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(54) **POLYOLEFIN SHEET**

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(57) **ABSTRACT**

A process for production of an article from a woven fabric of melt spun and drawn fibers or tapes of oriented polypropylene homopolymer or copolymer is disclosed, comprising subjecting the woven fabric of melt spun and drawn fibers or tapes to elevated temperature and pressure sufficient to melt a proportion of the polymer, characterised in that the draw ratio of said melt spun and drawn fibers or tapes is at least 7:1.

POLYOLEFIN SHEET

[0001] The present invention relates to polymer sheet materials made from oriented olefin polymer fibres or tapes, and to processes for making such materials.

[0002] In recent years, developments have been made in processes for compacting polyolefin fibres in order to make films of high-strength Two-step compaction processes for melt-spun fibres employing high compaction pressures are well known. An example is disclosed in GB 2253420A, in which an assembly of fibres of an oriented polymer are hot compacted in a two-step process to form a sheet having good mechanical properties. The process involves an initial step in which the fibres are brought to and held at the compaction temperature whilst subject to a pressure sufficient to maintain the fibres in contact, and thereafter compacted at a high pressure (40-50 MPa) for a few seconds (the compaction pressure). In this process a-proportion of the fibre surfaces, generally from 5 to 10 percent by weight, melt and subsequently recrystallise on cooling. This recrystallized phase binds the fibres together, resulting in good mechanical properties of the final sheet.

[0003] In WO 98/15397, an improvement to the above process is disclosed in which an assembly of melt-formed fibres is maintained in intimate contact at elevated temperature sufficient to melt a proportion of the fibres, whilst being subjected to a compaction pressure of no greater than 10 MPa. This single-step, low-pressure process also produces products having excellent mechanical properties.

[0004] In the above processes, the melt-formed fibres or tapes employed are commercially available products such as BP Amoco Propex® polypropylene tape. These tapes have a draw ratio of 6:1 (i.e. they are stretched to 6 times their original length during the melt-forming process).

[0005] In Plastics, Rubber and Composites Processing and Applications, 1998, Vol 27, No. 4, pgs 167-171, the present inventors disclose the compaction of unidirectional (unwoven) slit films and fibres, some of which are "highly drawn", i.e. they have a draw ratio greater than the usual 6:1. FIG. 5 (page 169) shows that the modulus of the compacted sheet formed from the highly drawn fibres is only slightly higher than that of the sheet formed from the tapes of lower modulus. As a result, it is concluded (beginning of page 170) that "there is therefore little point in using one of the more expensive, highly drawn polypropylene fibres, as their properties and structure revert to those of the much lower modulus, and much cheaper, tapes".

[0006] The modulus of woven fabrics is theoretically expected to be at least half that of the fibres forming those fabrics, as the consequence of cross-plying the fibres is a reduction in the modulus by a factor of at least 2. However, we have now discovered that if more highly drawn polypropylene tapes or fibres are compacted in the form of a woven fabric (rather than as a collection of unidirectional fibres or tapes), not only is it possible to obtain modulus values much greater than would be expected from the article above, but additionally it is possible to obtain products having mechanical properties which are improved in several other respects.

[0007] Accordingly in a first aspect, the present invention provides an article comprising melt-formed fibres of oriented polypropylene homopolymer or copolymer in the form of a woven fabric which has been subjected to hot compaction, characterised in that said melt-formed fibres have a draw ratio of at least 7:1.

[0008] A further aspect of the invention provides a process for production of an article from a woven fabric of melt-formed fibres of oriented polypropylene, homopolymer or copolymer, comprising subjecting the woven fabric of melt-formed fibres to elevated temperature and pressure sufficient to melt a proportion of the polymer, characterised in that the draw ratio of said melt-formed fibres is at least 7:1.

[0009] The article of the invention is preferably monolithic, which is to say that it is comprised of a single type of structure, namely an array of fibres or tapes surrounded by a solidified melt phase of the same material.

[0010] The term "melt-formed fibres" is used herein to mean strands of polypropylene which have been formed via molten polymer. They may be non-woven melt-spun and drawn fibres laid in a web, or melt-spun and drawn fibres comprised within yarns, or they may be in the form of woven bands or tapes, formed for example by initially slitting melt formed films prior to tensile drawing. The fibres are usually formed into a woven fabric by weaving or knitting. Optionally the fibres may have been subjected to a crosslinking process, as described in WO 98/15397.

[0011] The woven fabrics may comprise only fibres, or they may comprise a mixture of fibres and tapes. Most preferred are fabrics which are woven from flat tapes, as these have the best mechanical properties.

[0012] The term "hot compaction" means any process in which the polypropylene fibres are subjected to elevated temperature and pressure such that a proportion of the fibres is melted.

[0013] It is preferred that the hot compaction process of the invention uses a compaction pressure not exceeding 10 MPa. It is also preferred that a single pressure is used throughout the hot compaction process. Most preferred pressures are between 1 and 7 MPa, particularly between 2 and 5 MPa.

[0014] Preferably, the temperature at which the fibres are compacted is no greater than the peak temperature of melting at the ambient compaction pressure—i.e. the temperature of which the endotherm measured by Differential Scanning Calorimetry (DSC) of the constrained polymer fibres reaches its highest point. The minimum temperature at which the fibres should be compacted is preferably that at which the leading edge of the endotherm extrapolated to zero intersects the temperature axis. The proportion of the fibres which is melted during the hot compaction process is generally between 10 and 50 percent by weight.

[0015] Preferably the fibres used in the present invention have a weight average molecular weight (Mw) in the range of 100,000 to 800,000, preferably 250,000 to 450,000, for example 330,000 to 400,000. The polymer is preferably a polypropylene homopolymer, but may be a copolymer comprising polypropylene, in which case a copolymer comprising at least 50% polypropylene is preferred. Generally any copolymer containing polypropylene such as those disclosed in WO 98/15397 may be used.

[0016] Articles produced according to the present invention have improved mechanical properties compared with

those disclosed in the prior art in several different respects. We have found that the modulus of such articles is significantly higher than would be expected in view of the prior art; additionally, both the impact resistance and the thermal resistance are higher. The improvements in these latter properties are also surprising.

[0017] A preferred draw ratio is at least 8:1, more preferably at least 9:1. A draw ratio of 9:1 to 15:1, particularly 9:1 to 11:1, is preferred, as at higher draw ratios it is possible that polypropylene fibres or tapes may be too inelastic to be utilised effectively in the invention.

[0018] Compaction of the polypropylene may be carried out in an autoclave, or in a belt press or other apparatus in which the assembly is fed through a compaction zone where it is subjected to the required elevated temperature and pressure. Thus, the process may be operated as a continuous or semi-continuous process.

[0019] In one process, a woven fabric or assembly of woven fabrics of polypropylene fibre or tape is placed in a bench press and subjected to a slight contact pressure at elevated temperature, which is maintained until the required degree of melting has occurred. At this point, the compaction pressure is then applied after which the fabric is cooled under the compaction pressure before being removed from the bench press.

EXAMPLES

Example 1—Preparation of Compacted Sheet

[0020] Two fabrics having different draw ratios were compacted in a continuous process using a belt press. The fabrics were the following:

[0021] Fabric V1: woven polypropylene fabric available from Amoco as Propex® Geotextile type 6060, having a draw ratio of 6:1.

[0022] Fabric V2: woven polypropylene fabric available from Amoco as Propex® Geotextile type 6060, having a draw ratio of 10:1.

[0023] The two fabrics were compacted on a double belt press manufactured by Hymmen GmbH, of Bielefeld, Germany. The compaction conditions were slightly different, as the higher draw ratio V2 material has a higher melting point. The conditions were as follows:

[0024] V1: compaction was at 186° C., at a pressure of 4 MPa, and a belt speed of 3.0 m/min.

[0025] V2: compaction was at 192° C., at a pressure of 4 MPa, and a belt speed of 2.5 m/min.

[0026] The resulting compacted materials used for the tests below were in the form of sheets of 0.9 mm thickness.

Physical Properties

Example 2: Tensile Properties

[0027] Test method A of ASTM D882 (constant rate of separation of the grips) was used. The shape of the samples defined in this standard is a simple rectangle of gauge length 250 mm and width specified as a minimum of eight times the thickness (a width of 10 mm, approximately eleven times the thickness was used). An extra 50 mm length was allowed for gripping the sample, making a total length of 300 mm.

[0028] Samples of the product made in Example 1 were cut to the required dimensions by guillotine. This produced a high quality edge on the sample with no nicks or burrs. The thickness of the samples varied between 0-863 mm and 0-930 mm for V1 material and 0-870 mm and 0-931 mm for V2 material.

[0029] After preparation the samples were stored in polyethylene sample bags in a temperature controlled laboratory (20±2° C.) for 48 hours prior to testing.

[0030] The tests were performed on an Instron model 4505 testing machine, using a video extensometer supplied by RDP Howden Ltd. to track targets (white paint lines on the black polypropylene sheet) placed 50 mm apart on the samples. A previously untested sample was used for each test, and 5 samples were tested for each material for each property (modulus and strength) at a temperature of 20±2° C. The modulus samples were held in standard 1 kN pneumatic grips whilst the strength samples were held in 5 kN self tightening grips, which provided sufficient force to prevent slippage.

[0031] The crosshead speed for modulus determination was set at 25 mm min^{-1}, for strength determination it was 125 mm min^{-1}.

[0032] Nominal Strength

[0033] The nominal strength was determined from the peak load exhibited by the material, by dividing the peak load in Newtons by the cross sectional area in square metres. This peak load occurred immediately prior to the sample failing. The results are shown in Table 1 below.

TABLE 1

Material	Average Strength (MPa)	Standard Deviation
V1	86.2	5.01
V2	166	16.2

[0034] Elongation at Break

[0035] The elongation at break was determined from the extensometer as the point at which an instantaneous reduction in load of greater than 40% occurred. The results are shown in Table 2 below.

TABLE 2

Material	Average Elongation (%)	Standard Deviation
V1	20.6	2.20
V2	13.9	0.90

[0036] Modulus

[0037] Modulus was determined in the initial linear region of the stress strain curve using the software supplied with the video extensometer following ASTM D638. The results are shown in Table 3 below.

TABLE 3

Material	Average Modulus (GPa)	Standard Deviation
V1	3.25	0.16
V2	4.23	0.22

[0038] It can be seen from the above results of that the V2 material has 30% better modulus and 100% better strength than the V1 material. The lower elongation to break of the V2 compared with the V1 is attributable to the higher draw ratio of the V2 material, which is known to lead to a reduction in elasticity.

Example 3: Notched Izod Impact

[0039] Samples for testing were machined from thick sheets of compacted polypropylene, prepared by taking several 0.9 mm sheets prepared as above and gluing them together using Gluco (polypropylene) adhesive. The samples were as defined in the ASTM standard (rectangular bars 60.4 mm long, 12.7 mm high and approximately 5 mm thick with a notch of 2.5 mm depth 31.5 mm from one end).

[0040] The samples were tested on a Rosand Type 5 Instrumented Impact Tester with a specially designed anvil to hold the samples in place. The samples were struck with a wedge shaped dart with a rounded tip 22 mm from the notch at a speed of 3.46 m/sec. A 25 kg weight was attached to the dart to provide the necessary energy to break the sample.

[0041] Five samples were tested at each temperature tested. The energy per metre of notch was determined by dividing the energy recorded from the Rosand by the width of the sample.

[0042] The results are shown in Table 4 below. The samples exhibited two types of break:

[0043] H—Hinge break, the sample had broken more than 90% of the way through but was unable to support itself when held by one end.

[0044] N—No break, the sample had broken than less 90% of the way through.

TABLE 4

		Impact Energy		
Material	Temperature ° C.	$\bar{x}$	σ	Break Type
V1	−40	3976	378	H
V2	−40	7522	552	N
V1	20	3310	392	H
V2	20	4756	164	N

[0045] The above results show that the higher draw ratio V2 material exhibits a significant increase in the notched impact energy over the V1 material. This is surprising, as it is not possible to predict with any confidence from theory what effect increasing the draw ratio of the initial fibres would have on the impact performance of a compacted sheet.

Example 4: High Speed Puncture

[0046] As specified by the standard, these tests were performed on a Rosand Type 5 instrumented impact tester using a falling dart (with a spherical tip of 12.7 mm diameter) attached to a 25 kg weight with an impact speed of 200 m min^{-1}. The samples were gripped between steel plates 120 mm square with a 76 mm diameter aperture in the centre. The side of the steel plates in contact with the sheet had emery paper stuck to it to provide extra gripping force.

[0047] Samples 120 mm square were cut from the sheets prepared as in Example 1 above using a guillotine. These were then kept in polyethylene sample bags in a temperature controlled laboratory (20±2° C.) for 48 hours prior to testing. All samples were between 0.89 mm to 0.93 mm thick.

[0048] The tests were conducted at a variety of temperatures ranging from −40° C. to 100° C., and five samples were tested at each temperature. At temperatures other than room temperature (20° C.) the sample was allowed 10 minutes to stabilise at temperature before testing.

Definitions

[0049] Peak Force

[0050] The peak force is the maximum decelerating force experienced by the dart as it passes through the sample, and usually occurs at the point of rupture of the sample.

[0051] Distance to Peak

[0052] The distance to peak is the distance travelled by the dart from first contacting the sample to experiencing the peak force. It is therefore the amount of deflection that occurs in the sample.

[0053] Energy to Peak

[0054] The energy to peak is the energy absorbed by the material from the point at which the dart makes contact until the peak force is experienced. It is calculated by integrating to obtain the area under the force extension curve.

[0055] The results are shown in Tables 5 to 7 below.

TABLE 5

	Peak Force (kN) - $\bar{x}$			
	V1		V2	
Temperature (° C.)	$\bar{x}$	σ	$\bar{x}$	σ
−40	1.95	0.22	3.37	0.15
20	1.73	0.13	2.96	0.15
70	1.29	0.20	2.89	0.08
100	1.77	0.13	3.05	0.28

[0056]

TABLE 6

	Distance To Peak Force (mm) - $\bar{x}$			
Temperature	V1		V2	
(° C.)	$\bar{x}$	σ	$\bar{x}$	σ
−40	7.65	0.58	9.26	0.45
20	11.81	0.69	12.27	0.84

TABLE 6-continued

Temperature	Distance To Peak Force (mm) - $\bar{x}$			
	V1		V2	
(° C.)	$\bar{x}$	σ	$\bar{x}$	σ
70	10.69	0.74	13.63	0.97
100	12.75	1.35	14.97	0.56

[0057]

TABLE 7

Temperature	Energy to Peak (J) - $\bar{x}$			
	V1		V2	
(° C.)	$\bar{x}$	σ	$\bar{x}$	σ
−40	7.07	1.00	14.05	1.45
20	8.18	0.84	14.12	0.36
70	5.96	1.46	17.57	2.03
100	10.60	0.87	21.65	2.75

[0058] From the above results, it can be seen that the V2 material is better than the V1 material at all temperatures tested. It should be noted that the results obtained for the V1 material at 70° C. appear to be anomalous. As with the notched Izod results above, the superiority of the V2 material over the V1 material is not predictable from theory, and is therefore particularly unexpected. The increase in energy absorbed as the temperature is increased is likely to be caused by the increase in extensibility of the tape at the elevated temperature, resulting in greater energy absorption even though the strength and modulus of the tape will have decreased.

Example 5: Heat Deflection Temperature

[0059] Sheets of compacted polypropylene approximately 5 mm thick were prepared by using Gluco adhesive to stick together 6 sheets of 0.9 mm thick sheet prepared as in Example 1 above. The resulting thick sheets were then machined into the specimen geometry stated in the standard (rectangular bars 120 mm long and 13 mm high with a thickness of between 3 mm and 13 mm).

[0060] The bars were loaded into a three point bend apparatus with a 100 mm span which was then immersed in an silicon oil bath.

[0061] The mass placed on the centre point of the three point load mechanism was determined from the following equation:

$$P = \frac{2Sbd^2}{3L} \quad (1)$$

[0062] where

[0063] P=the applied load in Newtons

[0064] S=the desired stress level (455 kPa or 1820 kPa)

[0065] b=the width of the sample (m)

[0066] d=the depth of the sample (0.013 m)

[0067] L=the span (0.1 m)

[0068] The load was applied for five minutes before the dial gauge attached to the three point bend rig was zeroed and heating of the oil bath initiated. The bath was heated at a constant rate of 2° C. per minute and was stirred continuously.

[0069] The heat deflection temperature is defined as the temperature at which the centre of the test specimen has deflected by 0.25 mm, and the test was stopped at this point.

[0070] Two samples were tested at each stress level for each material. The results are shown in Table 8 below.

TABLE 8

Material	Stress Level (kPa)	Temperature (° C.)
V1	455	156
V2	455	160
V1	1820	92
V2	1820	102

[0071] The conclusion from the above results is that both materials exhibit a high heat deflection temperature at the low stress level, with heat deflection temperatures superior to unfilled polypropylene (100° C.) and comparable with 40% short glass fibre filled polypropylene (157° C.). The V2 material is slightly but significantly better than the V1 material at both stress levels.

1. Process for production of an article from a woven fabric of melt-formed fibres or tapes of oriented polypropylene homopolymer or copolymer, comprising subjecting the woven fabric of melt-formed fibres or tapes to elevated temperature and pressure sufficient to melt a proportion of the polymer, characterised in that the draw ratio of said fibres or tapes is at least 7:1.

2. Process according to claim 1, wherein the compaction pressure does not exceed 10 MPa.

3. Process according to claim 1 or **2**, wherein the compaction pressure is between 1 and 7 MPa, preferably between 2 and 5 MPa.

4. Process according to any preceding claim, wherein a single pressure is used throughout the hot compaction process.

5. Process according to any preceding claim, wherein the temperature at which the fibres or tapes are compacted is no greater than the peak temperature of melting at the ambient compaction pressure

6. Article comprising melt-formed fibres or tapes of oriented polypropylene homopolymer or copolymer in the form of a woven fabric which has been subjected to hot compaction, characterised in that said fibres or tapes have a draw ratio of at least 7:1.

7. Article or process according to any preceding claim, wherein the article is monolithic.

8. Article or process according to any preceding claim, wherein the draw ratio is at least 8:1, preferably at least 9:1.

9. Article or process according to claim 8, wherein the draw ratio is 9:1 to 15:1, preferably 9:1 to 11:1.

10. Article or process according to any preceding claim, wherein the fibres or tapes of the oriented polypropylene homopolymer or copolymer have a weight average molecular weight (Mw) in the range of 100,000 to 800,000.

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