United States Patent Office

3,314,847

Patented Apr. 18, 1967

3,314,847

TEXTILE

Herbert G. Lauterbach, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Filed Oct. 30, 1962, Ser. No. 234,215
4 Claims. (Cl. 161—173)

This invention relates generally to textiles and, more particularly, to high modulus elastomeric products reinforced with polymeric textile structures.

The practice of reinforcing high modulus elastomeric products such as pneumatic tires, conveyor belts, drive belts, hoses, and similar products with textile cord and yarn structures is well known. Particular utility is achieved with man-made cords and yarns of polyamides, polyesters, polyvinyl derivatives, polyolefines, and regenerated cellulose fibers. But these cords and yarns must be first plied and twisted and then dipped in adhesives and hot-stretched to make them useful for reinforcing such elastomeric products. The plied and twisted cords of such man-made fibers assure characteristics of tenacity and fatigue resistance superior to the characteristics that are attained with natural fibers. Adhesive dipping is necessary because of the substantially smooth outer surface of conventional man-made filaments. Nevertheless, failure in durability of such dipped-structure-reinforced elastomeric products is primarily due to separation at the adhesion bond. Cord hot-stretching increases cord strength and yield, and decreases cord growth. However, all these operations of plying, twisting, dipping, and hot-stretching, although they do result in an over-all superior elastomeric product, also add to the cost of fabricating that elastomeric product.

The most important objective of this invention is to provide more useful elastomeric products reinforced with textile structures prepared from man-made fibers.

Another objective of this invention is to provide novel elastomeric products which are reinforced with textile structures prepared from man-made fibers and which are constructed without adhesive dipping that textile structure.

Another objective of this invention is to provide high modulus elastomeric products reinforced with man-made textile structures which are not hot-stretched.

Another objective of this invention is to provide novel and more durable elastomeric products reinforced with textile structures prepared from man-made fibers.

Another objective of this invention is to provide high modulus elastomeric products reinforced with textile structures of zero twist prepared from man-made fibers.

A further objective of this invention is to provide improvements in the procedures followed in the preparation of such products. Other objectives will appear hereinafter.

These objectives are accomplished by covering and impregnating a bulky man-made yarn with elastomeric material, and fabricating a high modulus elastomeric product which is reinforced with this bulky, impregnated, substantially void-free, man-made yarn. The utility of this invention is available only for bulky yarn which has been bulked with at least about 5% overfeed. The bulky yarns of this invention, comprising either polyamide, polyester, polyvinyl derivative, polyolefine, or regenerated cellulose fibers, are composed of a plurality of randomly convoluted filaments having coils, loops, or whorls along their length, and are prepared with air bulking such as taught by the technology in U.S. Patents 2,783,609 and 2,852,906. The filament of the yarn bulked according to this invention has a molecular network structure that is not significantly changed when compared to the molecular network structure of the filament before bulking. This

fact is evidenced by the substantially unchanged mechanical properties (tenacity, elongation, and modulus of elasticity) of the filament before and after bulking. Impregnation of the bulky yarn is accomplished either by coating, with pressure, the yarn with a de-aerated plastisol or by calendering with an elastomeric material that flows into the yarn interstices during curing. The modulus of elasticity of the bulky yarn impregnated according to this invention is not less than 75% of the modulus of elasticity of the same yarn when both unbulked and unimpregnated. The impregnation of the yarn of this invention sets up a matrix for each filament so that stresses are transmitted to a not-easily-deformable mass.

The following examples are illustrative of the novel and more useful products of this invention and are not intended to limit it in any manner.

Example I

Two ends of 840 denier, 140 filament yarn composed of bright high tenacity polyhexamethylene adipamide continuous filaments are twisted to 2.8Z turns per inch, are passed through a water trough, and then are fed with 9.8% overfeed to a bulking jet as described in U.S. Patent 2,852,906. The air at the jet is 80 p.s.i.g. pressure and 70° F., and the exit speed of the yarn is 50 yards per minute. This bulked yarn, neither dipped nor hot-stretched, is impregnated with a natural-rubber-based elastomer typical of those used in skim stocks by being embedded between a conventional strip adhesive mold filled with that rubber and a 24-mil layer of that rubber, and then curing for one hour at 140° C. with a curing pressure of 20 tons. This preparation of the molded rubber containing the bulked yarn is substantially similar to the preparation of textile reinforced plies for fabrication of elastomeric products such as pneumatic tires, and the curing specified in this example is substantially the same curing carried out with a pneumatic tire. The impregnated yarn is cut from the mold, so that a small quantity of that rubber encases the yarn, inspected, and tested. Microscopic comparative inspection of the bulked, unimpregnated yarn with this yarn cut from the mold shows that the voids in the impregnated yarn are filled with cured rubber. Table I shows the properties of a control yarn unbulked and unimpregnated, of a bulked yarn, and of the bulked and impregnated yarn described above. None of the yarns in Table I are hot-stretched.

TABLE I

	Control Yarn	Bulked Yarn	Rubber Properties	Bulked and Impregnated Yarn
Overfeed, percent	0	9.8		9.8
Yarn bulk, cc./gm.	2.5	4.5		4.5
Yarn denier	1,694	1,918		1,918
Breaking tenacity, g.p.d.	8.4	4.5		7.0
Elongation at break, percent	20.3	19.4	0.15	17.4
Mod. of elasticity, g.p.d.	37.8	12.2	500	39.0
			0.03	

As is to be expected, bulking the yarn lowers the breaking tenacity and the modulus of elasticity; but, as is not to be expected, substantially complete recovery of these two properties is achieved when the bulked yarn is impregnated (undipped and not hot-stretched) according to this invention. Surprisingly, an additional useful property, a lower percent elongation at break is acquired by the yarn of this invention. Furthermore, as the degree of bulking (overfeed %) is increased, there is an increase in the ratio:

$$\frac{\text{Breaking tenacity of bulked and impregnated yarn}}{\text{Breaking tenacity of bulked yarn}}$$

It should be noted that the modulus of elasticity of the bulked and impregnated yarn is 103% of the modulus of elasticity of the same yarn when both unbulked and unimpregnated.

Example II

Six ends of 1680 denier, 280 filament yarn composed of bright high tenacity polyhexamethylene adipamide (66 nylon) continuous filaments are twisted to 0.5Z turn per inch, are passed through a water trough, and then are fed with 12% overfeed to a bulking jet as described in U.S. Patent 2,852,906. The air at the jet is 80 p.s.i.g. and 70° F., and the exit speed of the yarn is 50 yards per minute. This bulked yarn is used as the warp and as the fill to construct a plain weave 44 oz./yd.^{2} fabric and then, using a doctor-knife, the fabric is coated at 70° F. with a black de-aerated polyvinyl chloride formulation, similar to those formulations used to coat solid woven conveyor belt fabric. Then, a conventional firing step is carried out with the fabric in an oven at 300–400° F. for about 5 minutes. A conventional conveyor belt duck fabric (36 oz./yd.^{2}, 22 ends per inch 10S cotton warp, 14 picks per inch 6S cotton filling) is similarly coated with the black polyvinyl chloride formulation. Microscopic examination of a cross-section of this fabric composed of bulked 66 nylon yarn reveals that the yarn voids are substantially filled with the polyvinyl chloride. Tensile tests are performed with the Instrom machine on 1-inch wide samples of these fabrics. The coated fabrics are cut out and tested by the grab method while the uncoated fabrics are tested by the raveled-strip method. The results of these tests are on Table II. Both the grab method and the raveled-strip method are described in A.S.T.M. Std. D–39–59.

TABLE II

	Bulked 66 Nylon		Unbulked Cotton	
	Uncoated Fabric	Coated Fabric	Uncoated Fabric	Coated Fabric
Tensile Strength [1]	1,154	1,686	409.7	544.3
Elongation at Break (percent)	49.1	39.4	39.3	33.9
Elongation at 10% of Break Load (percent)	20	2.8	8.5	4.3

[1] lbs./in. of fabric width.

The results of these tests show the unexpected reduction (86%) of elongation at 10% of break load of the bulked 66 nylon yarn due to its impregnation with polyvinyl chloride whereas unbulked cotton, when coated with polyvinyl chloride is reduced only 49.5%. Not only is the impregnated fabric of bulked 66 nylon more than three times as strong as the similarly coated unbulked cotton (conventionally used for conveyor belting), but it has unexpectedly greater dimensional stability than the conventional fabric, and extremely low elongation at 10% of break load.

Example III

Six ends of 840 denier, 140 filament zero twist yarn composed of bright high tenacity polyhexamethylene adipamide (66 nylon) continuous filaments are passed through a water trough, and then are fed with a 15% overfeed to a bulking jet as described in U.S. Patent 2,852,906. The air at the jet is 80 p.s.i.g. and 70° F., and the exit speed of the yarn is 50 yards per minute. This bulked yarn is used as the warp (10 ends per inch) of a plain weave 14 oz./yd.^{2} fabric which contains a fill (5 picks per inch) of the same yarn bulked by the same procedure except that the overfeed is 5%. A natural-rubber-based elastomer, characterized by having a high scorch time of 45 minutes at 287° F. but otherwise being similar in properties to skim stock used for industrial rubber goods is hot calendered at 200° F. to both sides of this fabric. An approximately 10" x 24" slab composed of four layers of this calendered fabric is fabricated and cured under pressure for 50 minutes at 287° F. in a process which is substantially similar to the manufacturing of conveyor belts.

A conventional conveyor belt duck fabric (36 oz./yd.^{2}, 22 ends per inch 10S cotton warp, 14 picks per inch 6S cotton filling) is similarly calendered with rubber as is the 66 nylon fabric specified in this Example III above and made into a similar four-ply slab.

Two ends of 1050 denier, 175 filament unbulked yarn composed of bright high tenacity polyhexamethylene adipamide continuous filaments are twisted 3 turns per inch in the ply and ½ turn per inch in the single. This twisted product is then used as the warp (23½ ends per inch) and of the fill (23½ picks per inch) of a plain weave 14½ oz./yd.^{2} fabric. It should be noted that if the same number of picks and ends that are used with the bulked yarn (specified above) were used for this fabric of unbulked nylon, it would be so sleazy that it would not be comparable to the fabric of bulked yarn. This fabric is similarly calendered with rubber as is the 66 bulked nylon fabric specified above in this Example III, and made into a similar four-ply slab.

Four-inch wide straps of each of these three four-ply slabs are tested on an Instrom machine, and the results are on Table III shown below. The fastener strength to break is measured with an approximately 4-inch-wide fastener as manufactured by General Splice Corporation of 32 Woodworth Ave., Yonkers, New York. Deflection, or the slab stiffness, is determined by forming a simple beam of a 24-inch-long slab supported at a pair of symmetrically located points 16 inches apart and then measuring the deflection at the center below the horizontal. Adhesion is determined with a 1-inch-wide strip by measuring the applied force necessary to separate the third from the second ply of each slab. None of the yarns for this example are either hot stretched or dipped in an adhesive system, so it is adhesion between yarn and elastomer that is determined.

TABLE III

Fabric	Tensile Strength, pounds/in. of fabric width	Elongation With a 250 lb. Load (inches)	Fastener Strength (pounds)	Deflection (inches)	Adhesion, pounds/in. of fabric width
14 oz./yd.^{2} bulked 66 nylon yarn (in a 0.73" thick slab)	2,475	4.7	5,800	0.30	21.4
36 oz./yd.^{2} cotton (in a 0.93" thick slab)	1,290	3.9	4,100	0.35	14.0
14½ oz./yd.^{2} unbulked 66 nylon yarn (0.67" thick slab)	2,270	8.6	5,900	2.20	1.2

This example shows the unexpected utility for constructing conveyor belts of yarn that is neither twisted, dipped, nor hot-stretched, but is bulked and impregnated according to this invention. The fabric with the bulked yarn is substantially as strong as the fabric with the unbulked yarn, and substantially much stronger than the conventional cotton fabric. Furthermore, the elongation, deflection, and adhesion measurements show that the fabric with the bulked yarn has greater dimensional

stability and greater adhesiveness than either of the other two fabrics. The slightly lower elongation of the cotton slab is due to the approximately 2½ times greater weight of material that is present in the cotton slab. The high modulus of the yarn of this invention is shown by the significantly lower elongation with a 250 lb. load shown by the bulked nylon as compared to the unbulked nylon.

Example IV

Two ends of 840 denier, 140 filament yarn of bright high tenacity polyhexamethylene adipamide (66 nylon) continuous filaments are twisted together in a 12 x 12 turns per inch construction. This cord is passed through a water trough and then fed with approximately 25% overfeed to a bulking jet whose yarn inlet duct is aligned with a rectangular texturing chamber to which the texturing air is admitted at an angle of 22 degrees. The air at the jet is at 80 p.s.i.g. pressure and 70° F., and the exit speed of the yarn is 50 yards per minute. This bulked cord is cured into a natural-rubber-based elastomer similar in characteristics to passenger tire skim stocks, and an H-pull test is performed on the cured product.

This example shows that the utility of this invention is for polyamide, polyester, and polyolefine yarns which all show substantially similar adhesiveness despite their dissimilar polymeric composition because the bulking and the impregnating factors are substantially similar.

Example V

Polyhexamethylene adipamide yarn is piled and twisted to cords for pneumatic tires. One portion of these cords is conventionally dipped in a conventional resorcinol-formaldehyde latex adhesive system and hot stretched. Another portion is hot-stretched, but not dipped, and a third portion is bulked by being fed with 22% overfeed to a bulking jet as described in U.S. Patent 2,852,906. The air at the bulking jet is 80 p.s.i.g. and 70° F., and the exit speed of the yarn is 50 yards per minute. Then this bulked yarn is twisted and hot-stretched but not dipped. These three portions are used to construct conventional pneumatic tire plies which are in turn used to fabricate three standard 8.00 x 15 four-ply tires. Table V specifies cord properties and tire properties for these three. The H-pull test is as specified above in Example IV.

TABLE V

	Unbulked Cords are Hot Stretched and Dipped	Unbulked Cords are Hot Stretched but Not Dipped	Cords are Bulked and Hot Stretched but Not Dipped
Cord Properties:			
Twist	11.5×11.7	11.6×11.9	9.5×11.2
Denier	1,850	1,683	1,849
Breaking Tenacity (g.p.d.)	6.9	7.1	5.0
Breaking Elongation (percent)	20.0	14.5	13.7
H-Pull (at 25° C.) lbs	28	3.4	19.2
Tire Properties:			
Green Cord End Count (e.p.i.)	32	32	29
Ply Thickness (mils.)	44	42	44
Cord Shrinkage in Curing (Percent)	2.5	2.3	2.1
Speed at Failure	95	85	95
Total Mileage at Failure	495	347	503
Speed			

Two ends of 1100 denier, 250 filament yarn of high tenacity polyethylene terephthalate continuous filaments are twisted together in a 12 x 12 turns per inch construction. This cord is wet-bulked, cured, and H-pull tested as is the cord of 66 nylon specified above in this Example IV.

Two ends of 840 denier, 70 filament yarn of linear polypropylene continuous filaments are twisted together 3.5 turns per inch. This twisted product is wet-bulked, cured, and H-pull tested as is the cord of 66 nylon specified above in this Example IV, except that the overfeed is 10%.

In this example the H-pull is determined by first forming an H structure wherein the cord being tested takes the position of the horizontal bar in the H, and two ¼-inch wide pieces of elastomer take the positions of the two vertical legs of the H so that the outer surfaces of this H are approximately ¼ inch apart. This H sample is cured at 150° C. and 1000 p.s.i. for about 60 minutes. The H-pull is the applied force, when the H sample is at the indicated temperature, necessary to separate either vertical leg from the cord and is therefore a measure of the in-service-adhesion between the cord and the elastomer. The results of this H-pull test are given below in Table IV. The conventional adhesive dipping, hot-stretching operation is not used for any of these twisted products.

TABLE IV

	H-Pull at 70° F. (lbs.)
840/2 bulked 66 nylon cord	10.03
1100/2 bulked polyethylene terephthalate cord	9.62
840/2 bulked linear polypropylene yarn	11.5
840/2 unbulked 66 nylon cord	3.4

This example shows the unexpected durability of a pneumatic tire with cores made from bulked yarn with no adhesive. The H-pull test shows that conventional tire cords, to be useful, must be dipped in an adhesive system. An H-pull test of only 3.4 lbs. identifies an unacceptable tire cord.

This fact of the need for dipping is corroborated by the high speed test which shows failure for the tire with the undipped cords after traveling at a rate 10 miles per hour less for 30% less distance than a conventional tire with dipped cords. Surprisingly and unexpectedly, although the undipped but bulked cords, according to this invention, show almost 32% less adhesiveness in the H-pull test than do the dipped cords, the high speed test shows that tires from these two dissimilar cords are substantially equally durable. One explanation for this fact is the unexpectedly less (16%) cord shrinkage in curing observed in the tire with bulked and undipped cord. Unavoidable textile-structure-shrinkage in curing is a contribution to all failures of conventional cured, textile reinforced, elastomeric products, but the impregnation of the loopy bulky yarn according to this invention is significantly effective in controlling this shrinkage.

Example VI

Two ends of 840 denier, 140 filament yarn composed of bright high tenacity polyhexamethylene adipamide continuous filaments are twisted together 2.5 Z turns per inch. This twisted product is passed through a water trough and then is fed to the bulking jet specified in Example I above according to the bulking process specified in this Example I, except that 5% overfeed is used. Without additional twisting and with no dipping or hot-stretch-

ing, this bulked product is used as a 19-ends per inch fabric to construct conventional pneumatic tire plies which are in turn used to fabricate a standard 8.50 x 14 four-ply tire. This tire is subjected to a laboratory wheel test consisting of operating the tire underinflated. A pressure of 18 p.s.i.g. in the tire is used for this test in contrast to an ordinary operating pressure of 22 p.s.i.g. and the tire is overloaded to the extent that the tire is deflected 21% where 13% deflection is ordinary operating experience. This test tire is run on this laboratory wheel to 3000 miles without failure. A control tire is also laboratory wheel tested under the same conditions. This control tire is made to the same dimensions and from the same 2 ends of yarn as is the test tire, but this yarn for the control tire is twisted to cord with 12 x 12 turns per inch, dipped in a conventional adhesive dip system, hot-stretched, and then made into a ply fabric with 27 ends per inch.

This laboratory wheel test induces a weakening of the reinforcing textile structure, and this weakening is usually most significant in the sidewall of the tire. Nevertheless, gross inspection of both tires shows no incipient failure spots in the sidewall. It is very unexpected that a tire, reinforced with bulked yarn with negligible twist and with neither adhesive dipping nor hot-stretching, should survive this severe test unfailed as it did. Although Instron testing of comparable yarn and cord from the sidewalls of these two tires after the 3000 miles indicate somewhat more percent strength loss in the yarn of this invention than in the conventional cord, it should be noted that the tire of this invention has only about two-thirds of the amount of textile reinforcement that the conventional control tire has.

This example shows that a tire fabricated according to this invention is as durable as a conventional tire, and also is much more economical in material cost and fabrication cost.

The unobvious (1) increased strength, (2) increased adhesiveness, and (3) decreased elongation shown by the impregnated textile structures of this invention is due to the impregnation of the bulky yarn with its plurality of randomly convoluted filaments having coils, loops, or whorls along their length. Therefore, the unexpected increased utility is gained from using any continuous filament that may be processed by the technology which produces these randomly convoluted filaments.

However, it has been determined that, when the bulking overfeed is less than 5% (at which condition true impregnation does not occur), or, when conventional crimping or texturing is practiced with steam or mechanical means (at which condition the molecular network structure of the filament is changed and, therefore, the modulus of elasticity of this bulked yarn is less than 75% of the modulus of elasticity of the same yarn when unbulked) the yarn is unacceptable for use in high modulus elastomeric products.

Because of their relatively higher tenacity, structures of polyamides, polyesters, and polyolefines are preferred in this invention.

Typical of these polyamides are polyhexamethylene adipamide, polycaproamide, polyhexamethylene isophthalamide, polyundecanoamide, polyhexamethylene sebacamide, polymetaxylylene adipamide, polymetraxylylene sebacamide, and copolyamides and blends thereof. Typical of these polyesters are polyethylene terephthalate, polymethylene terephthalate, polyethylene isophthalate, polyhexahydro-p-xylylene terephthalate, polyesters from naphthalene dicarboxylic acids, and polyesters where bibenzoic acid is a replacement for terephthalic acid. Both polyethylene and polypropylene are comprehended by polyolefine synthetic fiber. Of all these polymers, the most preferred are polyhexamethylene adipamide, polyhexamethylene isophthalamide blended with polyhexamethylene adipamide, polyethylene terephthalate, and polypropylene.

For bulking, the preferred degree of yarn bulk is within the range of about 3.5 to 7.0 cc./gram for 66 nylon, and 2.9 to 6.0 cc./gram for polyethylene terephthalate. For other fibers, this range is a function of the ratio:

$$\frac{\text{Density of the particular fiber}}{\text{Density of 66 nylon fiber}}$$

i.e., when the particular fiber density is less than the density of 66 nylon fibers, the preferred range of bulk for the particular fiber is on a higher scale than 3.5 to 7.0.

The impregnating material used in this invention is preferably one that has good flow properties during manufacturing of the elastomeric article. Such materials are natural and synthetic rubbers, which have long scorch times (about 45 minutes at 287° F.) and low viscosity plastisols such as polyethylene, polyvinyl chloride, blocked isocyanate elastomeric material, polymerized chloroprene, and others. Scorch time is the time required by an elastomer stock to change from a flowing to a non-flowing condition during vulcanization (curing). A short scorch time would interfere with complete impregnation and with successful vulcanization.

Because of their high tensile strength, man-made cords may be used in lower quantity than textile structures of natural fibers. However, this equates to a less bulky and a less stiff fabric so that for such uses as conveyor belts, conventional polyamide and polyester fabrics have not been widely acceptable in the past. But now, with this invention, bulky polyamide and polyester fabrics make conveyor belts that are unexpectedly superior to conventional cotton conveyor belts.

Although twisted cord is preferred in this invention for such fatigue-resisting service as first-line pneumatic tires, a satisfactory tire can be made with unplied yarn that contains little or no twist.

It is apparent that many variations in the size, shape, and configuration of reinforced elastomeric articles and in the procedures followed in their fabrication may be adapted without departing from the spirit of the present invention which is therefore intended to be limited only by the scope of the appended claims.

I claim:

1. The process of preparing textile reinforced structures such as tires, conveyor belts, drive belts, hoses, and the like, which comprises bulking a synthetic, linear polymeric filament by overfeeding the filament by at least about five percent to a bulking jet and impregnating the bulked filament with an elastomer composition without dipping or hot stretching, and thereafter applying a layer of rubber thereto and curing the structure under high pressure at an elevated temperature.

2. The process of claim 1 in which the modulus of elasticity of the impregnated bulked yarn is not less than about 75% of the modulus of elasticity of the same yarn when unbulked and impregnated.

3. A structure such as a tire, conveyor belt, drive belt, hose, and the like, having a matrix of cured rubber, and embedded therein a synthetic, linear polymeric filament bulked with at least about five percent overfeed and impregnated with an elastomeric composition.

4. The structure of claim 3 in which the modulus of elasticity of the impregnated bulked yarn is not less than about 75% of the modulus of elasticity of the same yarn when unbulked and unimpregnated.

References Cited by the Examiner

UNITED STATES PATENTS

3,096,225	7/1963	Carr et al.	28—1
3,218,222	11/1965	Skeen et al.	117—138.8

ALEXANDER WYMAN, *Primary Examiner.*

R. A. FLORES, *Assistant Examiner.*