This invention relates to improved polyester filaments and like structures of novel constitution and to processes for the production of such filaments. It is well known that commercially available drawn and oriented synthetic fibres made from polyesters, derived from terephthalic acid, have a uniform constitution transversely through the fibre, so that properties such as strength, resistance to abrasion, dyeability etc., are all uniform throughout the cross section of the fibre.

Textile yarns made from filaments of these aromatic polyesters such as polyethylene terephthalate, are more difficult to dye than yarns made from natural fibres or regenerated cellulose or protein fibres. This difficulty is associated with the highly oriented and crystalline structure of the polyester fibre. This structure is not easily permeable by molecules of water and molecules of dye-stuffs during conventional dyeing procedures. It is known, however, that dyeing polyethylene terephthalate fibres at elevated temperatures improves the rate of dyeing considerably.

Textile fabrics made entirely from polyester fibres can be dyed at elevated temperatures e.g. 120–130°C, those containing mixtures of polyester fibre and natural fibres e.g. wool may be damaged by such temperatures and it is desirable to dye them by conventional techniques. Such conventional dyeing techniques employ aqueous dye-baths which operate at what is known commercially as "at the boil," i.e. at 90–95°C, and up to about 100°C. It is desirable, therefore, that a polyester staple fibre, particularly when intended for blending with other fibres should be dyeable at temperatures of about 100°C or below, and within commercially acceptable dyeing times.

It is known ("Wicksteed" The Physical Chemistry of Dyeing) that the improvement in the rate of dyeing with temperature is due to an improvement in the rate of diffusion of dye-stuff into the oriented drawn fibre which in turn is due to an increase in the molecular mobility of the structure of fibre with temperature. Physical measurements show that at temperatures up to 120°C, the molecules of polyethylene terephthalate in a dry fibre are substantially immobile. At temperatures above 120–125°C, however, molecules in the non-crystalline regions over- come their restraints and become free to move and rotate. Thus, parts of the fibre change from a rigid or "glassy" nature, to a mobile or "rubbery" nature and this transition is known as the glass-rubber transition, occurring at the glass-rubber transition temperature (Tg).

Our investigations also show that the glass-rubber transition temperature of a wet oriented and drawn polyethylene terephthalate fibre occurs at about 115°C, i.e. 10°C lower than that of the dry fibre, because of the influence of the water molecules.

Because of the physical changes in the nature of the polyethylene terephthalate fibre, which occur at the glass,rubber transition, several properties other than dyeing or diffusion rate, also change. Thus a fibre which has been bent, as in a pleated garment, will recover if heated above the transition temperature and the pleat will be removed. It is important that the transition temperature of the polyester fibre is not lowered to too near possible domestic washing temperatures because a garment made from polyester fibre with a lowered Tg will lose some of its permanent pleats if washed, or otherwise heat treated repeatedly at temperatures close to or above the transition temperature.

Whilst it is desirable to lower the transition temperature (Tg) of polyethylene terephthalate fibre so that the dyeability is improved, care must be taken that other desirable properties viz. pliability, retention, are not seriously impaired. Thus it would be desirable to have a region of better dyeability on the outside of the fibre, this better dyeability being due to a physical modification of the polyethylene terephthalate to produce a lower Tg, and a region of unmodified polyethylene terephthalate forming the inner core of the fibre, so that both improved dyeability and excellent pliability could be retained.

Such combinations of desirable properties obtained by the use of a fibre with an outer layer or skin of material surrounding an inner core of substantially the same material but in a different physical state, have not been recognised before for synthetic polyester fibres. Such fibre skin/core structure would be particularly advantageous for fibres made from polyethylene terephthalate.

According to our invention, therefore, we provide filaments and like shaped structures made from polyesters derived from terephthalic acid, particularly those made from polyethylene terephthalate, characterized in that the structure consists of a core portion and a physically modified skin or outer layer portion, the proportion of the cross-sectional area of the fibre skin portion may be as high as 70% and as low as 45%, preferably 50–60%. The modified skin portion is characterized by a transition temperature (Tg) 15–45°C lower than that of the core portion, preferably 20–40°C lower than that of the core portion. This confers on the fibre various improved properties, particularly dyeability.

The glass-rubber transition temperature is defined as the temperature at which the properties of the fibre change from those of a glass-like solid to those similar to a rubber. It can be determined by measurements of dynamic modulus, expansion coefficient, specific heat, etc. over a range of temperatures. For dynamic methods, the value is dependent on the frequency of measurement. We have measured the glass-rubber transition of our fibre samples using measurements of dynamic tensile modulus and dynamic torsional modules. In the method of measurement of dynamic tensile modulus we have followed a method similar in principle to that described by Thompson and Woods (Trans. Far. Soc. 2, 1583 (1856)) and we have measured the dynamic torsional modulus by extending the method described by Wakelin et al. (J. App. Phys. 26, 786 (1955)) so that measurements could be made over a wide range of temperatures and at frequencies comparable with those of the tensile measurements. The glass-rubber transition temperature (Tg) will be defined here as the temperature at which the plot of modulus against temperature has its maximum slope, the measurements being made at 10 c.p.s. or thereabouts. In a homogeneous sample; the glass-rubber temperature obtained from tensile or torsion measurements will be identical. We are concerned here with samples in which there is a modified skin and a core, the skin having a transition temperature 15–45°C lower than that of the core. It can be shown mathematically that the glass-rubber transition temperature of such a fibre measured by tensile modulus is not greatly different from that of the core, whereas the torsional modulus shows a much reduced glass-rubber transition temperature. This is because the deformations of the fibre torsional modulus are much greater in the skin than in the core, whereas in tension comparable deformation of skin and core are produced.
The improved polyester filaments provided by our invention have much improved dyeing properties whilst retaining the full pleating properties of unmodified polyesters, particularly of polyethylene terephthalate. These modified polyester filaments are superior to uniform structures made from e.g. poly(hexa hydro-para-xylene terephthalate) or copolymers of polyethylene terephthalate/sebacate, terephthalate/adipate, terephthalate/ isophthalate triacetate, etc. In that while such filamentary improved dyeing properties, they also have inferior pleat retention properties, as compared with fibres from 100% polyethylene terephthalate. It will be appreciated however that even such copolymer filaments and like structures containing at least 75% mole percent polyethylene terephthalate may be modified according to our invention.

The improved polyester structures of our invention may be obtained by treating the structures particularly in the form of filaments, in their undrawn, as spun, condition, with an inert organic liquid for a time and at a temperature, until at least 45% of the structures are converted into a skin portion, having a second order transition point (Tg) at least 15°C lower than that of the unaffected core portion. It will be appreciated that any liquid may be used for the treatment, which will bring about the desired modification of the structure.

The most suitable liquids for treatment are the polyethylene glycols and the nonyl phenyl polyethylene glycol ethers.

The effectiveness of these treating agents in our process, depends markedly on temperature and time of treatment and to a much diminished extent on the molecular size of the treating agent. Thus conditions can be found by which the desired skin/core modification of the fibre can be produced with temperatures up to 150°C, treatment times up to one minute duration and polyethylene glycols and their equivalent nonyl phenyl ethers up to 6000 molecular weight. Polyethylene glycols of molecular weight between 2000 and 20000, containing ethyl oxide condensate portions of similar molecular size, are preferred for use in the manufacture of our modified fibre because they have melting points below about 40°C and so can readily be washed off the drawn treated fibre with warm water.

If desired, the polyglycol ethers may be mixed and used together in the treatment bath. Immersion of a spun undrawn tow of polyethylene terephthalate in these treating agents at these temperatures produces complex changes in the structure of the fibre and these changes can render the fibre undrawable unless the treatment temperatures are below about 180°C and immersion times in the liquids are one minute or less, but more than one second.

For a commercially acceptable process, the final treated drawn product must have satisfactory tensile properties, i.e. a tenacity of 3.0-3.5 gpd or more, and be substantially free of liquid used for the treatment e.g. the polyethylene glycol or the nonyl phenyl polyethylene glycol ether. For these reasons, we prefer to operate at temperatures of between 110° and 125°C, with treatment times of 5 to 10 seconds using polyethylene glycol of molecular weight 400 to 1000 or the equivalent nonyl phenyl ethers. Under such conditions, the final treated drawn fibre has satisfactory tensile properties and can be washed free of treating agent at a stage between the drawing and the crimping operations.

The treatment conditions must always be designed to produce the desired ratio of modified skin to inner unmodified core of the fibre. This ratio must be so balanced so that they consist of at least 45% by cross-sectional area of skin portion. Otherwise, the improvement in dyeability will only be relatively small and more importantly, the colour shade of a dyed fibre will not be stable to further heat treatments, viz. ironing at 180°C. A shade change may occur upon such heat treatment because the dye penetrates into the unmodified inner core of the fibre.

If on the other hand, more than 70% of the structure is modified and converted to a skin portion, certain desirable properties will be lost such as pleat retention in garments containing the modified polyester fibre. In extreme cases, drawing of the undrawn and treated structures at least twice their length as spun may become impossible or at least very difficult.

For these reasons a number of properties must be taken into account such as modifying the polyester structures and we have found that this is achieved when 45-70% of the structures are converted into a skin or outer layer portion.

The structures after the treatment with the liquids should be capable of being drawn at least two and preferably up to six times their length as spun. This drawing may be carried out by heating the structures to between 75-100°C, but we have found that if the treatment has been effective, drawing to the required extent without heating becomes possible under adiabatic conditions, at high speeds of drawing. Although the polyester structures may be treated in batches in their relaxed condition, we prefer a continuous process in which the structures are conveniently passed through the liquid with or without tension. If tension is used, this should not be sufficient to cause drawing i.e. elongation beyond the yield point, during the actual application of the liquid treatment.

Usually the treatment is carried out by immersion in the presence of excess liquid, but other methods of treatment may be used, such as application by applicator rollers or by spraying, care being taken that at least 10%, preferably 20 to 40% of the liquid based on the dry weight of the structure is available at the selected treatment temperatures on the whole surface of the structure. If desired, various surfactant active agents may be added in small amounts to ensure a homogeneous treatment and should be taken to reduce the risk of entrapping air between the liquid and the surface of the structure during the treatment.

It will be appreciated that the liquids may be applied at low temperatures conveniently at room temperature, and that the structures may be subsequently heated to the required temperature for a sufficient time, providing the required amount of liquid is present during heating to effect a conversion of at least 45% of the structure to the modified constitution.

In the following examples which serve to illustrate, but not to limit our invention, the physical properties of the treated finished dry fibres were measured as follows:

The glass rubber transition temperature (Tg) was determined by measurement of the dynamic tensile and dynamic torsional modulus at various temperatures.

The dynamic tensile modulus was measured by taking a bundle of fibres, of total denier about 500, and applying to this a sinusoidal strain of means of a Scotch-yoke mechanism, the resultant stress being determined by a strain gauge transducer attached to the other end of the bundle of fibres. The sinusoidal strain was monitored by using the Scotch yoke mechanism to strain simultaneously an elastic spring also attached to a strain gauge transducer. The amplitudes of the signals from the two strain gauges were compared electrically, and this gave a value for the tensile modulus. The bundle of fibres was enclosed in a thermal cryostat and the temperature controlled by a flow of air which could be heated.

The plot of modulus against temperature was thus obtained and Tg determined from the position of point of maximum modulus of the polyester fibre. A single 3 denier filament of the treated yarn of length 10 cms. had a "Terylene" cross-bar of length 3 mm. and denier 100 fixed at its centre point by means of "Nurol." This fibre was held vertically so that the cross-bar can be interposed between two electrodes which are connected to an audio-frequency oscillator. The frequency of the oscillator is adjusted until the fibre cross bar system is in resonance vibration. The frequency at which this
occurs is a direct measure of the modulus of the fibre (Wakelin et al. J. App. Phys. 26, 786, 1955). This system is again held at various temperatures by means of an air flow and from the plot of modulus against temperature $T_g$ is obtained.

The relative extents of skin and core portions in our treated fibres have been measured by two techniques. Firstly, studies of the penetration of disperse dyes into our treated fibres show that when the treated fibres are dyed at the boil, the disperse dye (e.g. "Dispersol" Fast Scarlet B) rapidly penetrates the skin portion of the fibre. Thus, after one hour at the boil, the dye has penetrated into the whole of the skin portion, and the fibre has taken on a satisfactory stable shade of colour. Continuing dyeing for longer times only builds up the amount of dye in the skin portion, and makes only a very small difference to the degree of penetration into the fibre. For example a treated fibre was dyed with "Dispersol" Fast Scarlet B under indefinite bath conditions, at the boil for one, four and seven hours. After one hour, the fibre had taken up 15.8 mg. of dye/g. fibre and microscopic examination of cross-sections of this fibre showed that the dye had penetrated 50% of the cross-sectional area of the fibre. An untreated control fibre, dyed under the same conditions, had taken up 2.7 mg. of dye/g. fibre, and the dye had penetrated only 1-2% of the cross-sectional area into the fibre.

After four hours, the treated fibre had taken up 20 mg. of dye/g. fibre and the penetration was 52%. The untreated control had taken up 5.3 mg. of dye/g. fibre and the penetration had increased to about 15%.

After seven hours, the treated fibre had taken up 24 mg. of dye/g. fibre and the penetration was 55%, the untreated control had taken up 6.5 mg. of dye/g. fibre and the penetration had increased to about 30%.

In all cases, the inner core of the treated fibre remained virtually unstained, while in the untreated fibres the penetration was difficult to measure because of the diffuse edge of the dyed area.

Secondly, we find that the action of caustic alkalies e.g. sodium hydroxide on filaments of polyethylene terephthalate is confined almost entirely to the surface of the filaments. It is possible by continued action of such an alkali, to erode away the surface of the filament without reducing the molecular weight of the unattacked portion of the filament. We find that the action of sodium hydroxide on our treated filaments follows the same pattern of attack, but at a faster rate, this being due, of course, to the modified structure of the outer skin portion of the fibre. However, the action of alkali has proceeded until 50% of the fibre has been eroded away, the rate of attack decreases sharply and becomes the same as that observed on unmodified filaments of polyethylene terephthalate of the same denier.

**Example 1**

An undrawn tow of polyethylene terephthalate filaments (220 filaments, 10 denier per filament) was passed through a bath containing polyethylene glycol (molecular weight 600) heated to 125° C. at such a speed that the tow was continuously wound onto a take-up bobbin. The undrawn tow with polyethylene glycol 600 adhering to it then passed onto a set of feed rolls, through a hot water bath at 95° C. and onto a faster rotating set of draw rolls so that it was drawn to four times its original length. Sprays of warm water on the first three draw rolls and a rubber strip running alongside the final draw roll removed excess polyethylene glycol and water. The drawn tow was then dried for five minutes at 95° C. and set (to have zero shrinkage in boiling water) at 140° C. for ten minutes, in a hot air oven.

An undrawn tow of polyethylene terephthalate filaments, identical with that described above was wetted with cold water and fed directly onto the feed rolls of the drawing machine, drawn to four times its original length, and then processed as already described, to form a comparative but untreated, control fibre.

When dyed for one hour at the boil with "Dispersol" Fast Scarlet B, under "infinite" bath conditions, the treated drawn tow took up 15 mg. of dye per g. fibre while the untreated control fibre took up 2.4 mg. of dye per g. fibre.

The treated sample gave a $T_g$ by tensile modulus of 110° C. and by torsional modulus of 91° C. The control sample gave a $T_g$ in both tension and torsion of 120° C. Thus the skin of the treated fibre had a $T_g$ of 91° C. in the dry state and this corresponds to a $T_g$ of about 80° C. under wet conditions i.e. during dyeing. The inner unmodified core has a $T_g$ corresponding closely with that of the unmodified control fibre.

Examination of the treated fibre by the technique of dye penetration and alkali erosion showed that the modified skin portion was 53% of the cross-sectional area of the fibre.

**Example 2**

A similar undrawn tow, as in Example 1, of polyethylene terephthalate was treated for five seconds in a bath containing polyethylene glycol 400 heated to 125° C. and then dried and finished as in Example 1.

The dye uptake of this treated fibre was 14 mg. of dye/g. of fibre compared with a control fibre of 2.5 mg./g.

Measurements of $T_g$ gave a value of 93° C. for the skin portion (in the dry state) from the torsional method and 110° C. for $T_g$ by the tensile modulus method.

Dye penetration and alkali erosion showed that the skin portion formed 58% of the fibre.

**Example 3**

Treament as in Examples 1 and 2, but with "Tergitol" (R.T.M.) N.P. 35 (a nonyl phenyl polyethylene glycol ether) gave a treated fibre with a dye uptake of 15.5 mg./g. which had a skin portion, measured as before, of 51% having a $T_g$ of 90° C.

**Example 4**

Two undrawn threads each containing 336 undrawn 12 denier filaments of polyethylene terephthalate, were immersed in 100% "Carbowax" 600 (polyethylene glycol of average molecular weight 600) at 110° C. for 5 seconds and then manged to leave a residue of about 35% "Carbowax" on the filaments.

One of the treated threads was drawn over a 2" diameter pin heated to 110° C. The drawn thread had a dye uptake of 15 mg./gram. The other thread was drawn over a 2" diameter pin at room temperature, and the drawn thread had a dye uptake of 13 mg./gram.

The $T_g$ from the torsional method of the treated threads was 95° C. for the skin portion. Dye penetration indicated 50% of modified skin or outer layer portion of the filaments.

Similar threads to those used for Example 4 when drawn in a similar manner but without the previous treatment in "Carbowax" 600 had a dye uptake of only 3 mg. of dye per gram of fibre.

**Example 5**

An approximately 20,000 denier polyethylene terephthalate tow comprising 2,000 undrawn filaments each of about 10 d.p.f. and birefringence of $5.2 \times 10^{-4}$ was treated for five seconds in a bath of 100% "Carbowax" 600 at 130° C. before being drawn at a draw ratio of 3.6:1 through a 35% by weight aqueous solution of "Carbowax" 600 at 95° C. to give a drawn tow of 5,500. The physical properties of this tow were as follows:

- Tendency and percent extension 2.8 grams/denier—60% Dye uptake—19 mg. dye/gm fibre

A similar tow produced without the "Carbowax" treatment gave the following results:

- Tendency and extension 4.2 grams/denier—40% Dye uptake—3 mg. dye/gm fibre
The Tg was 87° C. from the torsional method of the treated modified filaments. The dye penetration and alkali erosion showed that the modified skin portion was 59%.

What we claim is:

1. A process for the manufacture of improved filaments, fibers and like shaped structures, made from polyesters derived from terephthalic acid, having a core portion and a modified outer layer portion comprising treating the structures in their undrawn, as spun condition with a heated inert organic liquid selected from the group consisting of polyethylene glycols, nonyl phenyl polyethylene glycol ethers, and mixtures thereof, at a temperature up to 150° C. for 1 to 60 seconds and until 45–70% of the structure is modified and converted into said outer layer portion, said outer layer portion having a second order transition point (Tg), after drawing, 15–45° C. lower than said core portion, and then drawing said structures at least twice and up to six times their length as spun in a zone maintained at 75–100° C.

2. A process as set forth in claim 1 in which the treatment is carried out at temperatures between 80° and 150° C.

3. A process as set forth in claim 1 in which the drawing is carried out under adiabatic conditions.

4. A process as set forth in claim 1 in which the structures are treated with said liquid in their relaxed condition.

5. A process as set forth in claim 1 in which said liquid is applied at about room temperature, and the structures are subsequently heated to a temperature of 80 to 150° C. and for a time to effect modification and conversion of 45–70% of the structure to said modified outer layer portion.

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