2
CE9	3	153	156	102.5	0.97	44.9	11.8	171	58%	0.98	150.9
CE10	3	154	154	100.7	1.94	102.8	22.8	270	92%	1.29	148.4
CE11	3	154	155	102.2	1.84	96.2	20.9	262	89%	1.17	149.1
CE12	3	154	156	107.1	0.91	42.5	11.7	173	59%	0.88	149.9
CE13	3	154	154	99.7	1.86	104.1	20.0	263	90%	1.74	148.0
CE14	3	154	155	99.7	1.95	102.4	22.3	263	90%	1.86	148.5
CE15	3	154	156	99.6	1.09	53.2	13.3	211	72%	1.36	150.0
CE16	3	155	154	100.7	1.81	95.3	21.5	240	82%	1.36	150.8
CE17	3	155	155	99.0	1.65	81.0	20.4	216	74%	1.25	150.9
CE18	3	155	156	104.4	1.45	70.1	19.2	206	70%	1.36	151.4
CE19	3	154	154	100.0	1.81	98.2	19.1	245	83%	1.88	148.8
CE20	3	154	155	100.7	1.80	96.2	19.9	265	90%	1.92	151.4
CE21	3	154	156	102.8	1.29	66.0	16.0	222	76%	1.64	150.9
CE22	3	155	155	98.8	1.84	97.5	21.9	238	81%	2.32	150.7
CE23	3	155	156	96.8	1.48	77.2	19.5	203	69%	2.00	151.7
CE24	3	154	154	112.7	1.72	105.1	19.7	262	89%	1.90	148.8
CE25	3	154	154	131.9	1.72	113.8	19.6	n.d.	n.d.	2.42	n.d.
CE26	3	154	154	149.0	1.72	123.0	19.5	n.d.	n.d.	2.71	n.d.
CE27	3	154	154	168.0	1.86	131.0	19.7	n.d.	n.d.	3.01	n.d.

Como puede ser visto de la Tabla 2, el uso de un polímero con una proporción PM/Mn de más de 6 y un módulo elástico de corte determinado directamente después de la fusión a 160°C de más de 0.9 MPa que resultan en un material

REIVINDICACIONES

1. Una película de UHMWPE que tiene una resistencia a la tensión de al menos 2.0 GPa, una energía de tensión para romperse de al menos 30 J/g, un PM de al menos 500000 gramos/mol, y una proporción PM/Mn de al menos 6.
2. La película de UHMWPE de la reivindicación 1 que tiene una Resistencia a la tensión de al menos 2.5 GPa, particularmente de al menos 3.0 GPa, mas particularmente al menos 3.5 GPa, o incluso al menos 4.0 GPa.
3. La película de UHMWPE de la reivindicación 1 o 2 que tiene una energía de tensión para romperse de al menos 35 J/g, particularmente de al menos 40 J/g GPa, más particularmente de al menos 50 J/g GPa.
4. La película de UHMWPE de una cualquiera de las reivindicaciones precedentes que tiene una proporción PM/Mn de a lo más 4, mas particularmente a lo más 3, aún más particularmente a lo más 2.
5. La película de UHMWPE de una cualquiera de las reivindicaciones precedentes que tiene un parámetro de orientación cristalina de al menos 3, en particular al

menos 4, mas particularmente al menos 5 , mas particularmente por lo menos 7, aun mas particularmente al menos 10, o por lo menos 15.

6. La película de UHMWPE de una cualquiera de las reivindicaciones precedentes que tiene un contenido de solvente orgánico de menos de 100 ppm.
7. Un proceso para la manufactura de una película de UHMWPE de acuerdo con una cualquiera de las reivindicaciones precedentes que comprende someter un UHMWPE inicial con un peso promedio del peso molecular de al menos 500000 gramos/mol, un módulo elástico de corte determinado directamente después de la fusión a 160°C de a lo más 0.9 MPa, y una proporción PM/Mn de a lo más 6 a una etapa de compactación y una etapa de estiramiento bajo condiciones tales que en ningún punto durante el procesamiento del polímero su temperatura es elevada a un valor por encima de su punto de fusión.
8. El proceso de la reivindicación 7 en donde el UHMWPE inicial tiene un módulo elástico de corte determinado directamente después de la fusión a 160°C a lo mas de 0.8 MPa, en particular a lo mas de 0.7 MPa.
9. El proceso de la reivindicación 7 u 8 en donde la etapa de compactación es llevada a cabo a una temperatura de al menos 1°C por debajo del punto de fusión del polímero sin restricción, en particular al menos 3°C, mas particularmente al menos 5°C, y la etapa de

estiramiento es llevada a cabo a una temperatura de al menos 1°C por debajo del punto de fusión del polímero bajo las condiciones del proceso, en particular al menos 3°C, mas particularmente al menos 5°C.

10. El proceso de una cualquiera de las reivindicaciones 7-9 en donde la proporción total de estiramiento obtenido es de al menos 120, en particular de al menos 140, mas particularmente de al menos 160.
11. El uso de una película de UHMWPE o los productos convertidos de la misma de una cualquiera de las reivindicaciones 1-6 como materia prima en aplicaciones balísticas, cuerdas, cables, redes, telas, y aplicaciones protectoras.
12. Cualidades Balísticas, cuerdas, cables, y redes, telas, y aplicaciones protectoras manufacturadas empleando la película de UHMWPE de acuerdo con una cualquiera de las reivindicaciones 1-6.

Polyethylene film with high tensile strength and high tensile energy to break

The present invention pertains to a polyethylene film with high tensile strength and high tensile energy to break, and to a method for manufacturing such a film from a specific ultra high molecular weight polyethylene. In this document ultra high molecular weight polyethylene will further be indicated as UHMWPE.

Methods for manufacturing high-strength high-modulus UHMWPE films are known in the art.

US 5,756,660 describes polymerisation of UHMWPE over a specific catalyst, followed by compression moulding, rolling and stretching to form a polymer film. In example 1, a material is obtained with a modulus of 160 GPa and a strength of 2.8 GPa.

US 5,106,555 describes a method for compression molding / stretching of UHMWPE.

US 5,503,791 describes a polyethylene film manufactured by extruding a solution of a polyolefin in a first solvent, followed by cooling, the removal of the solvent and stretching of the film. A disadvantage of the thus obtained film is that it always contains a certain amount of residual solvent, which may detrimentally affect the properties of the film. In general the amount of solvent present in solution of gel-cast films is at least 100 ppm. Further, the recovery of solvent is highly uneconomic.

EP 292 074 describes a UHMWPE film having a molecular weight of 4,000,000 g/mol, a Mw/Mn ratio of 4, a tensile strength of 2.3 GPa, and a tensile modulus of 92 GPa. Assuming a density of 0.97 g/ml, a tensile energy to break of 29.6 J/g can be calculated.

EP 269 151 describes a material having a tensile strength above 2.0 GPa, a modulus above 70 GPa. and a creep below $3 \times 10^{-7} \text{ sec}^{-1}$. This reference contains no information on the Mw/Mn ratio of the final product.

5 US 5,106,558 describes a method for the continuous preparation of a polyethylene having high strength and high modulus which comprises the steps of mixing 100 parts by weight of an ultra-high molecular weight polyethylene powder having an intrinsic viscosity of 5-50 dl/g in decalin at 135°C
10 with 2-50 parts of a liquid organic compound having a boiling point higher than the melting point of polyethylene, feeding the resulting mixture between a pair of rollers, and subjecting the mixture to compression moulding and drawing. This reference contains no information on the Mw/Mn ratio of
15 the final product.

US 6,017,480 describes a process for producing polyolefin materials comprising the steps of preparing a molded article of UHMW polyolefin, stretching the article by more than 30-fold, contacting the article , and restretching
20 the article. This reference contains no information on the Mw/Mn ratio of the final product.

It has been found that there is still room for improvement in the field of high-tensile strength UHMWPE films.
25 More in particular, there are numerous applications, including ballistic applications, ropes, cables, and nets, fabrics, and protective applications where PE films with high tensile energy to break, a high tensile strength, and other desirable properties will find application. The present invention
30 provides such a UHMWPE film.

The UHMWPE film according to the present invention has a tensile strength of at least 2.0 GPa, a tensile energy to

break of at least 30 J/g, an Mw of at least 500 000 gram/mole, and a Mw/Mn ratio of at most 6.

It has been found that the selection of a material with a Mw/Mn ratio of at most 6 in combination with a Mw of at least 500 000 is of importance to allow the final film to have the described high tensile strength and high energy to break in combination with further desirable properties, as will be discussed below. The materials described in US 5,756,660, US 5,106,555, and US 5,503,791 do not meet all of the above criteria.

As indicated above, the UHMWPE film according to the invention has a tensile strength of at least 2.0 GPa, determined in accordance with ASTM D882-00. Depending on the stretching ratio and stretching temperature, tensile strengths may be obtained of at least 2.5 GPa, in particular at least 3.0 GPa, more in particular at least 3.5 GPa. Tensile strengths of at least 4 GPa may also be obtained.

The tensile energy to break of the UHMWPE film according to the invention is at least 30 J/g. The tensile energy to break is determined in accordance with ASTM D882-00 using a strain rate of 50%/min. It is calculated by integrating the energy per unit mass under the stress-strain curve.

The tensile energy to break may be approximated by the following methods. These will give a fair approximation of the tensile energy to break as it is to be determined in accordance with ASTM D882-00 as discussed above.

An approximation of the tensile energy to break may be obtained by integrating the total energy absorbed and dividing it by the mass of the original gage region of the specimen. In particular, since the stress-strain curve of UHMWPE samples

with a tenacity over 2.0 GPa is approximately a straight line, the tensile energy to break can be calculated by the following formula

$$TEB = \frac{\sigma}{\rho} * \frac{EAB}{2} * 10$$

5 in which sigma is the tensile strength in GPa according to ASTM D882-00, rho is density in g/cm³, EAB is the elongation at break, expressed as a percentage according to ASTM D882-00, and TEB is the tensile energy to break in J/g.

Another approximation of the tensile energy to break
 10 TEB can be derived from tensile modulus and tensile strength in accordance with the following formula;

$$TEB = \frac{\sigma^2}{2 * Modulus * \rho} * 10^3$$

Depending on the stretching ratio, films may be obtained according to the invention which have a tensile
 15 energy to break of at least 35 J/g, in particular at least 40 J/g, more in particular at least 50 J/g.

The weight average molecular weight (Mw) of the polymer in the UHMWPE film of the present invention is at
 20 least 500 000 gram/mole in particular between 1.10⁶ gram/mole and 1.10⁸ gram/mole. The molecular weight distribution and molecular weigh averages (Mw, Mn, Mz) of the polymer are determined in accordance with ASTM D 6474-99 at a temperature of 160 °C using 1,2,4-trichlorobenzene (TCB) as solvent.
 25 Appropriate chromatographic equipment (PL-GPC220 from Polymer Laboratories) including a high temperature sample preparation device (PL-SP260) may be used. The system is calibrated using sixteen polystyrene standards (Mw/Mn <1.1) in the molecular weight range 5*10³ to 8*10⁶ gram/mole.

30 The molecular weight distribution of the UHMWPE present in the film according to the invention is relatively

narrow. This is expressed by the M_w (weight average molecular weight) over M_n (number average molecular weight) ratio of at most 6. More in particular the M_w/M_n ratio is at most 4, still more in particular at most 3, even more in particular at most 2.

The modulus of the UHMWPE film according to the invention is generally at least 80 GPa. The modulus is determined in accordance with ASTM D822-00. Depending on the stretching ratio, moduli may be obtained of at least 100, more in particular at least 120 GPa. It is possible to obtain moduli of at least 140 GPa, or at least 150 GPa.

In one embodiment of the present invention, the film according to the invention is characterised by a specific value for the uniplanar orientation parameter Φ . The uniplanar orientation parameter Φ is defined as the ratio between the 200 and the 110 peak areas in the X-ray diffraction (XRD) pattern of the film sample as determined in reflection geometry.

Wide angle X-ray scattering (WAXS) is a technique that provides information on the crystalline structure of matter. The technique specifically refers to the analysis of Bragg peaks scattered at wide angles. Bragg peaks result from long-range structural order. A WAXS measurement produces a diffraction pattern, i.e. intensity as function of the diffraction angle 2θ (this is the angle between the diffracted beam and the primary beam).

The uniplanar orientation parameter gives information about the extent of orientation of the 200 and 110 crystal planes with respect to the film surface. For a film sample with a high uniplanar orientation the 200 crystal planes are highly oriented parallel to the film surface. It has been found that the high tensile strength and high tensile energy

to break of the film according to the invention are generally accompanied by a high uniplanar orientation. The ratio between the 200 and 110 peak areas for a specimen with randomly oriented crystallites is around 0.4. However, the crystallites with indices 200 are preferentially oriented parallel to the film surface according to the invention, resulting in a higher value of the 200/110 peak area ratio and therefore in a higher value of the uniplanar orientation parameter.

The value for the uniplanar orientation parameter may be determined using an X-ray diffractometer. A Bruker-AXS D8 diffractometer equipped with focusing multilayer X-ray optics (Göbel mirror) producing Cu-K α radiation (K wavelength = 1.5418 Å) is suitable. Measuring conditions: 2 mm anti-scatter slit, 0.2 mm detector slit and generator setting 40kV, 35mA. The film specimen is mounted on a sample holder, e.g. with some double-sided mounting tape. The preferred dimensions of the film sample are 15 mm x 15 mm (l x w). Care should be taken that the sample is kept perfectly flat and aligned to the sample holder. The sample holder with the film specimen is subsequently placed into the D8 diffractometer in reflection geometry (with the normal of the film perpendicular to the goniometer and perpendicular to the sample holder). The scan range for the diffraction pattern is from 5° to 40° (2 θ) with a step size of 0.02° (2 θ) and a counting time of 2 seconds per step. During the measurement the sample holder spins with 15 revolutions per minute around the normal of the film, so that no further sample alignment is necessary. Subsequently the intensity is measured as function of the diffraction angle 2 θ . The peak area of the 200 and 110 reflections is determined using standard profile fitting software, e.g. Topas from Bruker-AXS. As the 200 and 110 reflections are single peaks, the fitting process is straightforward and it is within the scope of the skilled person to select and carry out an

appropriate fitting procedure. The uniplanar orientation parameter is defined as the ratio between the 200 and 110 peak areas. This parameter is a quantitative measure of the uniplanar orientation.

5

The high uniplanar orientation parameter is also related to the Mw/Mn ratio, in that polymers with a Mw/Mn ratio within the range specified in the present invention can be converted into films with a desirable value for the uniplanar orientation parameter. As indicated above, in one embodiment, the film according to the invention has a uniplanar orientation parameter of at least 3. It may be preferred for this value to be at least 4, more in particular at least 5, or at least 7. Higher values, such as values of at least 10 or even at least 15 may also be obtained. The theoretical maximum value for this parameter may be as high as infinite if the peak area 110 equals zero. High values for the uniplanar orientation parameter are often accompanied by high values for the strength and the energy to break.

20

The UHMWPE film according to the invention may be manufactured by a process which comprises subjecting a starting UHMWPE with a weight average molecular weight of at least 500 000 gram/mole, an elastic shear modulus G_N^0 , determined directly after melting at 160°C of at most 0.9 MPa, and a Mw/Mn ratio of at most 6 to a compacting step and a stretching step under such conditions that at no point during the processing of the polymer its temperature is raised to a value above its melting point.

30

The starting material of the process according to the invention is a highly disentangled UHMWPE. This can be seen from the combination of the weight average molecular weight, the Mw/Mn ratio, and the elastic shear modulus.

For further elucidation and preferred embodiments as regards the molecular weight and the Mw/Mn ratio of the starting UHMWPE, reference is made to what has been stated
 5 above for the film according to the invention.

As indicated above, the starting UHMWPE has an elastic shear modulus G_N^0 determined directly after melting at 160°C of at most 0.9 MPa, in particular at most 0.8 MPa, more in
 10 particular at most 0.7. The wording "directly after melting" means that the elastic shear modulus is determined as soon as the polymer has melted, in particular within 15 seconds after the polymer has melted. For this polymer melt G_N^0 typically increases from 0.6 to 2.0 MPa in several hours. The elastic
 15 shear modulus directly after melting at 160°C is one of the characterising features of the very disentangled UHMWPE used in the present invention.

G_N^0 is the elastic shear modulus in the rubbery plateau region. It is related to the average molecular weight between entanglements M_e , which in turn is inversely
 20 proportional to the entanglement density. In a thermodynamically stable melt having a homogeneous distribution of entanglements, M_e can be calculated from G_N^0 via the formula $G_N^0 = g_N \rho R T / M_e$, where g_N is a numerical factor
 25 set at 1, ρ is the density in g/cm³, R is the gas constant and T is the absolute temperature in K.

A low elastic shear modulus thus stands for long stretches of polymer between entanglements, and thus for a low degree of entanglement.

30 The UHMWPE used in the process according to the invention preferably has a DSC crystallinity of at least 74%,

more in particular at least 80%. The morphology of the films may be characterised using differential scanning calorimetry (DSC), for example on a Perkin Elmer DSC7. Thus, a sample of known weight (2 mg) is heated from 30 to 180°C at 10°C per minute, held at 180°C for 5 minutes, then cooled at 10°C per minute. The results of the DSC scan may be plotted as a graph of heat flow (mW or mJ/s; y-axis) against temperature (x-axis). The crystallinity is measured using the data from the heating portion of the scan. An enthalpy of fusion H (in J/g) for the crystalline melt transition is calculated by determining the area under the graph from the temperature determined just below the start of the main melt transition (endotherm) to the temperature just above the point where fusion is observed to be completed. The calculated H is then compared to the theoretical enthalpy of fusion (H_c of 293 J/g) determined for 100% crystalline PE at a melt temperature of approximately 140°C. A DSC crystallinity index is expressed as the percentage $100(H/H_c)$.

The film in accordance with the invention and the intermediate products of the manufacturing process according to the invention preferably also have crystallinities as indicated above.

The UHMWPE used in the present invention may have a bulk density which is significantly lower than the bulk density of conventional UWMWPEs. More in particular, the UHMWPE used in the process according to the invention may have a bulk density below 0.25 g/cm³, in particular below 0.18 g/cm³, still more in particular below 0.13 g/cm³. The bulk density is determined as follows. A sample of UHMWPE powder is poured into a measuring beaker of exact 100 ml. After scraping away the surplus of material, the weight of the content of the beaker is determined and the bulk density is calculated.

The UHMWPE used in the process according to the invention can be a homopolymer of ethylene or a copolymer of ethylene with a co-monomer which is another alpha-olefin or a cyclic olefin both with generally between 3 and 20 carbon atoms. Examples include propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, cyclohexene, etc. The use of dienes with up to 20 carbon atoms is also possible, e.g., butadiene or 1-4 hexadiene. The amount of (non-ethylene) alpha-olefin in the ethylene homopolymer or copolymer used in the process according to the invention preferably is at most 10 mole%, preferably at most 5 mole%, more preferably at most 1 mole%. If a (non-ethylene) alpha-olefin is used, it is generally present in an amount of at least 0.001 mol.%, in particular at least 0.01 mole%, still more in particular at least 0.1 mole%. Obviously, the ranges given above for the starting material also apply to the final polymer film.

The starting polymer for use in the present invention may be manufactured by a polymerisation process wherein ethylene, optionally in the presence of other monomers as discussed above, is polymerised in the presence of a single-site polymerisation catalyst at a temperature below the crystallisation temperature of the polymer, so that the polymer crystallises immediately upon formation. In particular, reaction conditions are selected such that the polymerisation speed is lower than the crystallisation speed. These synthesis conditions force the molecular chains to crystallize immediately upon their formation, leading to a rather unique morphology which differs substantially from the one obtained from the solution or the melt. The crystalline morphology created at the surface of a catalyst will highly depend on the ratio between the crystallization rate and the growth rate of the polymer. Moreover, the temperature of the synthesis, which is in this particular case also crystallization temperature,

will strongly influence the morphology of the obtained UHMW-PE powder. In one embodiment the reaction temperature is between -50 and +50°C, more in particular between -15 and +30°C. It is well within the scope of the skilled person to determine via routine trial and error which reaction temperature is appropriate in combination with which type of catalyst, polymer concentrations and other parameters influencing the reaction.

To obtain a highly disentangled UHMWPE it is important that the polymerisation sites are sufficiently far removed from each other to prevent entangling of the polymer chains during synthesis. This can be done using a single-site catalyst which is dispersed homogenously through the crystallisation medium in low concentrations. More in particular, concentrations less than $1 \cdot 10^{-4}$ mol catalyst per liter, in particular less than $1 \cdot 10^{-5}$ mol catalyst per liter reaction medium may be appropriate. Supported single site catalyst may also be used, as long as care is taken that the active sites are sufficiently far removed from each other to prevent substantial entanglement of the polymers during formation.

Suitable methods for manufacturing starting UHMWPE used in the present invention are known in the art. Reference is made, for example to WO01/21668 and US20060142521.

The polymer is provided in particulate form, for example in the form of a powder, or in any other suitable particulate form. Suitable particles have a particle size of up to 5000 micron, preferably up to 2000 micron, more in particular up to 1000 micron. The particles preferably have a particle size of at least 1 micron, more in particular at least 10 micron.

The particle size distribution may be determined by laser diffraction (PSD, Sympatec Quixel) as follows. The

sample is dispersed into surfactant-containing water and treated ultrasonic for 30 seconds to remove agglomerates/entanglements. The sample is pumped through a laser beam and the scattered light is detected. The amount of light
5 diffraction is a measure for the particle size.

The compacting step is carried out to integrate the polymer particles into a single object, e.g., in the form of a mother sheet. The stretching step is carried out to provide
10 orientation to the polymer and manufacture the final product. The two steps are carried out at a direction perpendicular to each other. It is noted that it is within the scope of the present invention to combine these elements in a single step, or to carry out the process in different steps, each step
15 performing one or more of the compacting and stretching elements. For example, in one embodiment of the process according to the invention, the process comprises the steps of compacting the polymer powder to form a mothersheet, rolling the plate to form rolled mothersheet and subjecting the rolled
20 mothersheet to a stretching step to form a polymer film.

The compacting force applied in the process according to the invention generally is $10\text{--}10000\text{ N/cm}^2$, in particular $50\text{--}5000\text{ N/cm}^2$, more in particular $100\text{--}2000\text{ N/cm}^2$. The density of the material after compacting is generally between 0.8 and 1
25 kg/dm^3 , in particular between 0.9 and 1 kg/dm^3 .

In the process according to the invention the compacting and rolling step is generally carried out at a temperature of at least 1°C below the unconstrained melting
30 point of the polymer, in particular at least 3°C below the unconstrained melting point of the polymer, still more in particular at least 5°C below the unconstrained melting point of the polymer. Generally, the compacting step is carried out at a temperature of at most 40°C below the unconstrained

melting point of the polymer, in particular at most 30°C below the unconstrained melting point of the polymer, more in particular at most 10°C.

5 In the process according to the invention the stretching step is generally carried out at a temperature of at least 1°C below the melting point of the polymer under process conditions, in particular at least 3°C below the melting point of the polymer under process conditions, still more in particular at least 5°C below the melting point of the polymer under process conditions. As the skilled person is aware, the melting point of polymers may depend upon the constraint under which they are put. This means that the melting temperature under process conditions may vary from case to case. It can easily be determined as the temperature at which the stress tension in the process drops sharply. Generally, the stretching step is carried out at a temperature of at most 30°C below the melting point of the polymer under process conditions, in particular at most 20°C below the melting point of the polymer under process conditions, more in particular at most 15°C.

25 The unconstrained melting temperature of the starting polymer is between 138 and 142°C and can easily be determined by the person skilled in the art. With the values indicated above this allows calculation of the appropriate operating temperature. The unconstrained melting point may be determined via DSC (differential scanning calorimetry) in nitrogen, over a temperature range of +30 to +180°C. and with an increasing temperature rate of 10°C/minute. The maximum of the largest endothermic peak at from 80 to 170°C. is evaluated here as the melting point.

In the conventional processing of UHMWPE it was necessary to carry out the process at a temperature which was

very close to the melting temperature of the polymer, e.g., within 1 to 3 degrees therefrom. It has been found that the selection of the specific starting UHMWPE used in the process according to the invention makes it possible to operate at
5 values which are more below the melting temperature of the polymer than has been possible in the prior art. This makes for a larger temperature operating window which makes for better process control.

Conventional apparatus may be used to carry out the
10 compacting step. Suitable apparatus include heated rolls, endless belts, etc.

The stretching step in the process according to the invention is carried out to manufacture the polymer film. The
15 stretching step may be carried out in one or more steps in a manner conventional in the art. A suitable manner includes leading the film in one or more steps over a set of rolls both rolling in process direction wherein the second roll rolls faster than the first roll. Stretching can take place over a
20 hot plate or in an air circulation oven. In general it is difficult to control the temperature of this type of equipment within 1 degree, which will allow the skilled person to appreciate the broadened operating window provided by the process of the present invention.

25 It is one of the features of the present invention that the total stretching ratio of the film can be very high indeed. For example, the total stretching ratio may be at least 120, in particular at least 140, more in particular at
30 least 160. The total draw ratio is defined as the area of the cross-section of the compacted mothersheet divided by the cross-section of the drawn film produced from this mothersheet.

The process according to the invention is carried out in the solid state. The final polymer film has a polymer solvent content of less than 0.05 wt.%, in particular less than 0.025 wt.%, more in particular less than 0.01 wt.%.

5

The film according to the invention is a three-dimensional object which is characterised in that two of its dimensions are substantially larger than the third. More in particular, the ratio between the second smallest dimension, the width of the film, and the smallest dimension, the thickness of the film, is at least 10, in particular at least 50.

10

The polymer film or the converted products thereof according to the invention can be used as starting material for numerous applications, including ballistic applications, ropes, cables, nets, fabrics, and protective applications.

15

Ballistic attributes, ropes, cables, nets, fabrics, and protective appliances derived from the UHMWPE film according to the invention are also part of the present invention.

20

The present invention will be illustrated by way of the following examples. It is to be understood that the invention is not limited in any way thereto or thereby.

25

Experimental

Compaction is executed in a mould with dimensions 610x30mm. After the mould is filled with the polymer, the polymer is compacted in a hot press for several minutes. After cooling down to a temperature $<40^{\circ}\text{C}$ the sheet is removed from the mould. Subsequently, the sheet is fed to a pair of upper and

30

lower heated rolls. The distance between the rolls is 150 micron. Directly after rolling, the film was stretched over the surface of the upper roll. Further stretching of the rolled film was executed on an oil-heated hotplate located
5 between two roller sets that run on accurately defined speeds.

Example 1

Polymerization

10 All air-and/or water-sensitive activities were performed under an argon atmosphere using Schlenk techniques or in a conventional nitrogen-filled glove box (Braun MB-150 GI). Methylalumoxane was purchased from WITCO GmbH as a 10 wt % toluene solution. Ethylene was obtained from Air Liquide.
15 Dried toluene was used as the polymerization solvent. The catalyst $[3\text{-tBu-2-O-C}_8\text{H}_3\text{CH=N(C}_6\text{F}_5\text{)}_2\text{TiCl}_2$ was synthesized according to Mitani et al. (M. Mitani, T. Nakano, T. Fujita, Chem. Eur. J. 2003, 9, 2396-2403) and EP0874005. The molecular weight and molecular weight distribution was measured at 135°C.
20 by gel-permeation chromatography (GPC; GPC220, Polymer Labs) using 1,2,4-trichlorobenzene as solvent. The polymerizations were carried out under atmospheric pressure using a 2000 ml round bottom flask, equipped with a thermocouple and a mechanical stirrer. Toluene (1000 ml) was introduced to the
25 argon-purged reactor after which the solvent was saturated by bubbling ethylene into the solution for 30 minutes at +10° C. The polymerization was initiated by addition of a toluene solution of methylalumoxane (20 ml) after which a toluene solution of the catalyst (1 μmol) was introduced into the
30 reactor while stirring vigorously. After 30 minutes the ethylene feed was stopped and isobutyl alcohol was added to terminate the polymerization. HCl and water were added to the resulting mixture. The solid UHMWPE was recovered by filtration, washed with water and acetone and dried (vacuum

oven 60° C., overnight). The yield was 75 grams. Its weight and number average molecular weight was 3 600 000 and 2 300 000, respectively. The Mw/Mn ratio was 1.56. The bulk density was 0.11 g/cm³. The unconstrained melting temperature of the polymer was 141°C. The elastic shear modulus determined directly after melting at 160°C was 0.65 MPa.

16 gram disentangled ultrahigh molecular weight polyethylene (as synthesized above) was compacted at an average pressure of 160 bar at a maximum temperature of 115°C maintained for 6 minutes. The resulted sheet was 0.9 mm thick, 610 mm long and 30mm wide. Its density was 0.95 g/cm³. The sheet was pre-heated to 125°C and directly rolled and stretched into a film according to the above-mentioned procedure. Based on the dimensional changes, the rolling ratio was calculated as 4.5, the ratio of elongation of the integrated rolling/stretching process was 20. The surface temperature of the roller-set was 125°C. A number of experiments were carried out in which one, two, or three stretching steps were carried out, at different temperatures and stretching ratios. The stretching speed was adjusted so that the temperature and stretching ratios could be obtained. The number of stretching steps, the temperature of the stretching steps and the total stretching ratio, which includes the rolling step, are given in table 1. The mechanical properties, Uniplanar Orientation Parameter and DSC results of the films thus obtained are given in Table 1.

As can be seen from Table 1, the process according to the invention allows the manufacture of films with a high strength in combination with a high tensile energy to break. These films also show a high tensile modulus.

There is a positive correlation between the DSC crystallinity and the physical properties of the film, in that films with a higher crystallinity often have a higher strength and TEB.

The uniplanar orientation parameter is a measure for the alignment of the polymers in the film, and therewith related to the total stretching ratio. With the present invention, a uniplanar orientation parameter of above 3 can already be
5 obtained at stretching ratio's of the order of 80. As will be illustrated in the comparative Example below, where a conventional polymer is used as starting material, a uniplanar orientation parameter of of the order of 3 can only be obtained at very high stretching ratios, and there it will not
10 be accompanied by the high strength and high TEB values that are part of the present invention.

Table1.

Stretched Sample	Stretching steps	Temp. at (third) drawing (°C)	Total Stretching Ratio	Tensile Strength (GPa)	Tensile Modulus (GPa)	TEB (J/g)	Heat of Fusion (J/g)	DSC crystallinity (%)	Uniplanar Orientation Parameter Φ (°)	Unconstrained melting temperature (°C)
E1	2	132	79	2.34	94	42.3	259	88.2%	3.7	153
E2	2	132	79	2.40	92	40.4	252	85.8%	3.0	151
E3	2	132	106	2.42	116	37.8	270	92.2%	4.5	154
E4	2	132	139	2.94	142	44.5	251	85.7%	5.7	154
E5	2	132	168	3.06	149	45.8	270	92.0%	10.2	153
E6	2	132	194	3.27	146	51.6	261	88.9%	12.6	151
E7	3	132 (132)	136	2.89	128	50.9	281	95.7%	3.7	154
E8	3	132 (132)	164	2.75	128	45.8	268	91.5%	4.2	153
E9	3	132 (132)	178	3.01	135	55.4	273	93.0%	5.9	153
E10	3	132 (132)	132	2.98	138	43.9	268	91.5%	6.1	152
E11	3	132 (132)	152	3.19	144	46.9	266	90.6%	5.8	155
E12	3	132 (132)	156	2.92	137	49.6	269	91.6%	5.9	154
E13	3	132 (132)	150	3.15	124	54.0	262	89.2%	8.6	153
E14	2	124	119	3.32	142	40.7	n.d.	n.d.	10.4	n.d.
E15	2	124	116	3.38	139	43.2	n.d.	n.d.	8.1	n.d.
E16	2	124	118	3.22	132	41.4	n.d.	n.d.	8.5	n.d.
E17	2	124	114	3.44	140	44.6	n.d.	n.d.	8.6	n.d.
E18	2	124	113	3.73	137	53.4	n.d.	n.d.	14.3	n.d.
E19	2	124	72	3.06	109	45.0	n.d.	n.d.	8.3	n.d.
E20	2	134	88	3.06	118	41.8	n.d.	n.d.	7.4	n.d.

E21	2	134	114	3.48	137	46.5	n.d.	n.d.	8.6	n.d.
E22	2	134	142	3.77	149	50.1	n.d.	n.d.	14.8	n.d.
E23	2	134	174	3.71	158	46.0	n.d.	n.d.	10.4	n.d.
E24	2	134	196	3.81	160	47.6	n.d.	n.d.	17.9	n.d.
E25	2	134	221	3.72	152	48.0	n.d.	n.d.	11.0	n.d.
E26	2	136	67	2.48	92	47.2	n.d.	n.d.	4.3	n.d.
E27	2	136	62	2.31	92	48.6	n.d.	n.d.	3.1	n.d.
E28	2	136	113	2.99	115	51.6	n.d.	n.d.	6.8	n.d.
E29	2	136	155	3.46	135	60.0	n.d.	n.d.	12.7	n.d.
E30	2	136	96	2.35	97	44.6	n.d.	n.d.	3.2	n.d.
E31	2	136	151	3.14	137	53.8	n.d.	n.d.	6.5	n.d.
E32	2	136	132	3.06	120	52.0	n.d.	n.d.	5.5	n.d.
E33	2	136	142	3.60	146	66.2	n.d.	n.d.	12.0	n.d.
E34	2	136	116	2.97	133	42.8	n.d.	n.d.	6.6	n.d.
E35	2	136	243	3.08	156	50.2	n.d.	n.d.	6.7	n.d.
E36	2	136	122	3.16	122	54.9	n.d.	n.d.	7.5	n.d.
E37	2	136	162	3.18	130	52.3	n.d.	n.d.	6.8	n.d.
E38	2	136	131	3.26	129	51.7	n.d.	n.d.	9.2	n.d.
E39	2	136	137	3.16	141	52.7	n.d.	n.d.	7.3	n.d.
E40	2	136	120	2.93	107	51.5	n.d.	n.d.	5.2	n.d.
E41	3	136 (138)	162	2.96	149	48.6	n.d.	n.d.	5.8	n.d.
E42	3	136 (138)	235	3.05	168	53.5	n.d.	n.d.	6.5	n.d.

n.d. = not determined

Comparative example 1

20 gram powder of a conventional Ziegler-Natta ultrahigh
5 molecular weight polyethylene (Ticona GUR series UHMWPE)
having a Mw of about 2 600 000, an Mn of about 360 000, an
Mw/Mn ratio of 7.22, a bulk density of 0.25 g/cm^3 , and an
elastic shear modulus determined directly after melting at
160°C of 1.65 MPa was used as starting material. The starting
10 polymer was compacted at an average pressure of 160 bar at a
maximum temperature of 134°C maintained for 6 minutes. The
resulted sheet was 1.15 mm thick, 610 mm long and 30mm wide.
Its density was 0.95 g/cm^3 . The sheet was pre-heated to 135°C
and directly rolled and stretched into a film according to the
15 above-mentioned procedure. Based on the dimensional changes
the rolling ratio was calculated as 4, the ratio of elongation
of the integrated rolling/stretching process was around 20..
The surface temperature of the roller-set was 138°C. A number
of experiments were carried out in which one, two, or three
20 stretching steps were carried out, at different temperatures
and stretching ratios. The stretching speed was adjusted so
that the temperature and stretching ratios could be obtained.
The number of stretching steps, the temperature of the
stretching steps and the total stretching ratio, which
25 includes the rolling step, are given in table 2. The
mechanical properties, Uniplanar Orientation Parameter and DSC
results of the films thus obtained are given in Table 2

Table 2.

Stretched Sample	Stretching steps	Temp. at second drawing (°C)	Temp. at third drawing (°C)	Total Stretching Ratio	Tensile Strength (GPa)	Tensile Modulus (GPa)	TEB (J/g)	Heat of Fusion (J/g)	DSC crystallinity	Uniplanar Orientation Parameter Φ (°)	Unconstrained melting temperature (°C)
CE1	2	153	-	53.6	1.43	73.2	16.9	250	85%	1.04	147.0
CE2	2	154	-	52.8	1.37	71.4	16.1	233	80%	1.18	148.8
CE3	2	154	-	51.4	1.40	70.8	18.9	264	90%	1.61	149.2
CE4	2	155	-	53.2	1.25	50.2	17.1	222	76%	1.02	151.2
CE5	2	154	-	52.4	1.45	73.1	18.1	243	83%	2.02	149.0
CE6	2	155	-	51.3	1.27	64.7	15.3	210	72%	2.09	148.9
CE7	3	153	154	101.1	1.81	103.3	19.2	272	93%	1.23	149.6
CE8	3	153	155	101.1	1.86	96.8	22.0	256	87%	1.33	148.2
CE9	3	153	156	102.5	0.97	44.9	11.8	171	58%	0.98	150.9
CE10	3	154	154	100.7	1.94	102.8	22.8	270	92%	1.29	148.4
CE11	3	154	155	102.2	1.84	96.2	20.9	262	89%	1.17	149.1
CE12	3	154	156	107.1	0.91	42.5	11.7	173	59%	0.88	149.9
CE13	3	154	154	99.7	1.86	104.1	20.0	263	90%	1.74	148.0
CE14	3	154	155	99.7	1.95	102.4	22.3	263	90%	1.86	148.5
CE15	3	154	156	99.6	1.09	53.2	13.3	211	72%	1.36	150.0
CE16	3	155	154	100.7	1.81	95.3	21.5	240	82%	1.36	150.8
CE17	3	155	155	99.0	1.65	81.0	20.4	216	74%	1.25	150.9
CE18	3	155	156	104.4	1.45	70.1	19.2	206	70%	1.36	151.4
CE19	3	154	154	100.0	1.81	98.2	19.1	245	83%	1.88	148.8
CE20	3	154	155	100.7	1.80	96.2	19.9	265	90%	1.92	151.4
CE21	3	154	156	102.8	1.29	66.0	16.0	222	76%	1.64	150.9
CE22	3	155	155	98.8	1.84	97.5	21.9	238	81%	2.32	150.7
CE23	3	155	156	96.8	1.48	77.2	19.5	203	69%	2.00	151.7
CE24	3	154	154	112.7	1.72	105.1	19.7	262	89%	1.90	148.8
CE25	3	154	154	131.9	1.72	113.8	19.6	n.d.	n.d.	2.42	n.d.
CE26	3	154	154	149.0	1.72	123.0	19.5	n.d.	n.d.	2.71	n.d.
CE27	3	154	154	168.0	1.86	131.0	19.7	n.d.	n.d.	3.01	n.d.

As can be seen from Table 2, the use of a polymer with a Mw/Mn ratio of more than 6 and an elastic shear modulus determined directly after melting at 160°C of at more than 0.9 MPa results in a material with a tensile strength and TEB which are well outside the range of the present invention. It is noted that in these Examples the films were stretched as far as they would go. It was not possible to obtain higher stretching ratios.

CLAIMS

1. UHMWPE film having a tensile strength of at least 2.0 GPa, a tensile energy to break of at least 30 J/g, an Mw of at least 500 000 gram/mole, and a Mw/Mn ratio of at most 6.

2. The UHMWPE film of claim 1 which has a tensile strength of at least 2.5 GPa, in particular at least 3.0 GPa, more in particular at least 3.5 GPa, or even at least 4.0 GPa.

3. The UHMWPE film of claim 1 or 2 which has a tensile energy to break of at least 35 J/g, in particular at least 40 J/g GPa, more in particular at least 50 J/g GPa.

4. The UHMWPE film of any one of the preceding claims which has a Mw/Mn ratio of at most 4, more in particular at most 3, even more in particular at most 2.

5. The UHMWPE film of any one of the preceding claims which has a crystalline orientation parameter of at least 3, in particular at least 4, more in particular at least 5, even more in particular at least 7, still more in particular at least 10, or at least 15.

6. The UHMWPE film of any one of the preceding claims which has an organic solvent content of less than 100 ppm.

7. A process for manufacturing the UHMWPE film according to any one of the preceding claims which comprises subjecting a starting UHMWPE with a weight average molecular weight of at least 500 000 gram/mole, an elastic shear modulus determined directly after melting at 160°C of at most 0.9 MPa, and a Mw/Mn ratio of at most 6 to a compacting step and a

stretching step under such conditions that at no point during the processing of the polymer its temperature is raised to a value above its melting point.

5 8. The process of claim 7 wherein the starting UHMWPE has an elastic shear modulus determined directly after melting at 160°C of at most 0.8 MPa, in particular at most 0.7 MPa.

10 9. The process of claim 7 or 8 wherein the compacting step is carried out at a temperature of at least 1°C below the unconstrained melting point of the polymer, in particular at least 3°C, more in particular at least 5°C, and the stretching step is carried out at a temperature of at
15 least 1°C below the melting point of the polymer under process conditions, in particular at least 3°C, more in particular at least 5°C.

20 10. The process of any one of claims 7-9 wherein the total stretching ratio obtained is at least 120, in particular at least 140, more in particular at least 160.

25 11. Use of a UHMWPE film or the converted products thereof of any one of claims 1-6 as starting material in ballistic applications, ropes, cables, nets, fabrics, and protective applications.

30 12. Ballistic attributes, ropes, cables, and nets, fabrics, and protective appliances manufactured using the UHMWPE film according to any one of claims 1-6.

ABSTRACT

The present invention pertains to a UHMWPE film having a tensile strength of at least 2.0 GPa, a tensile energy to break of at least 30 J/g, an Mw of at least 500 000 gram/mole, and a Mw/Mn ratio of at most 6.

The film may be manufactured via a process which comprises subjecting a starting UHMWPE with a weight average molecular weight of at least 500 000 gram/mole, an elastic shear modulus determined directly after melting at 160°C of at most 0.9 MPa, and a Mw/Mn ratio of at most 6 to a compacting step and a stretching step under such conditions that at no point during the processing of the polymer its temperature is raised to a value above its melting point.

The film may be used as starting material in any applications where high tensile strength and high energy to break are important. Suitable applications include ballistic applications, ropes, cables, nets, fabrics, and protective applications.

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(54) Title: POLYETHYLENE FILM WITH HIGH TENSILE STRENGTH AND HIGH TENSILE ENERGY TO BREAK

(57) Abstract: The present invention pertains to a UHMWPE film having a tensile strength of at least 2.0 GPa, a tensile energy to break of at least 30 J/g, an Mw of at least 500 000 gram/mole, and a Mw/Mn ratio of at most 6. The film may be manufactured via a process which comprises subjecting a starting UHMWPE with a weight average molecular weight of at least 500 000 gram/mole, an elastic shear modulus determined directly after melting at 160 °C of at most 0.9 MPa, and a Mw/Mn ratio of at most 6 to a compacting step and a stretching step under such conditions that at no point during the processing of the polymer its temperature is raised to a value above its melting point. The film may be used as starting material in any applications where high tensile strength and high energy to break are important. Suitable applications include ballistic applications, ropes, cables, nets, fabrics, and protective applications.

Polyethylene film with high tensile strength and high tensile energy to break

The present invention pertains to a polyethylene film with high tensile strength and high tensile energy to break, and to a method for manufacturing such a film from a specific ultra high molecular weight polyethylene. In this document ultra high molecular weight polyethylene will further be indicated as UHMWPE.

Methods for manufacturing high-strength high-modulus UHMWPE films are known in the art.

US 5,756,660 describes polymerisation of UHMWPE over a specific catalyst, followed by compression moulding, rolling and stretching to form a polymer film. In example 1, a material is obtained with a modulus of 160 GPa and a strength of 2.8 GPa.

US 5,106,555 describes a method for compression molding / stretching of UHMWPE.

US 5,503,791 describes a polyethylene film manufactured by extruding a solution of a polyolefin in a first solvent, followed by cooling, the removal of the solvent and stretching of the film. A disadvantage of the thus obtained film is that it always contains a certain amount of residual solvent, which may detrimentally affect the properties of the film. In general the amount of solvent present in solution of gel-cast films is at least 100 ppm. Further, the recovery of solvent is highly uneconomic.

EP 292 074 describes a UHMWPE film having a molecular weight of 4,000,000 g/mol, a Mw/Mn ratio of 4, a tensile strength of 2.3 GPa, and a tensile modulus of 92 GPa. Assuming a density of 0.97 g/ml, a tensile energy to break of 29.6 J/g can be calculated.

EP 269 151 describes a material having a tensile strength above 2.0 GPa, a modulus above 70 GPa. and a creep below $3 \times 10^{-7} \text{ sec}^{-1}$. This reference contains no information on the Mw/Mn ratio of the final product.

5 US 5,106,558 describes a method for the continuous preparation of a polyethylene having high strength and high modulus which comprises the steps of mixing 100 parts by weight of an ultra-high molecular weight polyethylene powder having an intrinsic viscosity of 5-50 dl/g in decalin at 135°C
10 with 2-50 parts of a liquid organic compound having a boiling point higher than the melting point of polyethylene, feeding the resulting mixture between a pair of rollers, and subjecting the mixture to compression moulding and drawing. This reference contains no information on the Mw/Mn ratio of
15 the final product.

US 6,017,480 describes a process for producing polyolefin materials comprising the steps of preparing a molded article of UHMW polyolefin, stretching the article by more than 30-fold, contacting the article , and restreching
20 the article. This reference contains no information on the Mw/Mn ratio of the final product.

It has been found that there is still room for improvement in the field of high-tensile strength UHMWPE films.
25 More in particular, there are numerous applications, including ballistic applications, ropes, cables, and nets, fabrics, and protective applications where PE films with high tensile energy to break, a high tensile strength, and other desirable properties will find application. The present invention
30 provides such a UHMWPE film.

The UHMWPE film according to the present invention has a tensile strength of at least 2.0 GPa, a tensile energy to

break of at least 30 J/g, an Mw of at least 500 000 gram/mole, and a Mw/Mn ratio of at most 6.

It has been found that the selection of a material
5 with a Mw/Mn ratio of at most 6 in combination with a Mw of at least 500 000 is of importance to allow the final film to have the described high tensile strength and high energy to break in combination with further desirable properties, as will be discussed below. The materials described in US 5,756,660, US
10 5,106,555, and US 5,503,791 do not meet all of the above criteria.

As indicated above, the UHMWPE film according to the invention has a tensile strength of at least 2.0 GPa,
15 determined in accordance with ASTM D882-00. Depending on the stretching ratio and stretching temperature, tensile strengths may be obtained of at least 2.5 GPa, in particular at least 3.0 GPa, more in particular at least 3.5 GPa. Tensile strengths of at least 4 GPa may also be obtained.

20 The tensile energy to break of the UHMWPE film according to the invention is at least 30 J/g. The tensile energy to break is determined in accordance with ASTM D882-00 using a strain rate of 50%/min. It is calculated by integrating the energy per unit mass under the stress-strain
25 curve.

The tensile energy to break may be approximated by the following methods. These will give a fair approximation of the tensile energy to break as it is to be determined in
30 accordance with ASTM D882-00 as discussed above.

An approximation of the tensile energy to break may be obtained by integrating the total energy absorbed and dividing it by the mass of the original gage region of the specimen. In particular, since the stress-strain curve of UHMWPE samples

with a tenacity over 2.0 GPa is approximately a straight line, the tensile energy to break can be calculated by the following formula

$$TEB = \frac{\sigma}{\rho} * \frac{EAB}{2} * 10$$

5 in which sigma is the tensile strength in GPa according to ASTM D882-00, rho is density in g/cm³, EAB is the elongation at break, expressed as a percentage according to ASTM D882-00, and TEB is the tensile energy to break in J/g.

10 Another approximation of the tensile energy to break TEB can be derived from tensile modulus and tensile strength in accordance with the following formula;

$$TEB = \frac{\sigma^2}{2 * Modulus * \rho} * 10^3$$

15 Depending on the stretching ratio, films may be obtained according to the invention which have a tensile energy to break of at least 35 J/g, in particular at least 40 J/g, more in particular at least 50 J/g.

The weight average molecular weight (Mw) of the polymer in the UHMWPE film of the present invention is at least 500 000 gram/mole in particular between 1.10⁶ gram/mole and 1.10⁸ gram/mole. The molecular weight distribution and molecular weigh averages (Mw, Mn, Mz) of the polymer are determined in accordance with ASTM D 6474-99 at a temperature of 160 °C using 1,2,4-trichlorobenzene (TCB) as solvent.

25 Appropriate chromatographic equipment (PL-GPC220 from Polymer Laboratories) including a high temperature sample preparation device (PL-SP260) may be used. The system is calibrated using sixteen polystyrene standards (Mw/Mn <1.1) in the molecular weight range 5*10³ to 8*10⁶ gram/mole.

30 The molecular weight distribution of the UHMWPE present in the film according to the invention is relatively

narrow. This is expressed by the Mw (weight average molecular weight) over Mn (number average molecular weight) ratio of at most 6. More in particular the Mw/Mn ratio is at most 4, still more in particular at most 3, even more in particular at most 2.

The modulus of the UHMWPE film according to the invention is generally at least 80 GPa. The modulus is determined in accordance with ASTM D822-00. Depending on the stretching ratio, moduli may be obtained of at least 100, more in particular at least 120 GPa. It is possible to obtain moduli of at least 140 GPa, or at least 150 GPa.

In one embodiment of the present invention, the film according to the invention is characterised by a specific value for the uniplanar orientation parameter Φ . The uniplanar orientation parameter Φ is defined as the ratio between the 200 and the 110 peak areas in the X-ray diffraction (XRD) pattern of the film sample as determined in reflection geometry.

Wide angle X-ray scattering (WAXS) is a technique that provides information on the crystalline structure of matter. The technique specifically refers to the analysis of Bragg peaks scattered at wide angles. Bragg peaks result from long-range structural order. A WAXS measurement produces a diffraction pattern, i.e. intensity as function of the diffraction angle 2θ (this is the angle between the diffracted beam and the primary beam).

The uniplanar orientation parameter gives information about the extent of orientation of the 200 and 110 crystal planes with respect to the film surface. For a film sample with a high uniplanar orientation the 200 crystal planes are highly oriented parallel to the film surface. It has been found that the high tensile strength and high tensile energy

to break of the film according to the invention are generally accompanied by a high uniplanar orientation. The ratio between the 200 and 110 peak areas for a specimen with randomly oriented crystallites is around 0.4. However, the crystallites with indices 200 are preferentially oriented parallel to the film surface according to the invention, resulting in a higher value of the 200/110 peak area ratio and therefore in a higher value of the uniplanar orientation parameter.

The value for the uniplanar orientation parameter may be determined using an X-ray diffractometer. A Bruker-AXS D8 diffractometer equipped with focusing multilayer X-ray optics (Göbel mirror) producing Cu-K α radiation (K wavelength = 1.5418 Å) is suitable. Measuring conditions: 2 mm anti-scatter slit, 0.2 mm detector slit and generator setting 40kV, 35mA. The film specimen is mounted on a sample holder, e.g. with some double-sided mounting tape. The preferred dimensions of the film sample are 15 mm x 15 mm (l x w). Care should be taken that the sample is kept perfectly flat and aligned to the sample holder. The sample holder with the film specimen is subsequently placed into the D8 diffractometer in reflection geometry (with the normal of the film perpendicular to the goniometer and perpendicular to the sample holder). The scan range for the diffraction pattern is from 5° to 40° (2 θ) with a step size of 0.02° (2 θ) and a counting time of 2 seconds per step. During the measurement the sample holder spins with 15 revolutions per minute around the normal of the film, so that no further sample alignment is necessary. Subsequently the intensity is measured as function of the diffraction angle 2 θ . The peak area of the 200 and 110 reflections is determined using standard profile fitting software, e.g. Topas from Bruker-AXS. As the 200 and 110 reflections are single peaks, the fitting process is straightforward and it is within the scope of the skilled person to select and carry out an

appropriate fitting procedure. The uniplanar orientation parameter is defined as the ratio between the 200 and 110 peak areas. This parameter is a quantitative measure of the uniplanar orientation.

5

The high uniplanar orientation parameter is also related to the Mw/Mn ratio, in that polymers with a Mw/Mn ratio within the range specified in the present invention can be converted into films with a desirable value for the uniplanar orientation parameter. As indicated above, in one embodiment, the film according to the invention has a uniplanar orientation parameter of at least 3. It may be preferred for this value to be at least 4, more in particular at least 5, or at least 7. Higher values, such as values of at least 10 or even at least 15 may also be obtained. The theoretical maximum value for this parameter may be as high as infinite if the peak area 110 equals zero. High values for the uniplanar orientation parameter are often accompanied by high values for the strength and the energy to break.

20

The UHMWPE film according to the invention may be manufactured by a process which comprises subjecting a starting UHMWPE with a weight average molecular weight of at least 500 000 gram/mole, an elastic shear modulus G_N^0 , determined directly after melting at 160°C of at most 0.9 MPa, and a Mw/Mn ratio of at most 6 to a compacting step and a stretching step under such conditions that at no point during the processing of the polymer its temperature is raised to a value above its melting point.

30

The starting material of the process according to the invention is a highly disentangled UHMWPE. This can be seen from the combination of the weight average molecular weight, the Mw/Mn ratio, and the elastic shear modulus.

For further elucidation and preferred embodiments as regards the molecular weight and the Mw/Mn ratio of the starting UHMWPE, reference is made to what has been stated
5 above for the film according to the invention.

As indicated above, the starting UHMWPE has an elastic shear modulus G_N^0 determined directly after melting at 160°C of at most 0.9 MPa, in particular at most 0.8 MPa, more in
10 particular at most 0.7. The wording "directly after melting" means that the elastic shear modulus is determined as soon as the polymer has melted, in particular within 15 seconds after the polymer has melted. For this polymer melt G_N^0 typically increases from 0.6 to 2.0 MPa in several hours. The elastic
15 shear modulus directly after melting at 160°C is one of the characterising features of the very disentangled UHMWPE used in the present invention.

G_N^0 is the elastic shear modulus in the rubbery plateau region. It is related to the average molecular weight
20 between entanglements M_e , which in turn is inversely proportional to the entanglement density. In a thermodynamically stable melt having a homogeneous distribution of entanglements, M_e can be calculated from G_N^0 via the formula $G_N^0 = g_N \rho RT / M_e$, where g_N is a numerical factor
25 set at 1, ρ is the density in g/cm³, R is the gas constant and T is the absolute temperature in K.

A low elastic shear modulus thus stands for long stretches of polymer between entanglements, and thus for a low degree of entanglement.
30

The UHMWPE used in the process according to the invention preferably has a DSC crystallinity of at least 74%,

more in particular at least 80%. The morphology of the films may be characterised using differential scanning calorimetry (DSC), for example on a Perkin Elmer DSC7. Thus, a sample of known weight (2 mg) is heated from 30 to 180°C at 10°C per minute, held at 180°C for 5 minutes, then cooled at 10°C per minute. The results of the DSC scan may be plotted as a graph of heat flow (mW or mJ/s; y-axis) against temperature (x-axis). The crystallinity is measured using the data from the heating portion of the scan. An enthalpy of fusion H (in J/g) for the crystalline melt transition is calculated by determining the area under the graph from the temperature determined just below the start of the main melt transition (endotherm) to the temperature just above the point where fusion is observed to be completed. The calculated H is then compared to the theoretical enthalpy of fusion (H_c of 293 J/g) determined for 100% crystalline PE at a melt temperature of approximately 140°C. A DSC crystallinity index is expressed as the percentage $100(H/H_c)$.

The film in accordance with the invention and the intermediate products of the manufacturing process according to the invention preferably also have crystallinities as indicated above.

The UHMWPE used in the present invention may have a bulk density which is significantly lower than the bulk density of conventional UWMWPEs. More in particular, the UHMWPE used in the process according to the invention may have a bulk density below 0.25 g/cm³, in particular below 0.18 g/cm³, still more in particular below 0.13 g/cm³. The bulk density is determined as follows. A sample of UHMWPE powder is poured into a measuring beaker of exact 100 ml. After scraping away the surplus of material, the weight of the content of the beaker is determined and the bulk density is calculated.

The UHMWPE used in the process according to the invention can be a homopolymer of ethylene or a copolymer of ethylene with a co-monomer which is another alpha-olefin or a cyclic olefin both with generally between 3 and 20 carbon atoms. Examples include propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, cyclohexene, etc. The use of dienes with up to 20 carbon atoms is also possible, e.g., butadiene or 1-4 hexadiene. The amount of (non-ethylene) alpha-olefin in the ethylene homopolymer or copolymer used in the process according to the invention preferably is at most 10 mole%, preferably at most 5 mole%, more preferably at most 1 mole%. If a (non-ethylene) alpha-olefin is used, it is generally present in an amount of at least 0.001 mol.%, in particular at least 0.01 mole%, still more in particular at least 0.1 mole%. Obviously, the ranges given above for the starting material also apply to the final polymer film.

The starting polymer for use in the present invention may be manufactured by a polymerisation process wherein ethylene, optionally in the presence of other monomers as discussed above, is polymerised in the presence of a single-site polymerisation catalyst at a temperature below the crystallisation temperature of the polymer, so that the polymer crystallises immediately upon formation. In particular, reaction conditions are selected such that the polymerisation speed is lower than the crystallisation speed. These synthesis conditions force the molecular chains to crystallize immediately upon their formation, leading to a rather unique morphology which differs substantially from the one obtained from the solution or the melt. The crystalline morphology created at the surface of a catalyst will highly depend on the ratio between the crystallization rate and the growth rate of the polymer. Moreover, the temperature of the synthesis, which is in this particular case also crystallization temperature,

will strongly influence the morphology of the obtained UHMW-PE powder. In one embodiment the reaction temperature is between -50 and +50°C, more in particular between -15 and +30°C. It is well within the scope of the skilled person to determine via routine trial and error which reaction temperature is appropriate in combination with which type of catalyst, polymer concentrations and other parameters influencing the reaction.

To obtain a highly disentangled UHMWPE it is important that the polymerisation sites are sufficiently far removed from each other to prevent entangling of the polymer chains during synthesis. This can be done using a single-site catalyst which is dispersed homogenously through the crystallisation medium in low concentrations. More in particular, concentrations less than $1 \cdot 10^{-4}$ mol catalyst per liter, in particular less than $1 \cdot 10^{-5}$ mol catalyst per liter reaction medium may be appropriate. Supported single site catalyst may also be used, as long as care is taken that the active sites are sufficiently far removed from each other to prevent substantial entanglement of the polymers during formation.

Suitable methods for manufacturing starting UHMWPE used in the present invention are known in the art. Reference is made, for example to WO01/21668 and US20060142521.

The polymer is provided in particulate form, for example in the form of a powder, or in any other suitable particulate form. Suitable particles have a particle size of up to 5000 micron, preferably up to 2000 micron, more in particular up to 1000 micron. The particles preferably have a particle size of at least 1 micron, more in particular at least 10 micron.

The particle size distribution may be determined by laser diffraction (PSD, Sympatec Quixel) as follows. The

sample is dispersed into surfactant-containing water and treated ultrasonic for 30 seconds to remove agglomerates/entanglements. The sample is pumped through a laser beam and the scattered light is detected. The amount of light
5 diffraction is a measure for the particle size.

The compacting step is carried out to integrate the polymer particles into a single object, e.g., in the form of a mother sheet. The stretching step is carried out to provide
10 orientation to the polymer and manufacture the final product. The two steps are carried out at a direction perpendicular to each other. It is noted that it is within the scope of the present invention to combine these elements in a single step, or to carry out the process in different steps, each step
15 performing one or more of the compacting and stretching elements. For example, in one embodiment of the process according to the invention, the process comprises the steps of compacting the polymer powder to form a mothersheet, rolling the plate to form rolled mothersheet and subjecting the rolled
20 mothersheet to a stretching step to form a polymer film.

The compacting force applied in the process according to the invention generally is $10\text{-}10000\text{ N/cm}^2$, in particular $50\text{-}5000\text{ N/cm}^2$, more in particular $100\text{-}2000\text{ N/cm}^2$. The density of the material after compacting is generally between 0.8 and 1
25 kg/dm^3 , in particular between 0.9 and 1 kg/dm^3 .

In the process according to the invention the compacting and rolling step is generally carried out at a temperature of at least 1°C below the unconstrained melting
30 point of the polymer, in particular at least 3°C below the unconstrained melting point of the polymer, still more in particular at least 5°C below the unconstrained melting point of the polymer. Generally, the compacting step is carried out at a temperature of at most 40°C below the unconstrained

melting point of the polymer, in particular at most 30°C below the unconstrained melting point of the polymer, more in particular at most 10°C.

5 In the process according to the invention the stretching step is generally carried out at a temperature of at least 1°C below the melting point of the polymer under process conditions, in particular at least 3°C below the melting point of the polymer under process conditions, still more in particular at least 5°C below the melting point of the polymer under process conditions. As the skilled person is aware, the melting point of polymers may depend upon the constraint under which they are put. This means that the melting temperature under process conditions may vary from case to case. It can easily be determined as the temperature at which the stress tension in the process drops sharply. Generally, the stretching step is carried out at a temperature of at most 30°C below the melting point of the polymer under process conditions, in particular at most 20°C below the melting point of the polymer under process conditions, more in particular at most 15°C.

The unconstrained melting temperature of the starting polymer is between 138 and 142°C and can easily be determined by the person skilled in the art. With the values indicated above this allows calculation of the appropriate operating temperature. The unconstrained melting point may be determined via DSC (differential scanning calorimetry) in nitrogen, over a temperature range of +30 to +180°C. and with an increasing temperature rate of 10°C/minute. The maximum of the largest endothermic peak at from 80 to 170°C. is evaluated here as the melting point.

In the conventional processing of UHMWPE it was necessary to carry out the process at a temperature which was

very close to the melting temperature of the polymer, e.g., within 1 to 3 degrees therefrom. It has been found that the selection of the specific starting UHMWPE used in the process according to the invention makes it possible to operate at values which are more below the melting temperature of the polymer than has been possible in the prior art. This makes for a larger temperature operating window which makes for better process control.

Conventional apparatus may be used to carry out the compacting step. Suitable apparatus include heated rolls, endless belts, etc.

The stretching step in the process according to the invention is carried out to manufacture the polymer film. The stretching step may be carried out in one or more steps in a manner conventional in the art. A suitable manner includes leading the film in one or more steps over a set of rolls both rolling in process direction wherein the second roll rolls faster than the first roll. Stretching can take place over a hot plate or in an air circulation oven. In general it is difficult to control the temperature of this type of equipment within 1 degree, which will allow the skilled person to appreciate the broadened operating window provided by the process of the present invention.

It is one of the features of the present invention that the total stretching ratio of the film can be very high indeed. For example, the total stretching ratio may be at least 120, in particular at least 140, more in particular at least 160. The total draw ratio is defined as the area of the cross-section of the compacted mothersheet divided by the cross-section of the drawn film produced from this mothersheet.

The process according to the invention is carried out in the solid state. The final polymer film has a polymer solvent content of less than 0.05 wt.%, in particular less than 0.025 wt.%, more in particular less than 0.01 wt.%.

5

The film according to the invention is a three-dimensional object which is characterised in that two of its dimensions are substantially larger than the third. More in particular, the ratio between the second smallest dimension, the width of the film, and the smallest dimension, the thickness of the film, is at least 10, in particular at least 50.

10

The polymer film or the converted products thereof according to the invention can be used as starting material for numerous applications, including ballistic applications, ropes, cables, nets, fabrics, and protective applications.

15

Ballistic attributes, ropes, cables, nets, fabrics, and protective appliances derived from the UHMWPE film according to the invention are also part of the present invention.

20

The present invention will be illustrated by way of the following examples. It is to be understood that the invention is not limited in any way thereto or thereby.

25

Experimental

Compaction is executed in a mould with dimensions 610x30mm. After the mould is filled with the polymer, the polymer is compacted in a hot press for several minutes. After cooling down to a temperature <40°C the sheet is removed from the mould. Subsequently, the sheet is fed to a pair of upper and

30

lower heated rolls. The distance between the rolls is 150 micron. Directly after rolling, the film was stretched over the surface of the upper roll. Further stretching of the rolled film was executed on an oil-heated hotplate located
5 between two roller sets that run on accurately defined speeds.

Example 1

Polymerization

10 All air-and/or water-sensitive activities were performed under an argon atmosphere using Schlenk techniques or in a conventional nitrogen-filled glove box (Braun MB-150 GI). Methylalumoxane was purchased from WITCO GmbH as a 10 wt % toluene solution. Ethylene was obtained from Air Liquide.
15 Dried toluene was used as the polymerization solvent. The catalyst $[3\text{-tBu-2-O-C}_8\text{H}_3\text{CH=N(C}_6\text{F}_5)]_2\text{TiCl}_2$ was synthesized according to Mitani et al. (M. Mitani, T. Nakano, T. Fujita, Chem. Eur. J. 2003, 9, 2396-2403) and EP0874005. The molecular weight and molecular weight distribution was measured at 135°C.
20 by gel-permeation chromatography (GPC; GPC220, Polymer Labs) using 1,2,4-trichlorobenzene as solvent. The polymerizations were carried out under atmospheric pressure using a 2000 ml round bottom flask, equipped with a thermocouple and a mechanical stirrer. Toluene (1000 ml) was introduced to the
25 argon-purged reactor after which the solvent was saturated by bubbling ethylene into the solution for 30 minutes at +10° C. The polymerization was initiated by addition of a toluene solution of methylalumoxane (20 ml) after which a toluene solution of the catalyst (1 μmol) was introduced into the
30 reactor while stirring vigorously. After 30 minutes the ethylene feed was stopped and isobutyl alcohol was added to terminate the polymerization. HCl and water were added to the resulting mixture. The solid UHMWPE was recovered by filtration, washed with water and acetone and dried (vacuum

oven 60° C., overnight). The yield was 75 grams. Its weight and number average molecular weight was 3 600 000 and 2 300 000, respectively. The Mw/Mn ratio was 1.56. The bulk density was 0.11 g/cm³. The unconstrained melting temperature of the polymer was 141°C. The elastic shear modulus determined directly after melting at 160°C was 0.65 MPa.

16 gram disentangled ultrahigh molecular weight polyethylene (as synthesized above) was compacted at an average pressure of 160 bar at a maximum temperature of 115°C maintained for 6 minutes. The resulted sheet was 0.9 mm thick, 610 mm long and 30mm wide. Its density was 0.95 g/cm³. The sheet was pre-heated to 125°C and directly rolled and stretched into a film according to the above-mentioned procedure. Based on the dimensional changes, the rolling ratio was calculated as 4.5, the ratio of elongation of the integrated rolling/stretching process was 20. The surface temperature of the roller-set was 125°C. A number of experiments were carried out in which one, two, or three stretching steps were carried out, at different temperatures and stretching ratios. The stretching speed was adjusted so that the temperature and stretching ratios could be obtained. The number of stretching steps, the temperature of the stretching steps and the total stretching ratio, which includes the rolling step, are given in table 1. The mechanical properties, Uniplanar Orientation Parameter and DSC results of the films thus obtained are given in Table 1.

As can be seen from Table 1, the process according to the invention allows the manufacture of films with a high strength in combination with a high tensile energy to break. These films also show a high tensile modulus.

There is a positive correlation between the DSC crystallinity and the physical properties of the film, in that films with a higher crystallinity often have a higher strength and TEB.

The uniplanar orientation parameter is a measure for the alignment of the polymers in the film, and therewith related to the total stretching ratio. With the present invention, a uniplanar orientation parameter of above 3 can already be
5 obtained at stretching ratio's of the order of 80. As will be illustrated in the comparative Example below, where a conventional polymer is used as starting material, a uniplanar orientation parameter of of the order of 3 can only be
10 obtained at very high stretching ratios, and there it will not be accompanied by the high strength and high TEB values that are part of the present invention.

Table1.

Stretched Sample	Stretching steps	Temp. at second (third) drawing (°C)	Total Stretching Ratio	Tensile Strength (GPa)	Tensile Modulus (GPa)	TEB (J/g)	Heat of Fusion (J/g)	DSC crystallinity (%)	Uniplanar Orientation Parameter Φ (°)	Unconstrained melting temperature (°C)
E1	2	132	79	2.34	94	42.3	259	88.2%	3.7	153
E2	2	132	79	2.40	92	40.4	252	85.8%	3.0	151
E3	2	132	106	2.42	116	37.8	270	92.2%	4.5	154
E4	2	132	139	2.94	142	44.5	251	85.7%	5.7	154
E5	2	132	168	3.06	149	45.8	270	92.0%	10.2	153
E6	2	132	194	3.27	146	51.6	261	88.9%	12.6	151
E7	3	132 (132)	136	2.89	128	50.9	281	95.7%	3.7	154
E8	3	132 (132)	164	2.75	128	45.8	268	91.5%	4.2	153
E9	3	132 (132)	178	3.01	135	55.4	273	93.0%	5.9	153
E10	3	132 (132)	132	2.98	138	43.9	268	91.5%	6.1	152
E11	3	132 (132)	152	3.19	144	46.9	266	90.6%	5.8	155
E12	3	132 (132)	156	2.92	137	49.6	269	91.6%	5.9	154
E13	3	132 (132)	150	3.15	124	54.0	262	89.2%	8.6	153
E14	2	124	119	3.32	142	40.7	n.d.	n.d.	10.4	n.d.
E15	2	124	116	3.38	139	43.2	n.d.	n.d.	8.1	n.d.
E16	2	124	118	3.22	132	41.4	n.d.	n.d.	8.5	n.d.
E17	2	124	114	3.44	140	44.6	n.d.	n.d.	8.6	n.d.
E18	2	124	113	3.73	137	53.4	n.d.	n.d.	14.3	n.d.
E19	2	124	72	3.06	109	45.0	n.d.	n.d.	8.3	n.d.
E20	2	134	88	3.06	118	41.8	n.d.	n.d.	7.4	n.d.

E21	2	134	114	3.48	137	46.5	n.d.	n.d.	8.6	n.d.
E22	2	134	142	3.77	149	50.1	n.d.	n.d.	14.8	n.d.
E23	2	134	174	3.71	158	46.0	n.d.	n.d.	10.4	n.d.
E24	2	134	196	3.81	160	47.6	n.d.	n.d.	17.9	n.d.
E25	2	134	221	3.72	152	48.0	n.d.	n.d.	11.0	n.d.
E26	2	136	67	2.48	92	47.2	n.d.	n.d.	4.3	n.d.
E27	2	136	62	2.31	92	48.6	n.d.	n.d.	3.1	n.d.
E28	2	136	113	2.99	115	51.6	n.d.	n.d.	6.8	n.d.
E29	2	136	155	3.46	135	60.0	n.d.	n.d.	12.7	n.d.
E30	2	136	96	2.35	97	44.6	n.d.	n.d.	3.2	n.d.
E31	2	136	151	3.14	137	53.8	n.d.	n.d.	6.5	n.d.
E32	2	136	132	3.06	120	52.0	n.d.	n.d.	5.5	n.d.
E33	2	136	142	3.60	146	66.2	n.d.	n.d.	12.0	n.d.
E34	2	136	116	2.97	133	42.8	n.d.	n.d.	6.6	n.d.
E35	2	136	243	3.08	156	50.2	n.d.	n.d.	6.7	n.d.
E36	2	136	122	3.16	122	54.9	n.d.	n.d.	7.5	n.d.
E37	2	136	162	3.18	130	52.3	n.d.	n.d.	6.8	n.d.
E38	2	136	131	3.26	129	51.7	n.d.	n.d.	9.2	n.d.
E39	2	136	137	3.16	141	52.7	n.d.	n.d.	7.3	n.d.
E40	2	136	120	2.93	107	51.5	n.d.	n.d.	5.2	n.d.
E41	3	136 (138)	162	2.96	149	48.6	n.d.	n.d.	5.8	n.d.
E42	3	136 (138)	235	3.05	168	53.5	n.d.	n.d.	6.5	n.d.

n.d. = not determined

Comparative example 1

20 gram powder of a conventional Ziegler-Natta ultrahigh
5 molecular weight polyethylene (Ticona GUR series UHMWPE)
having a Mw of about 2 600 000, an Mn of about 360 000, an
Mw/Mn ratio of 7.22, a bulk density of 0.25 g/cm³, and an
elastic shear modulus determined directly after melting at
160°C of 1.65 MPa was used as starting material. The starting
10 polymer was compacted at an average pressure of 160 bar at a
maximum temperature of 134°C maintained for 6 minutes. The
resulted sheet was 1.15 mm thick, 610 mm long and 30mm wide.
Its density was 0.95 g/cm³. The sheet was pre-heated to 135°C
and directly rolled and stretched into a film according to the
15 above-mentioned procedure. Based on the dimensional changes
the rolling ratio was calculated as 4, the ratio of elongation
of the integrated rolling/stretching process was around 20.
The surface temperature of the roller-set was 138°C. A number
of experiments were carried out in which one, two, or three
20 stretching steps were carried out, at different temperatures
and stretching ratios. The stretching speed was adjusted so
that the temperature and stretching ratios could be obtained.
The number of stretching steps, the temperature of the
stretching steps and the total stretching ratio, which
25 includes the rolling step, are given in table 2. The
mechanical properties, Uniplanar Orientation Parameter and DSC
results of the films thus obtained are given in Table 2

Table 2.

Stretched Sample	Stretching steps	Temp. at second drawing (°C)	Temp. at third drawing (°C)	Total Stretching Ratio	Tensile Strength (GPa)	Tensile Modulus (GPa)	TEB (J/g)	Heat of Fusion (J/g)	DSC crystallinity	Uniplanar Orientation Parameter Φ (°)	Unconstrained melting temperature (°C)
CE1	2	153	-	53.6	1.43	73.2	16.9	250	85%	1.04	147.0
CE2	2	154	-	52.8	1.37	71.4	16.1	233	80%	1.18	148.8
CE3	2	154	-	51.4	1.40	70.8	18.9	264	90%	1.61	149.2
CE4	2	155	-	53.2	1.25	50.2	17.1	222	76%	1.02	151.2
CE5	2	154	-	52.4	1.45	73.1	18.1	243	83%	2.02	149.0
CE6	2	155	-	51.3	1.27	64.7	15.3	210	72%	2.09	148.9
CE7	3	153	154	101.1	1.81	103.3	19.2	272	93%	1.23	149.6
CE8	3	153	155	101.1	1.86	96.8	22.0	256	87%	1.33	148.2
CE9	3	153	156	102.5	0.97	44.9	11.8	171	58%	0.98	150.9
CE10	3	154	154	100.7	1.94	102.8	22.8	270	92%	1.29	148.4
CE11	3	154	155	102.2	1.84	96.2	20.9	262	89%	1.17	149.1
CE12	3	154	156	107.1	0.91	42.5	11.7	173	59%	0.88	149.9
CE13	3	154	154	99.7	1.86	104.1	20.0	263	90%	1.74	148.0
CE14	3	154	155	99.7	1.95	102.4	22.3	263	90%	1.86	148.5
CE15	3	154	156	99.6	1.09	53.2	13.3	211	72%	1.36	150.0
CE16	3	155	154	100.7	1.81	95.3	21.5	240	82%	1.36	150.8
CE17	3	155	155	99.0	1.65	81.0	20.4	216	74%	1.25	150.9
CE18	3	155	156	104.4	1.45	70.1	19.2	206	70%	1.36	151.4
CE19	3	154	154	100.0	1.81	98.2	19.1	245	83%	1.88	148.8
CE20	3	154	155	100.7	1.80	96.2	19.9	265	90%	1.92	151.4
CE21	3	154	156	102.8	1.29	66.0	16.0	222	76%	1.64	150.9
CE22	3	155	155	98.8	1.84	97.5	21.9	238	81%	2.32	150.7
CE23	3	155	156	96.8	1.48	77.2	19.5	203	69%	2.00	151.7
CE24	3	154	154	112.7	1.72	105.1	19.7	262	89%	1.90	148.8
CE25	3	154	154	131.9	1.72	113.8	19.6	n.d.	n.d.	2.42	n.d.
CE26	3	154	154	149.0	1.72	123.0	19.5	n.d.	n.d.	2.71	n.d.
CE27	3	154	154	168.0	1.86	131.0	19.7	n.d.	n.d.	3.01	n.d.

As can be seen from Table 2, the use of a polymer with a Mw/Mn ratio of more than 6 and an elastic shear modulus determined directly after melting at 160°C of at more than 0.9 MPa results in a material with a tensile strength and TEB which are well outside the range of the present invention. It is noted that in these Examples the films were stretched as far as they would go. It was not possible to obtain higher stretching ratios.

CLAIMS

1. UHMWPE film having a tensile strength of at least 2.0 GPa, a tensile energy to break of at least 30 J/g, an Mw of at least 500 000 gram/mole, and a Mw/Mn ratio of at most 6.

2. The UHMWPE film of claim 1 which has a tensile strength of at least 2.5 GPa, in particular at least 3.0 GPa, more in particular at least 3.5 GPa, or even at least 4.0 GPa.

3. The UHMWPE film of claim 1 or 2 which has a tensile energy to break of at least 35 J/g, in particular at least 40 J/g GPa, more in particular at least 50 J/g GPa.

4. The UHMWPE film of any one of the preceding claims which has a Mw/Mn ratio of at most 4, more in particular at most 3, even more in particular at most 2.

5. The UHMWPE film of any one of the preceding claims which has a crystalline orientation parameter of at least 3, in particular at least 4, more in particular at least 5, even more in particular at least 7, still more in particular at least 10, or at least 15.

6. The UHMWPE film of any one of the preceding claims which has an organic solvent content of less than 100 ppm.

7. A process for manufacturing the UHMWPE film according to any one of the preceding claims which comprises subjecting a starting UHMWPE with a weight average molecular weight of at least 500 000 gram/mole, an elastic shear modulus determined directly after melting at 160°C of at most 0.9 MPa, and a Mw/Mn ratio of at most 6 to a compacting step and a

stretching step under such conditions that at no point during the processing of the polymer its temperature is raised to a value above its melting point.

5 8. The process of claim 7 wherein the starting UHMWPE has an elastic shear modulus determined directly after melting at 160°C of at most 0.8 MPa, in particular at most 0.7 MPa.

10 9. The process of claim 7 or 8 wherein the compacting step is carried out at a temperature of at least 1°C below the unconstrained melting point of the polymer, in particular at least 3°C, more in particular at least 5°C, and the stretching step is carried out at a temperature of at
15 least 1°C below the melting point of the polymer under process conditions, in particular at least 3°C, more in particular at least 5°C.

 10. The process of any one of claims 7-9 wherein the
20 total stretching ratio obtained is at least 120, in particular at least 140, more in particular at least 160.

 11. Use of a UHMWPE film or the converted products thereof of any one of claims 1-6 as starting material in
25 ballistic applications, ropes, cables, nets, fabrics, and protective applications.

 12. Ballistic attributes, ropes, cables, and nets, fabrics, and protective appliances manufactured using the
30 UHMWPE film according to any one of claims 1-6.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/005385

A. CLASSIFICATION OF SUBJECT MATTER
INV. B29C55/00 B29C55/04
ADD. B29K23/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 292 074 A (STAMICARBON [NL]) 23 November 1988 (1988-11-23) cited in the application examples 3,1 column 4, line 31 - line 37	1-6, 11, 12
X	EP 0 269 151 A (DYNEEMA VOF [NL]) 1 June 1988 (1988-06-01) cited in the application example VIII; table 2 page 3, line 42 - line 43	1-6, 11, 12
X	US 5 106 558 A (KOBAYASHI KEIZO [JP] ET AL) 21 April 1992 (1992-04-21) cited in the application example 5; table 1	1-6, 11, 12
	-/---	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

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- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

27 August 2008

Date of mailing of the international search report

05/09/2008

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
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Authorized officer

Attalla, Giancarlo

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/005385

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 017 480 A (YOSHIDA SUMIO [JP] ET AL) 25 January 2000 (2000-01-25) cited in the application example 15; table 1	1-6, 11, 12
A	LI-HUI WANG ET AL: "ROLLING AND ROLL-DRAWING OF ULTRAHIGH MOLECULAR WEIGHT POLYETHYLENE REACTOR POWDERS" JOURNAL OF APPLIED POLYMER SCIENCE, JOHN WILEY AND SONS INC. NEW YORK, US, vol. 43, no. 8, 20 October 1991 (1991-10-20), pages 1559-1564, XP000240175 ISSN: 0021-8995 abstract	7-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2008/005385

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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			JP 9254252 A	30-09-1997
			NL 1005575 C2	08-07-1998
			NL 1005575 A1	23-09-1997

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)*If none of the following sub-boxes is used, this sheet should not be included in the request.*

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

DE WEIJER, Anton Peter
Driehuizer Weg 338
NL-6525 PN Nijmegen
The Netherlands

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:
NL

State (that is, country) of residence:
NL

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

VAN DE HEE, Hendrik
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NL-6716 JC Ede
The Netherlands

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:
NL

State (that is, country) of residence:
NL

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

PETERS, Martinus Wilhelmis Maria Gemma
van Nispenstraat 103
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The Netherlands

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:
NL

State (that is, country) of residence:
NL

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

RASTOGI, Sanjay
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The Netherlands

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:
NL

State (that is, country) of residence:
NL

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

☒ Further applicants and/or (further) inventors are indicated on another continuation sheet.

Supplemental Box*If the Supplemental Box is not used, this sheet should not be included in the request.*

1. *If, in any of the Boxes, except Boxes Nos. VIII(i) to (v) for which a special continuation box is provided, the space is insufficient to furnish all the information: in such case, write "Continuation of Box No." (indicate the number of the Box) and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient, in particular:*
 - (i) *if more than one person is to be indicated as applicant and/or inventor and no "continuation sheet" is available: in such case, write "Continuation of Box No. III" and indicate for each additional person the same type of information as required in Box No. III. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below;*
 - (ii) *if, in Box No. II or in any of the sub-boxes of Box No. III, the indication "the States indicated in the Supplemental Box" is checked: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the applicant(s) involved and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is applicant;*
 - (iii) *if, in Box No. II or in any of the sub-boxes of Box No. III, the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the inventor(s) and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is inventor;*
 - (iv) *if, in addition to the agent(s) indicated in Box No. IV, there are further agents: in such case, write "Continuation of Box No. IV" and indicate for each further agent the same type of information as required in Box No. IV;*
 - (v) *if, in Box No. VI, there are more than three earlier applications whose priority is claimed: in such case, write "Continuation of Box No. VI" and indicate for each additional earlier application the same type of information as required in Box No. VI.*
2. *If the applicant intends to make an indication of the wish that the international application be treated, in certain designated States, as an application for a patent of addition, certificate of addition, inventor's certificate of addition or utility certificate of addition: in such a case, write the name or two-letter code of each designated State concerned and the indication "patent of addition," "certificate of addition," "inventor's certificate of addition" or "utility certificate of addition," the number of the parent application or parent patent or other parent grant and the date of grant of the parent patent or other parent grant or the date of filing of the parent application (Rules 4.11(a)(iii) and 49bis.1(a) or (b)).*
3. *If the applicant intends to make an indication of the wish that the international application be treated, in the United States of America, as a continuation or continuation-in-part of an earlier application: in such a case, write "United States of America" or "US" and the indication "continuation" or "continuation-in-part" and the number and the filing date of the parent application (Rules 4.11(a)(iv) and 49bis.1(d)).*

FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

WANG, Bing
 Wevestraat 20
 NL-6164 XC Geleen
 The Netherlands

x applicant and inventor

State of nationality: NL
 State of residence: NL

Box No. V DESIGNATIONS

The filing of this request constitutes under Rule 4.9(a), the designation of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents. However,

- ☐ DE Germany is not designated for any kind of national protection
☐ JP Japan is not designated for any kind of national protection
☐ KR Republic of Korea is not designated for any kind of national protection
☐ RU Russian Federation is not designated for any kind of national protection

(The check-boxes above may only be used to exclude (irrevocably) the designations concerned if, at the time of filing or subsequently under Rule 26bis.1, the international application contains in Box No. VI a priority claim to an earlier national application filed in the particular State concerned, in order to avoid the ceasing of the effect, under the national law, of this earlier national application.)

Box No. VI PRIORITY CLAIM

The priority of the following earlier application(s) is hereby claimed:

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country or Member of WTO	regional application: regional Office	international application: receiving Office
item (1) 09. July 2007 (09.07.2007)	07013377.2		EP	
item (2)				
item (3)				

☐ Further priority claims are indicated in the Supplemental Box.

Transmit certified copy: the receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of this international application is the receiving Office) identified above as:

☐ all items ☒ item (1) ☐ item (2) ☐ item (3) ☐ other, see Supplemental Box

Restore the right of priority: the receiving Office is requested to restore the right of priority for the earlier application(s) identified above or in the Supplemental Box as item(s) (). (See also the Notes to Box No. VI: further information must be provided to support a request to restore the right of priority.)

Incorporation by reference: where an element of the international application referred to in Article 11(1)(iii)(d) or (e) or a part of the description, claims or drawings referred to in Rule 20.5(a) is not otherwise contained in this international application but is completely contained in an earlier application whose priority is claimed on the date on which one or more elements referred to in Article 11(1)(iii) were first received by the receiving Office, that element or part is, subject to confirmation under Rule 20.6, incorporated by reference in this international application for the purposes of Rule 20.6.

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA / EP

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year) Number Country (or regional Office)

Box No. VIII DECLARATIONS

The following declarations are contained in Boxes Nos. VIII (i) to (v) (mark the applicable check-boxes below and indicate in the right column the number of each type of declaration):

		Number of declarations
☐ Box No. VIII (i)	Declaration as to the identity of the inventor	:
☐ Box No. VIII (ii)	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent	:
☐ Box No. VIII (iii)	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application	:
☒ Box No. VIII (iv)	Declaration of inventorship (only for the purposes of the designation of the United States of America)	1
☐ Box No. VIII (v)	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	:

Box No. IX CHECK LIST; LANGUAGE OF FILING

This international application contains:	This international application is accompanied by the following item(s) (mark the applicable check-boxes below and indicate in right column the number of each item):	Number of items
(a) on paper, the following number of sheets:	1. ☒ fee calculation sheet	1
request (including declaration and supplemental sheets) :	2. ☐ original separate power of attorney	:
description (excluding sequence listing and/or tables related thereto) :	3. ☐ original general power of attorney	:
claims :	4. ☒ copy of general power of attorney; reference number, if any: 42651	1
abstract :	5. ☐ statement explaining lack of signature	:
drawings :	6. ☐ priority document(s) identified in Box No. VI as item(s):	:
Sub-total number of sheets :	7. ☐ translation of international application into (language):	:
sequence listing :	8. ☐ separate indications concerning deposited microorganism or other biological material	:
tables related thereto :	9. ☐ sequence listing in electronic form (indicate type and number of carriers)	:
(for both, actual number of sheets if filed on paper, whether or not also filed in electronic form; see (c) below)	(i) ☐ copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application)	:
Total number of sheets :	(ii) ☐ (only where check-box (b)(i) or (c)(i) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Rule 13ter	:
31	(iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listing mentioned in left column	:
	10. ☐ tables in electronic form related to sequence listing (indicate type and number of carriers)	:
	(i) ☐ copy submitted for the purposes of international search under Section 802(b-quater) only (and not as part of the international application)	:
	(ii) ☐ (only where check-box (b)(ii) or (c)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Section 802(b-quater)	:
	(iii) ☐ together with relevant statement as to the identity of the copy or copies with the tables mentioned in left column	:
	11. ☐ other (specify):	:
(b) ☐ only in electronic form (Section 801(a)(i))		
(i) ☐ sequence listing		
(ii) ☐ tables related thereto		
(c) ☐ also in electronic form (Section 801(a)(ii))		
(i) ☐ sequence listing		
(ii) ☐ tables related thereto		
Type and number of carriers (diskette, CD-ROM, CD-R or other) on which are contained the		
☐ sequence listing:		
☐ tables related thereto:		
(additional copies to be indicated under items 9(ii) and/or 10(ii), in right column)		

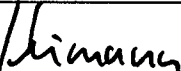
Figure of the drawings which should accompany the abstract:

Language of filing of the international application:

english

Box No. X SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).



Dr. A. Heimann

A.P. De Weijer

H. van de Hee

M.W.M.G. Peters

S. Rastogi

B. Wang

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1. Date of actual receipt of the purported international application: (02.07.08) 02 JUL 2008	2. Drawings: ☐ received: ☐ not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):	
5. International Searching Authority (if two or more are competent): ISA /	6. ☐ Transmittal of search copy delayed until search fee is paid

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From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF RECEIPT OF
RECORD COPY

LAD	HEI	OBE	SCR	REI
BEN	CPW	GmbH	HEIMANN, Anette	
	08. OKT. 2008		CPW GmbH	
			Kasinostrasse 19-21	
			42103 Wuppertal	
			ALLEMAGNE	
			Tax: 0202. 32.4224	
			SK	SV

Date of mailing (day/month/year)
07 October 2008 (07.10.2008)

IMPORTANT NOTIFICATION

Applicant's or agent's file reference
CQN 2722 WO

International application No.
PCT/EP2008/005385

The applicant is hereby notified that the International Bureau has received the record copy of the international application as detailed below.

Name(s) of the applicant(s) and State(s) for which they are applicants:

TEIJIN ARAMID B.V. (for all designated States except US)
DE WEIJER, Anton, Peter et al (for US)

International filing date:

02 July 2008 (02.07.2008)

Priority date(s) claimed:

09 July 2007 (09.07.2007)

Date of receipt of the record copy by the International Bureau:

21 July 2008 (21.07.2008)

List of designated Offices:

AP: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW

EA: AM, AZ, BY, KG, KZ, MD, RU, TJ, TM

EP: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR

OA: BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG

National: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW

ATTENTION: The applicant should carefully check the data appearing in this notification. In case of any discrepancy between these data and the indications in the international application, the applicant should immediately inform the International Bureau. In addition, the applicant's attention is drawn to the information contained in the Annex, relating to:

- time limits for entry into the national phase - see updated important information (as of April 2002)
- requirements regarding priority documents (if applicable)

A copy of this notification is being sent to the receiving Office and to the International Searching Authority.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer

Rochaix Thomas

Facsimile No. +41 22 338 89 70

e-mail pt06.pct@wipo.int

Telephone No. +41 22 338 74 06

Form PCT/IB/301 (October 2005)

1/DTREEZISZ0

PATENT COOPERATION TREATY

PCT/EP2008/005385

LAD	HEI	OBE	SCR	REI
BEN	CPW GmbH			AMA
BUL	03. DEZ. 2008			ULR
DK	PT	US	CA	SV

PCT

NOTIFICATION OF THE RECORDING
OF A CHANGE

From the INTERNATIONAL BUREAU

To:

HEIMANN, Anette
CPW GmbH
Kasinostrasse 19-21
42103 Wuppertal
ALLEMAGNE

(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

Date of mailing (day/month/year) 20 November 2008 (20.11.2008)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference CQN 2722 WO	
International application No. PCT/EP2008/005385	International filing date (day/month/year) 02 July 2008 (02.07.2008)

1. The following indications appeared on record concerning:

☒ the applicant ☒ the inventor ☐ the agent ☐ the common representative

Name and Address

WANG, Bing
Wevestraat 20
NL-6164 XC Geleen
Netherlands

State of Nationality

NL

State of Residence

NL

Telephone No.

Facsimile No.

E-mail address

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☒ the person ☐ the name ☐ the address ☐ the nationality ☐ the residence

Name and Address

State of Nationality

State of Residence

Telephone No.

Facsimile No.

E-mail address

☐ Notifications by e-mail authorized

3. Further observations, if necessary:

The person identified in Box 1 is now recorded as applicant for the United States of America only and inventor for all designated States.

4. A copy of this notification has been sent to:

☒ the receiving Office ☐ the designated Offices concerned
☐ the International Searching Authority ☐ the elected Offices concerned
☐ the International Preliminary Examining Authority ☐ other:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer

Fourné-Godbersen Margret

e-mail pt06.pct@wipo.int

Telephone No. +41 22 338 74 06

Facsimile No. +41 22 338 89 70

Form PCT/IB/306 (July 2008)

1/DU40WA6S0

110

PATENT COOPERATION TREATY

PCT

From the INTERNATIONAL SEARCHING AUTHORITY

To:

CPW GMBH
Attn. Heimann, Anette
Kasinostrasse 19-21
D-42103 Wuppertal
ALLEMAGNE

LAD	~~BE~~	OBE	SCR	REL
BEN	CPW GmbH			AMA
BUL	23. DEZ. 2008			ULR
DK	PT		UE	SK/3V

NOTIFICATION OF DECISION CONCERNING REQUEST FOR RECTIFICATION

(PCT Rule 91.3(a) and (d))

Applicant's or agent's file reference

CQN 2722 WO

International application N°.

PCT/EP2008/005385

Applicant

TEIJIN ARAMID B.V.

Date of mailing
(day/month/year)

18/12/2008

REPLY-DUE

NONE

However, see last paragraph below

International filing date
(day/month/year)

02/07/2008

The applicant is hereby notified that this International Searching Authority has considered the request for rectification of obvious errors in the international application/in other papers submitted by the applicant to this Authority, and that it has decided:

1. a. ☒ to authorize the rectification:

☒ as requested by the applicant.

☐ to the extent set forth below*:

b. ☒ The rectification **will be or has been taken into account** for the purposes of the international search (Rule 43.6bis (a)).

☐ The rectification **has not been taken into account** because it was authorized by this Authority after this Authority has begun to draw up the international search report (Rule 43.6bis (b)).

2. ☐ to refuse to authorize the rectification or part of it for the following reasons*:

A copy of this notification, together with a copy of the applicant's request for rectification, has been sent to the receiving Office and to the International Bureau.

* **If the authorization of the rectification has been refused in whole or in part**, the applicant may request the International Bureau, within two months from the date of the refusal and subject to the payment of a special fee, to publish the request for rectification and the reasons for refusal by this Authority and any further brief comments that may be submitted by the applicant together with the international application. See rule 91.3(d) and, for the amount of the fee, see the **PCT Applicant's Guide**, Volume I, Annex B2(1B).

Name and mailing address of the International Searching Authority



European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Marie-Laure Dupont-Hüper

CPW

REC'D 03 NOV 2008

WIPO PCT

Intellectual Property Services

RECEIVED AT ISA/EP ON 17-11-2008

CPW GmbH * Postfach 10 01 49 * D-42097 Wuppertal

World Intellectual
Property Organization
34, chemin des Colombettes
P.O. Box 18

CH-1211 Geneva
Switzerland

Your reference

Our reference
CQN 2722 WO
LAD

Phone/Telefax
Tel. +49 (202) 32-4210
Fax +49 (202) 32-4224

Wuppertal
28.10.2008
Sch.462

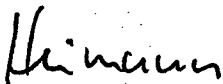
International Patent Application No. PCT/EP2008/005385
Applicant: Teijin Aramid B.V.

Herewith a request for a correction is filed.

In claim 5 of the above named application a "crystalline orientation parameter" is mentioned. The term "crystalline" is incorrect and an obvious error. On page 5, line 13 to 20 and page 7, line 10 to 15 of the specification the parameter is specified as "uniplanar orientation parameter".

Therefore, the applicant files a new page 24, which should replace the present page 24. In claim 5 of new page 24 the term "crystalline orientation parameter" is amended to "uniplanar orientation parameter".

We kindly ask for correction.



Dr. A. Heimann
(GA 42651)

CPW GmbH

Kasinostraße 19-21
D-42103 Wuppertal
Telefon +49 (202) 32-4212
Telefax +49 (202) 32-4224
kontakt@cpw-wuppertal.de

CLAIMS

1. UHMWPE film having a tensile strength of at least 2.0 GPa, a tensile energy to break of at least 30 J/g, an Mw of at least 500 000 gram/mole, and a Mw/Mn ratio of at most 6.

2. The UHMWPE film of claim 1 which has a tensile strength of at least 2.5 GPa, in particular at least 3.0 GPa, more in particular at least 3.5 GPa, or even at least 4.0 GPa.

3. The UHMWPE film of claim 1 or 2 which has a tensile energy to break of at least 35 J/g, in particular at least 40 J/g GPa, more in particular at least 50 J/g GPa.

4. The UHMWPE film of any one of the preceding claims which has a Mw/Mn ratio of at most 4, more in particular at most 3, even more in particular at most 2.

5. The UHMWPE film of any one of the preceding claims which has a uniplanar orientation parameter of at least 3, in particular at least 4, more in particular at least 5, even more in particular at least 7, still more in particular at least 10, or at least 15.

6. The UHMWPE film of any one of the preceding claims which has an organic solvent content of less than 100 ppm.

7. A process for manufacturing the UHMWPE film according to any one of the preceding claims which comprises subjecting a starting UHMWPE with a weight average molecular weight of at least 500 000 gram/mole, an elastic shear modulus determined directly after melting at 160°C of at most 0.9 MPa, and a Mw/Mn ratio of at most 6 to a compacting step and a

From the INTERNATIONAL BUREAU

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SECOND AND SUPPLEMENTARY NOTICE
INFORMING THE APPLICANT OF THE
COMMUNICATION OF THE INTERNATIONAL
APPLICATION (TO DESIGNATED OFFICES
WHICH APPLY THE 30 MONTH TIME
LIMIT UNDER ARTICLE 22(1))

(PCT Rule 47.1(c))

To:

HEIMANN, Anette
CPW GmbH
Kasinostrasse 19-21
42103 Wuppertal
ALLEMAGNE

LAD	HEI	OBE	SCR	REI
BER	CPW GmbH			AMA
BUL	23. NOV. 2009			ULR
DK	BT		UE	SK SV

Date of mailing (day/month/year)

12 November 2009 (12.11.2009)

Applicant's or agent's file reference

CQN 2722 WO

IMPORTANT NOTICE

International application No.

PCT/EP2008/005385

International filing date (day/month/year)

02 July 2008 (02.07.2008)

Priority date (day/month/year)

09 July 2007 (09.07.2007)

Applicant

TEIJIN ARAMID B.V. et al

- ATTENTION:** For any designated Office(s), for which the time limit under Article 22(1), as in force from 1 April 2002 (30 months from the priority date), **does not apply**, please see Form PCT/IB/308(First Notice) issued previously.
- Notice is hereby given that the following designated Office(s), for which the time limit under Article 22(1), as in force from 1 April 2002, **does apply**, has/have requested that the communication of the international application, as provided for in Article 20, be effected under Rule 93bis.1. The International Bureau has effected that communication on the date indicated below:
15 January 2009 (15.01.2009)

AU, AZ, BY, CN, CO, DZ, EP, HU, KG, KP, KR, MD, MK, MY, MZ, NA, NG, PG, RU, SY, TM, US

In accordance with Rule 47.1(c-bis)(i), those Offices will accept the present notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

- The following designated Offices, for which the time limit under Article 22(1), as in force from 1 April 2002, **does apply**, have not requested, as at the time of mailing of the present notice, that the communication of the international application be effected under Rule 93bis.1:

AE, AG, AL, AM, AO, AP, AT, BA, BB, BG, BH, BR, BW, BZ, CA, CH, CR, CU, CZ, DE, DK, DM, DO, EA, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, ID, IL, IN, IS, JP, KE, KM, KN, KZ, LA, LC, LK, LR, LS, LT, LY, MA, ME, MG, MN, MW, MX, NI, NO, NZ, OA, OM, PH, PL, PT, RO, RS, SC, SD, SE, SG, SK, SL, SM, SV, TJ, TN, TR, TT, UA, UZ, VC, VN, ZA, ZM, ZW

In accordance with Rule 47.1(c-bis)(ii), those Offices accept the present notice as conclusive evidence that the Contracting State for which that Office acts as a designated Office does not require the furnishing, under Article 22, by the applicant of a copy of the international application.

4. TIME LIMITS for entry into the national phase

For the designated or elected Office(s) listed above, the applicable time limit for entering the national phase will, **subject to what is said in the following paragraph**, be **30 MONTHS** from the priority date.

In practice, **time limits other than the 30-month time limit** will continue to apply, for various periods of time, in respect of certain of the designated or elected Office(s) listed above. For **regular updates on the applicable time limits** (30 or 31 months, or other time limit), Office by Office, refer to the *PCT Gazette*, the *PCT Newsletter* and the *PCT Applicant's Guide*, Volume II, National Chapters, all available from WIPO's Internet site, at <http://www.wipo.int/pct/en/index.html>.

It is the applicant's **sole responsibility** to monitor all these time limits.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer

Agnes Wittmann-Regis

Facsimile No. +41 22 338 82 70

e-mail: pt06.pct@wipo.int

From the INTERNATIONAL BUREAU

PCT

FIRST NOTICE INFORMING THE APPLICANT OF
THE COMMUNICATION OF THE INTERNATIONAL
APPLICATION (TO DESIGNATED OFFICES WHICH
DO NOT APPLY THE 30 MONTH TIME LIMIT
UNDER ARTICLE 22(1))

(PCT Rule 47.1(c))

To:	LAD	HEI	OBE	S. R.	REI
HEIMANN, Anette	CPW GmbH		20. FEB. 2009		
CPW GmbH			ARMA		
Kasinostrasse 19-21			ULR		
42103 Wuppertal					
ALLEMAGNE	DK	BT		DF	SV

Date of mailing (day/month/year) 12 February 2009 (12.02.2009)		IMPORTANT NOTICE	
Applicant's or agent's file reference CQN 2722 WO			
International application No. PCT/EP2008/005385	International filing date (day/month/year) 02 July 2008 (02.07.2008)	Priority date (day/month/year) 09 July 2007 (09.07.2007)	
Applicant TEIJIN ARAMID B.V. et al			

1. **ATTENTION:** For any designated Office(s), for which the time limit under Article 22(1), as in force from 1 April 2002 (30 months from the priority date), **does apply**, please see Form PCT/IB/308(Second and Supplementary Notice) (to be issued promptly after the expiration of 28 months from the priority date).

2. Notice is hereby given that the following designated Office(s), for which the time limit under Article 22(1), as in force from 1 April 2002, **does not apply**, has/have requested that the communication of the international application, as provided for in Article 20, be effected under Rule 93bis.1. The International Bureau has effected that communication on the date indicated below:
15 January 2009 (15.01.2009)

None

In accordance with Rule 47.1(c-bis)(i), those Offices will accept the present notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

3. The following designated Offices, for which the time limit under Article 22(1), as in force from 1 April 2002, **does not apply**, have not requested, as at the time of mailing of the present notice, that the communication of the international application be effected under Rule 93bis.1 :

LU, TZ, UG

In accordance with Rule 47.1(c-bis)(ii), those Offices accept the present notice as conclusive evidence that the Contracting State for which that Office acts as a designated Office does not require the furnishing, under Article 22, by the applicant of a copy of the international application.

4. TIME LIMITS for entry into the national phase

For the designated Office(s) listed above, and unless a demand for international preliminary examination has been filed before the expiration of **19 months** from the priority date (see Article 39(1)), the applicable time limit for entering the national phase will, **subject to what is said in the following paragraph**, be **20 MONTHS** from the priority date.

In practice, **time limits other than the 20-month time limit** will continue to apply, for various periods of time, in respect of certain of the designated Offices listed above. For **regular updates on the applicable time limits** (20 or 21 months, or other time limit), Office by Office, refer to the *PCT Gazette*, the *PCT Newsletter* and the *PCT Applicant's Guide*, Volume II, National Chapters, all available from WIPO's Internet site, at <http://www.wipo.int/pct/en/index.html>.

It is the applicant's **sole responsibility** to monitor all these time limits.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

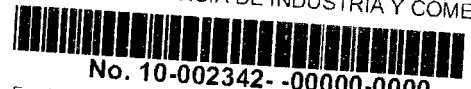
Facsimile No. +41 22 338 82 70

Authorized officer

Agnes Wittmann-Regis

e-mail: pt06.pct@wipo.int

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 10-002342- -00000-0000

Fecha: 2010-01-12 16:24:58 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 115



LISTA DE CHEQUEO
ADMISIÓN A TRÁMITE - NUEVAS CREACIONES

PATENTE DE INVENCION ☐

MODELO DE UTILIDAD ☐

Art 33 Decisión 486/00

☐	Indicación que se solicita una patente.
☐	Datos de identificación del solicitante o de la persona que presenta la solicitud
☐	Descripción de la invención
☐	Dibujos de ser estos pertinentes
☐	Comprobante de pago de las tasas establecidas (De ser el caso formato de descuento)
Completa ☐ Incompleta ☐	

PATENTE DE INVENCION PCT ☒

MODELO DE UTILIDAD PCT ☐

Art.33 Decisión 486/00, Circular Única

☒	Indicación que se solicita una PCT
☒	Copia de la solicitud en español, tal como fue presentada inicialmente (capítulo descriptivo, reivindicatorio, resumen)
☐	Dibujos de ser estos pertinentes
☒	Comprobante de pago de las tasas establecidas (de ser el caso formato de descuento)
Completa ☒ Incompleta ☐	

DISEÑO INDUSTRIAL ☐

(Art. 119 Decisión 486/00)

☐	Indicación que se solicita Diseño industrial
☐	Datos de identificación del solicitante o de la persona que presenta la solicitud
☐	Representación gráfica y fotográfica del Diseño industrial o muestra del material que incorpora el diseño
☐	Comprobante de pago de las tasas establecidas
Completa ☐ Incompleta ☐	

ESQUEMA DE TRAZADO ☐

(Art. 92 Decisión 486/00)

☐	Indicación que se solicita un esquema de trazado
☐	Datos de identificación del solicitante o de la persona que presenta la solicitud
☐	Representación gráfica de un esquema de trazado
☐	Comprobante de pago de las tasas establecidas
Completa ☐ Incompleta ☐	