Chemistry

EFFECTS OF CHEMICAL MODIFICATIONS ON POLYESTER FIBRES

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SUMMARY : A general review on polyester fibres formation is given illustrating its structure, polymerization reactions as well as chemical, physical and mechanical properties. Modifications of polyester fibres are also reported. Alkalies, amines, solvents either aqueous or non-aqueous attack polyester fibres differently. Their effects in inducing structural and properties changes are thoroughly reviewed.

Key Words: Polyester fibers, polymerization.

INTRODUCTION

Polyester fibres are Man-made fibres in which the forming substance is a long chain polymer composed of at least 85% by weight of an ester of dihydric alcohol and terephthalic acid (1).

Polyester fibres found immediate acceptance in easy-care, wash-and-wear, and durable press garments. It had excellent wrinkle recovery, either wet or dry.

Structure of polyester

The linear homopolymer poly (ethylene-terephthalate) is the dominant composition for polyester fibres. Number average molecular weights of about 15.000 are required for useful textile-fibre properties, but lower values give staple of low tendency to pilling, and higher values provide high strength fibres for industrial use (2,3).

The length of the repeated unit in poly (ethylene terephthalate) along the chain is 10.75°A, a value only slightly less than that expected for a fully extended chain with one chemical unit to the geometric repeating unit, and successive ester groups in the trans configuration to each other (10.9°A). The chains are therefore nearly planar. The unit cell is triclinic (4), the atomic positions in the crystallite indicate that no special forces of attraction exist between the molecules. The spacings between atoms of neighboring molecules is of the order expect if Van der Waals forces operate (4).

Drawn polyester fibres may be considered to be composed of crystalline and non-crystalline regions. The theoretical density of pure crystalline material can be determined mathematically from the dimensions of the unit cell. Percentage crystallinity and molecular orientation relate to tensile strength and shrinkage; however, the various methods of measurement are problematic (5).
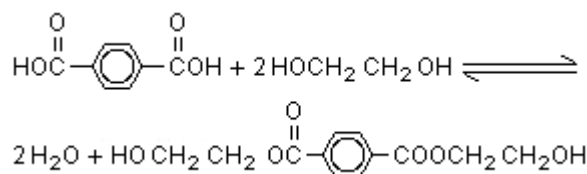
Polymerization reactions

Polyester polymer is produced commercially in a two-step polymerization process, ie, monomer formation by ester interchange of dimethyl terephtalate with glycol or esterification of terephthalic acid with glycol followed by polycondensation by removing excess glycol:
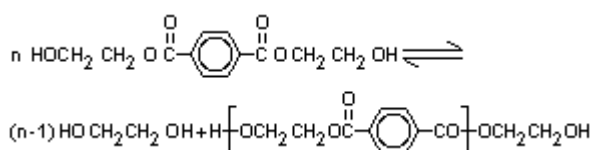
STEP 1: Ester interchange:
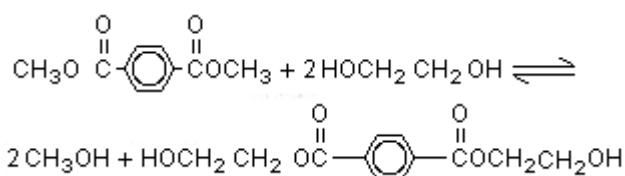
Esterification:

STEP 2: Polycondensation:

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Monomer formation (STEP 1) by the catalyzed ester-interchange reaction between molten dimethyl terephthalate and glycol takes place at about 200°C. The product is a mixture of monomer, very low molecular weight polymer, and as a methanol by - product, which distills at 150°C. Ester-interchange catalysts are divalent salts of manganese, cobalt, magnesium, zinc, or calcium. An alternative monomer formation system involves terephthalic acid rather than dimethyl terephthalicpthalate and an uncatalyzed direct esterification rather than ester-interchange. The monomer which is the same from both methods expect for some end groups, usually is polymerized (STEP 2) in the presence of an antimony catalyst. Chain extension is promoted by removal of excess glycol from the very viscous melt at about 280°C, with carefully controlled agitation and a progressive reduction of pressure to about 200 Pa. Heating is continued at about 280°C until the desired degree of condensation is obtained (6).

Properties of polyester fibres
Chemical properties
Effect of alkalies: Polyester fibres have good resistance to weak alkalies high temperatures. It exhibits only moderate resistance to strong alkalies at room temperature and is degraded at elevated temperatures.

Effect of acids: Weak acids, even at the boiling point, have no effect on polyester fibres unless the fibres are exposed for several days. Polyester fibres have good resistance to strong acids at room temperature. Prolonged exposure to boiling hydrochloric acid destroys the fibres, and 96% sulfuric acid and causes disintegration of the fibres.

Effect of solvents: Polyester fibres are generally resistant to organic solvents. Chemicals used in cleaning and stain removal do not damage it, but hot m-cresol destroys the fibres, and certain mixtures of phenol with trichloromethane dissolve polyester fibres. Oxidizing agents and bleachers do not damage polyester fibres.

Miscellaneous properties: Polyester fibres exhibit good resistance to sunlight, and it also resists abrasion very well. Soaps, synthetic detergents, and other laundry aids do not damage it. One of the most serious faults with polyester is its oleophilic quality. It absorbs oily materials easily and holds the oil tenaciously (7).

Physical properties
Moisture regain: The moisture regain of polyester is low, ranges between 0.2 to 0.8 percent. Although polyesters are non-absorbent, they do not have wicking ability. In wicking, moisture can be carried on the surface of the fibre without absorption (8).

Specific gravity: The specific gravity 1.38 or 1.22 depending on type of polyester fibres is moderate. Polyester fibres have a density greater than polyamide fibres and lower than rayon. Fabrics made from polyester fibres are medium in weight (8).

Heat effect: The melting point of polyester is close to that of polyamide, ranging from 250 to 300°C. Polyester fibres shrink from flame and melt, leaving a hard black residue. The fabric burns with a strong, pungent odor. Heat setting of polyester fibres, not only stabilizes size and shape, but also enhances wrinkle resistance of the fibres (8).

Mechanical properties: A wide of polyester fibres properties is possible depending on the method of manufacture. Generally, as the degree of stretch is increased, which yields higher crystallinity and greater molecular orientation, so are the properties, e.g., tensile strength and initial Young's modulus. At the same time elongation normally decreases. An increase in molecular weight further increases tensile strength, modulus and extensibility (9).

Shrinkage of the fibres also varies with the mode of treatment. If relaxation of stress and strain in the oriented fibre occurs, shrinkage decreases but the initial modulus may be also reduced. Yarns maintained at a fixed length and constant tension during heat setting are less affected with respect to changes in modulus, and reduced shrinkage values are still obtained (10).

Poly (ethylene terephthalate) shows nonlinear and time-dependant elastic behavior. Creep occurs under load with subsequent delay in recovery on removal of the load, but compared to that of other melt-spun fibres, creep is small.

Chemical modification of polyester fibres
Polyester fibres have taken the major position in textiles all over the world although they have many drawbacks e.g., (a) low moisture regain (0.4%), (b) the fibres has a tendency to accumulate static electricity, (c) the cloth made up of polyester fibres picks up more soil during wear and it also difficult to clean during washing (11), (d) the polyester garments from pills and thus, the appearance of a garment is spoiled, (e) the polyester fibre is flammable. Thus, it has been suggested that surface modifications can have an effect on hand, thermal properties, permeability, and hydrophilicity.

Numerous research papers and patents are available and considerable amount of research works is in progress on the hydrolysis (12-32) and aminolysis (33-52) of polyester fibres to overcome their disadvantages.

Alkali treatment

Polyester fabrics have been widely accepted by consumers for their easy care properties, versatility and long life (12,13). Inspite of such acceptance, complaints concerning their hand, thermal properties and moisture absorbency have been cited (13). Improved moisture absorbency of polyester fibres can be achieved by introducing hydrophilic block copolymers. However, this modification can lead to problems of longer drying time, excessive wrinkling and wet cling (14). In addition, penetration of water into the interior of the fibres has not been clearly shown to improve perceived comfort (12,15). It has been suggested that surface modifications can have an effect on hand, thermal properties, permeability, and hydrophilicity (13).

Polyester fibres are susceptible to the action of bases depending on their ionic character. Ionizable bases like caustic soda, caustic potash and lime water only effect the outer surface of polyester filaments. Primary and secondary bases and ammonia, on the other hand, can diffuse into polyester fibre and attack in depth resulting in breaking of polyester chain molecules by amide formation (16-19).

One of the surface modifications is the controlled hydrolysis of polyester. The action of strong base leads to cleavage of ester linkages on the fibre surfaces (20). The result is the formation of terminal hydroxyl and carboxylase groups on the fibre surface. Hydrolysis is believed to increase the number of polar functional groups at the fibre surface.

Alkali-treatment in organic solvent medium: Treatment of polyester fabric was carried out with a mixture of 0.3% sodium hydroxide in ethanol, squeezed to 50% pick up and then stored after covering it with a nylon film at room temperature for 24 hours (19). There was a loss in weight of 21% of treated fabric and the fabric achieved uniform silk-like handle. Polyester fabric was treated with a mixture containing 60 g/l of alkali and about 5% ethanol with 50% pick up and then the treated fabric was stored at the room temperature, while rotating to minimize the uneven deposition or drying of the alkali solution on fabric. In this case too, the fabric suffered a weight loss of 21%.

It was shown (19) that the treatment of the polyester fibres with 6 g/l of sodium methoxide in methanol and also similar alkoxides of K, Li, Cs, or Rb causes weight loss of fibre, and the fibre acquires the silk-handle.

Namboodri and Haith (21) carried out a comparative study by treating the polyester fibres with alkalies and various alkoxides (e.g., sodium hydroxide in water, sodium methoxide in methanol, sodium ethoxide in ethanol, sodium isopropoxide in isopropanol, and potassium tertiary butoxide in tertiary butanol) at 60°C and at different concentrations. It was found that the loss in weight of the polyester fibre was in the order sodium hydroxide < tertiary butoxide < secondary propoxide < methoxide and ethoxide. It was suggested that the observed order followed the nucleophilicity of the bases, and the relatively lower reactivity of the secondary propoxide and tertiary butoxide was assumed to be due to the steric retardation during the equilibrium reactions. The hydrolysis of the polyester fibre was assumed to be taking place on the surface of the fibre. It was assumed that a random attack of the base on the carboxyl groups of the surface polymer molecules took place with removal of the shorter chains from the surface, which were further hydrolyzed by the base present in the solution.

Bendak (22) studied the topochemical degradation of polyester fibres caused by methanolic sodium hydroxide solutions treatment. Methanolic medium and higher temperature of treatment resulted in a steeper tendency in the loss in weight. Pretreated samples with methanolic sodium hydroxide solutions, which had lost about 5-8% of their original weight, showed a significant decrease in wicking time, and a relatively slight improvement in reducing the time sinking. The pretreatment of the fibres did not alter significantly the moisture regain characteristics; a little part of the fibres seemed to be affected by the treatment.

Hot alkali treatment: The deteriorating action of the alkali on the polyester fibres was carried out by a 4% solution of sodium hydroxide at 100°C giving a 30% loss in weight after a two-hour treatment (19).

Rudakova *et al.* (23) studied the kinetics of the hydrolysis of polyester films with solutions of potassium hydroxide of various concentrations at different temperatures. It was found that the hydrolysis occurred only in the surface layer, and it was of zero order with respect to polyester substrate. The kinetics of hydrolysis showed that the rate-controlling step was attack of a water molecule on the ionized from of the ester links. The activation energy was calculated and found to be 18.0 K cal/mole.

Ko Sohk Won *et al.* (24) have reported that the treatment of a polyester fabric with aqueous sodium hydroxide solution caused a decrease of weight and breaking strength and improved handle with increasing sodium hydroxide concentration, treatment time and temperature. It has been reported that these effects were further enhanced in the presence of a carrier, such as Palanil Carrier A. The molecular weight of the fibre was also decreased, but crystallinity was not affected by the alkali treatment.

Timmis (25) reported that pilling-resistant polyester fabric can be prepared by treating it with a 2 g/l sodium hydroxide solution at 60°C for 30 min, washing, drying and heat-setting. This was accompanied by a small decrease in the tensile strength of the fabric.

Bukosek and Coworkers (26) have reported that heat treatment and treatment with alkalies affect differently the diameter, tensile strength, the degree of orientation and the dye sorption of polyester fibres. The weight loss of the polyester fibres increase linearly with increasing time of the fibre treatment with 30% sodium hydroxide solution. It has been reported that the molecular weight of polyester was not changed on boiling in water for one hour, heating at 200°C and treatment with alkalies. But sorption of disperse dyes decreased on treating of the fibres with alkalies. The fibre orientation of the multifilament polyester yarns decreased on heat and alkali treatments.

Shenai et al. (19) reported that Cashmere-like polyester fibres could be prepared by first singing the surface of the raised fibres and then treating the fibres with a hydrolyzing agent. Thus, a polyester serge was scoured, heat-set, dyed, napped, singed, immersed in aqueous 20% sodium hydroxide solution at 120°C for 10 min, washed to give a fabric with Cashmere-like hand.

Shenai and Lokre (27) have studied the action of sodium hydroxide solution on polyester fibres at various alkali concentrations and various treatment time and temperature, in terms of the weight loss of the fibres. They have reported that the weight loss increased linearly with the increase of treatment conditions.

Shet (28) carried out treatment of padding in 25% NaOH followed by hot air drying at 60°C for 5-15 minutes and subsequent washing. Improvement in feel was observed for polyester along with wet ability without effecting, the strength or dimensional stability.

Achwal (16) found that for a satisfactory improvement in feel to a silk-like level, a high weight loss of 15% was necessary. Improvement in static charge development needed at least a weight loss of 10%. Adequate improvement in hydrophilicity could be achieved by a weight loss of 5%.

The effects of hydrolysis of polyester fibres in aqueous NaOH on the handle, strength, dye ability, and electrostatic properties of the fabric were examined (29). Hollows were observed on the fibres after hydrolysis, indicating that hydrolysis did not occur uniformly on the fibre surface. After 15% wt. loss, a fabric had electrostatic voltage 100 and half-life time 2.5 s, as compared with 280 and 5 s, for the untreated fabric. Hydrolysis improved the smoothness of the fabric and decreased the electrostatic charge from friction (29). Elisson et al. (30) observed that untreated polyester fibres have relatively smooth surface, while NaOH treatment causes pitting of the fibre surface. The pits increase in number and depth as the time of hydrolysis was lengthened.

Song and Kim (31) found that the weight loss of poly (ethylene terepthalate) fibres by alkali treatment decreased in the order of KOH > NaOH > Na_2CO_3 and increased with increasing alkali concentration and treatment temperature and time. With increasing weight loss, drape and flex stiffness and tear strength decreased, and tear strength retention at weight loss 17% was >70%. At the same weight loss, handle was affected by the treatment conditions. Zhang and Co-workers (32) observed that the addition of dodecyl-dimethybenzeneammonium bromide cationic surfactant reduced the concentration of NaOH and thus lowered the degree of degradation of poly (ethylene terepthalate) fibres.

Amine treatment: Polyester fibres generally exhibited low surface energy and limited chemical reactivity, resulting in poor wettability and weak adhesive bonding. When polyester fibres were used as reinforcing elements in composites, appropriate treatment procedures might be followed to achieve adequate interfacial adhesion. The introduction of new functional groups by means of chemical modification reactions was one possible mean for altering the physical and chemical nature of the fibre. By choosing the proper experimental conditions, it would be possible to restrict the chemical modification to the surface of the fibre, leaving the interior structure unchanged.

The presence of amine groups would increase wettability, and also provide potential sites for the formation of covalent chemical bonds with polymeric matrices as in a composite. Amine groups were able to react with epoxides, isocyanates, and methylol compounds, forming chemical bonds with epoxies, polyurethanes, and phenol and resorcinol-formaldehyde resins (33).

Reaction of an amine with an ester group of the poly ethylene terephthalate led to chain scission at the reacting site giving rise to amide formation:
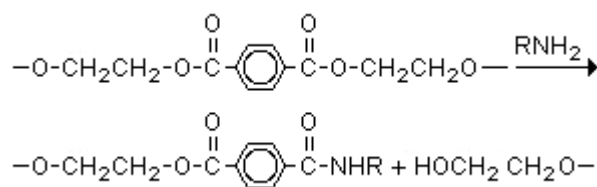
Farrow et al. (34) have expressed doubts about the selective nature of amine treatment for polyester, many other workers (35-38) have reported that amine etching was selective enough to discriminate between the crystalline and amorphous regions.

Chu and Wilkes (38) as well as Adams (39) have shown that the etched samples exhibited a surface network structure dependant on the mechanical and thermal history of the sample. Murray et al. (35) have concluded the under graded polyester possessed a fibrous morphology similar to that proposed by Prevorsek (40) and that the amine etching destroyed this fibrous

278

texture, leaving a weak granular structure which still showed some orientation.

Prevosek's model (40) suggested the presence of two types of amorphous domains: inter micro-or macro-fibrillar regions and intra micro- or macro-fibrillar regions. During drawing the micro- or macro-fibrils slip past each other, and as a result the interfibrillar tie molecules were highly stressed, while the intrafibrillar tie chains were relatively less affected. It was also proposed by Prevorsek that near the surface area parallel to the fibre surface, and in the domains between micro-fibrils one often observed longitudinal cracks that separate clusters of several hundreds of microfibrils. During chemical etching, the highly stressed intermicrofibrillar matter was preferentially etched. As the etching continued the intrafibrillar chains were attacked, and transverse cracks began to appear.

Miyagi and Co-workers (41) found that etching of semi-crystalline polyester began in the poorly crystallized portion of the sample. The crystalline polyester portions were thus initially not affected except for cutting of chain folds and tie molecules. Once the chains in the poorly crystallized portions of the samples were cut, fast loss of monomer occurred between 200 and 300 min of reaction time. At this time most crystalline polyester was still unchanged in amount and X-ray structure. Beyond 300 min, the rate of loss of monomer slowed down considerably, as practically only crystalline oligomer in fully extended chain crystal morphology remained.

Treatment with methyl amine: The effect of alkyl amines on the ester bonds in polyester gave rise to a nucleophilic substitution of basic amine-group into the ester carbonyl. The consequence of the reaction was chain splitting with the formation of amide end-groups : (42)
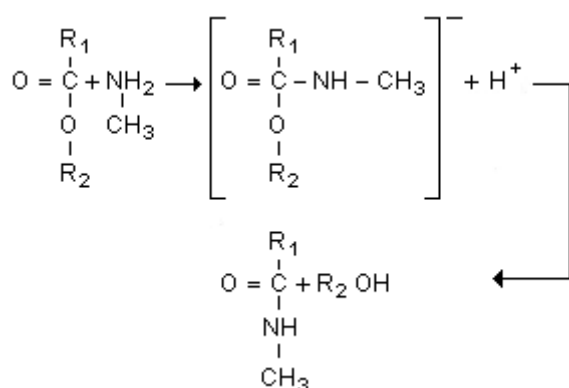
The reaction rate depend on the rate of diffusion of amine into the fibre. The reaction rate, as well as the changes in polymer and the possibility of separation of the amorphous and crystalline phases were investigated (43).
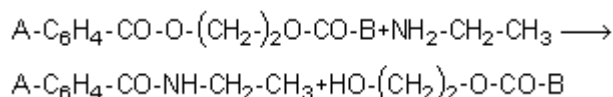
Kudlacek *et al.* (42) have degraded polyester fibres in 30% aqueous methyl amine (1:150) at 20°C for various intervals of time. Fine gradually growing cracks along and across the or in an oblique direction to the axis were the first morphological changes. These cracks enabled the amine to diffuse in the interior. The crystals of oligomers and monomer appeared already in the first phase of aminolysis, these grew on fibres to dimensions being much greater than the fibre diameter. At the end of the fibres, fibrillary structure and a distinctly greater extent of core destruction appeared. It could be concluded that the aminolysis might be useful for relative comparison of accessibility, especially in the phase of the maximum reaction rate, where the sensibility to the structure differences seemed to be the greatest. The morphology of destruction was complicated by secondary changes in the structure of the fibres.

Chauhan, Rao and Dweltz (37) observed that chemical etching of polyester filaments with aqueous methyl amine has revealed a complex stress cracking behavior which varied with orientation and thermal crystallization conditions. The etching experiments were carried out at room temperature (27°C) using a 40% aqueous methyl amine solution. The fibre to liquor ratio was kept high. After etching the surfaces of polyester filaments exhibited a complex mosaic pattern of cracks.

Hinrichsen and Co-workers (44) treated polyester fibres in 40 aqueous methyl amine at room temperature for 420 min. The fibres showed a smaller number of cracks in the fibre direction (44).

Treatment with ethyl amine: A study of the etching of polyester fibres in aqueous ethyl amine at room temperature was shown (34) to lead to chain cleavage as summarized by the equation:

$$A\text{-}C_6H_4\text{-}CO\text{-}O\text{-}(CH_2\text{-})_2O\text{-}CO\text{-}B + NH_2\text{-}CH_2\text{-}CH_3 \longrightarrow$$
$$A\text{-}C_6H_4\text{-}CO\text{-}NH\text{-}CH_2\text{-}CH_3 + HO\text{-}(CH_2)_2\text{-}O\text{-}CO\text{-}B$$

The author concluded that amorphous and crystalline polyester was attacked simultaneously with too little differentiation for useful etching. Solvent treatment of semi crystalline polyester resulted in the separation of isolated spherulites of crystalline polyester imbedded in an amorphous, swollen matrix (45); however, dissolution did not sever the molecular backbone chains, a condition necessary for removal of amorphous portions of molecules.

In order to investigate the structure and morphology of polyester fibres, the fibres have been degraded in 50 and 60% aqueous ethyl amine solutions at 30±1°C for various time intervals by Cho and Co-workers (46). The changes of such properties as weight loss, crystallinity, crystallite size, and morphology were measured and observed on

the insoluble fraction during amine degradation. The conclusions obtained from this study were as follows:

1. Weight loss, increase in crystallinity, and decrease in crystallite size were found to increase gradually with increased time of treatment;

2. Initially ethyl amine diffused and permeated into polyester fibres. In the second stage, decomposition and dissolution of polyester fibres occurred mainly in the amorphous regions. During the third stage, there was a gradual decrease in the reaction rate and this might be attributed to a relatively, slow attack on crystalline regions in the sample. This indicated that amine degradation of polyester fibre was a permeant reaction;

3. Stress crack occurred on fibre surfaces in proportion to reaction time with ethyl amine solution, and finally this resulted in the breaking of polyester fibres;

4. Change patterns of weight loss and crystallinity of polyester fibres upon amine degradation were in accordance with those from the morphological study.

Cho and co-workers (47) have worked in the same trend in order to investigate the physical properties of polyester. Changes of properties as tensile property, dynamic viscoelasticity, and thermal behavior were measured on the insoluble fraction during amine degradation. The conclusions obtained from this study were as follows:

1. Decrease in specific stress and breaking extension, decrease in the intensity and temperature of the maximum tan and peak, and depression in the melting point, etc. were found to gradually increase with increased ethyl amine treatment time;

2. Both intensity and temperature of maximum tan and peak decreased during the initial course of aminolysis. This phenomena could be ascribed not only to the decrease of the amorphous regions but also to the decrease of lateral order, to chain scission in low order regions;

3. Melting point decreased with the decrease of crystallite size. The double melting peaks were observed for the aminolyzed fibres, suggesting that two kinds of different fine crystal structures existed in polyester fibres;

4. Change patterns of specific stress and breaking extension, maximum tan and peak, and thermal behavior of polyester fibres upon amine degradation were in accordance with those from the morphological study.

Chauhan *et al.* (37) reported two stages of decomposition during aminolysis of polyester with 70% aqueous monoethylamine. The first stage gave rise to a rapid degradation of amorphous regions as indicated by a rapid weight loss, increased crystallinity and amide group content, accompanied by a sharp drop in molecular weight. The second stage was a slower degradation of crystalline regions as indicated by a slow and constant values of molecular weight and crystallinity.

Treatment with butyl amine: Zeronian and co-workers (48) have treated polyester fibres with n-butyl amine at 21°C. As fabric weight loss did not occur after treatment, thus it would be expected that the warp yarn was not affected by this treatment. Small decreases in the bending length were obtained, indicating that factors other than weight change could affect the hand of amine-treated polyester fabric.

Large losses in yarn strength, expressed either as breaking load or specific stress occurred.

Both the moisture regain and the yarn contact angle of the polyester did not appear to be markedly affected by the butyl amine treatment. However, hydrophilicity of the fabric after treatment, as measured by the water drop absorption technique appeared to be improved.

Treatment with diethyl amine: Bendak (22) studied the per meant degradation of polyester fibres caused by diethyl amine treatment. Methanolic medium and higher temperature of treatment resulted in a steeper tendency in the loss in weight. Treatment of the polyester substrate with methanolic diethyl amine imparted a significant reduction in the time of sinking and an increase in capillary rise. Lateral migration was appreciably improved with increasing time of treatment with the alcoholic reagent.

Wicking properties of polyester were found to be significantly improved with increasing the percentage loss in weight of the substrate. Diethyl amine treatment caused a relatively significant increase in the moisture regain.

Treatment with multifunctional amines: During the reaction of multifunctional amines with polyester (49), only one of the amine groups is consumed in the chain scission reaction, being converted to an amide group, while the remaining amine groups might be incorporated into the polyester structure. Ideally the reaction sequence might be visualized as follows:

Most of the amines used were low-molecular weight monofunctional amines such as methyl amine, ethyl amine, n-propyl amine, benzyl amine, piperidine, and aniline. Attempts to react polyester with bifunctional amines such as ethylene diamine and hexamethylene diamine also were reported (49).
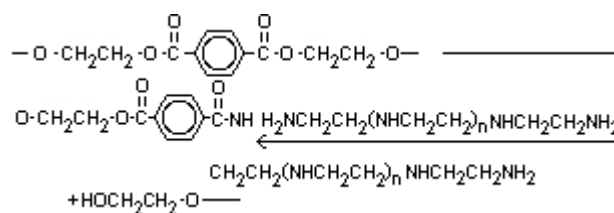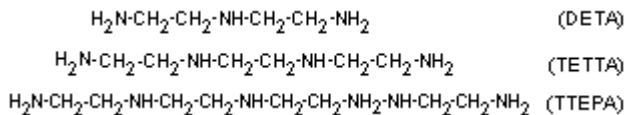
Differences in reactivity between different amines were observed (49). Some amines caused complete degradation of the polyester to the corresponding diamides of terephthalic acid, some caused formation of mixtures of oligomers, and some hardly reacted at all. On reacting with hydrazine and benzyl amine, the corresponding polyester degradation products terephthalic dihydride, terephthalic-bis-benzylamide, and bis-benzlamides of oligomers were obtained. On reaction with ethylenediamine, only a mixture of oligomeric bis-ethylenediamides was isolated. Reactions with hexaethylene diamine, piperidine, and aniline were not as vigorous, and no definite low-molecular weight polyester degradation products were given (49).

It was reported that treatment of polyester fibres with 23% aqueous ethylenediamine solution in the presence of NaOH at pH 9-10 produced an increased adhesion of the modified fibres which was attributed to the incorporation of amide groups in the polyester chains (50).

An attempt to promote adhesions of polyester to polyethylene by absorbing poly (ethylenimine) (PEI) on polyester fibres has also been reported (51). Adsorption of 0.3-0.5% polyethylemine on polyester fibres appeared to increase the tensile strength of the composite.

Avny and Rebenfeld (52) studied the reactions of diethylenetriamine (DETA), triethylenetetramine (TETTA) and tetraethylenepentamine (TTEPA) with polyester monofilaments and with a multifilament yarn.

$$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH_2 \quad \text{(DETA)}$$

$$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH_2 \quad \text{(TETTA)}$$

$$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH_2 \quad \text{(TTEPA)}$$

As reaction progressed and the molecular weight of the polyester decreased as a result of chain scission, oligomers and low-molecular weight polyester fractions might be extracted, leading to a decrease in the polyester mass. Thus the dependence of the polyester weight change during reaction was indicative of the interaction of the amine with the polymer involving the diffusion behavior of the amine, its reactivity toward the ester group, and the solubility and diffusivity of the low-molecular weight reaction products that were formed. Results obtained indicate the large differences in the interactive capability in the order: DETA > TETTA > TTEPA

Organic solvent treatment

The use of non-aqueous organic solvents as processing media in textile wet-finishing operations had received considerable attention during the last few years. It was found that the treatments of synthetic fibres with strongly-interacting solvents such as dimenhylformamide (DMF), butanol, benzyl alcohol, tetrachloroethylene and tetra-

chloroethane led to structural modifications of the fibres and that the morphological events taking place in the solvent-treated fibres were very large (53). Presumably these solvents caused a breaking down of intermolecular cohesive forces thereby increasing segmental mobility in the polymer, allowing relaxation of orientation stresses that were introduced during the spinning and drawing processes. These events might be associated with a simultaneous or subsequent re-crystallization process (54).

Jin and co-workers (55) studied the effects of a number of organic solvents on an oriented polyester yarn. In these studies, shrinkage was not measured but the analogous process of force generation was recorded. Thus, when the yarn was held under constant length constraints, a force was generated when the yarn was exposed either to thermal energy or to the chemical environment that would cause yarn shrinkage in an unconstrained condition.

In chemically induced shrinkage, the chemical energy which led to the disruption of intermolecular cohesive forces was presumably generated by the formation of solvated bonding sites. The formation and existence of these solvates within the polymer structure constituted a major difference between thermal and solvent induced shrinkage. While crystallization could occur during thermal shrinkage at higher temperatures, the crystallization of solvated polymer chains required a dissociation of the solvate and the exclusion of the solvent molecules. It would be expected that this process was quite slow at room temperature and that therefore the predominant mechanism in solvent induced shrinkage was a disruption of intermolecular forces and a release of some residual orientational stresses (56).

Weigmann and co-workers (57) found that the formation of void-containing structures by solvent treatment depends on the ability of the solvent to swell the polymer and to cause crystallization in the swollen state. If the polyester yarn undergoes heat treatment prior to the solvent treatment the requisite swellable and crystallizable domains in the fibre structure might no longer exist.

Action of non-aqueous solvents on Polyester Fibre

The extent of interaction of non-aqueous solvents with polyester fibre depends on the temperature, concentration of solvent, the chemical and physical nature of the polymer and the nature of the solvent (58).

Ribnick and co-workers (56) studied the effect of solvents on the mechanical properties of polyester yarns and reported the effects of a number of organic solvents differing widely in the chemical and physical characteristics on the mechanical properties of a polyesterl yarn. The plasticizing action of different solvents on polyester fibres has been studied from the load-extension behavior and they suggested that dimethyl form amide has a strong

plasticizing action and that it decreased the yield point considerably, causing an extended flow region. It was interesting to note that the degree of interaction between chlorinated solvents as methylene chloride, tetrachloro-ethane, trichloroethylene and perchloroethylene, and polyester fibres appeared to be related to the presence of active hydrogen atoms on the carbon back-bone of the solvents. The presence of active hydrogen atoms appea-red to be required for an interaction to occur suggesting the importance of specific chemical interactions between the organic solvent and the polymer.

Ribnick and Co-workers (56) also suggested that even at room temperature, strong interactions could be observed between some solvents and the polyester fibres, while many solvents were found to have only minor effects on the mechanical properties of the fibres. The recovery of the original mechanical properties after treat-ment with the stronger plasticizers was incomplete, with the exception of the tensile strength, which in few instances, shoved a small increase. Shrinkage in these solvents was completely irreversible, indicating perma-nent changes in the fibre structure. It was apparent from these results that some of the solvents investigated have the capability of lowering glass transition temperature (Tg) of the polyester well below room temperature.

Similarly, the absence of appreciable interactions of the polyester yarns with solvents indicated that the Tg of each of these polyester/solvent systems might be at or above the room temperature. Because of the wide differences in the polarity and H-bonding capacity between most of these solvents and the polyester, no significant effect on the segmental mobility and on the Tg of the polyester solvent system would be expected at the room tempera-ture.

One of the most important concepts relating to the capacity of a solvent to swell or dissolve a polymer was the solubility parameter that was first enunciated by Moore and Co-workers (59). It was recognized that the solubility parameter was only directly applicable to amorphous polymers, and thus its application to semi-crystalline fibres might be considered as a first approxi-mation.

The solubility parameter might briefly be described by applying the free energy equation to the process of mixing of solvent and the polymer.

$$\ddot{A}Fm = \ddot{A}Hm - T\ddot{A}Sm$$

Where the molar free energy of mixing (ΔFm) at a particular temperature (T) is composed of the heat of mixing term (ΔHm) and the entropy term (ΔSm). For a two-component system, consisting of a solute and a solvent,

$$\ddot{A}Hm = \ddot{A}Vm\left[\left(\frac{\ddot{A}E_1}{V_1}\right)^{1/2} - \left(\frac{\ddot{A}E_2}{V_2}\right)^{1/2}\right]^2 \varnothing_1\varnothing_2$$

Where Vm is the total number of molecules in mixture, $\Delta E_{1,2}$ is the energy of vaporization of the component 1,2 , $V_{1,2}$ is the molar volume fraction of the components 1 and 2, $\varnothing_{1,2}$ is the volume fraction of the component 1 and 2, E/V is the energy of vaporization per unit volume of each component and is defined as the cohesive energy density (C.E.D) and the square root of the C.E.D. is defined as the "solubility parameter " of the component (∂). Therefore,

$$\ddot{A}Hm = Vm\,\varnothing_1\varnothing_2\left(ó_1 - ó_2\right)^2$$

It could be seen that ΔHm would be zero when $ó_1 = \partial_2$ and therefore ΔFm would be negative indicating spon-taneity of mixing.

It was observed that the maximum interactions of the various solvents with polyester yarns took place with the solvents whose solubility parameter approached that of polyester. A solubility parameter of 10.7 $(cal/cm^3)^{1/2}$ could be calculated for the terephthalate unit by the methods of Small (60).

Knox and Co-workers (61) have shown that the inter-action of non-aqueous solvents with polyester might poly-ester might be characterized as bimodal in nature, giving rise to two interaction maximal at ∂ values of 9.85 and 12.1 as a consequence of the preferential interaction of solvents with the aromatic and aliphatic ester residues of the polyester monomer repeated unit.

Ribnick *et al.* (54) reported that a number of organic solvents have been shown to cause a high level of shrink-age in oriented, semi-crystalline polyester. In chemically induced shrinkage, the chemical energy which led to the disruption of the intermolecular cohesive forces was presumably generated by the formation of solvated bond-ing sites. They have examined the kinetics of the shrink-age of a drawn polyester yarn in a number of organic solvents at several temperatures. The shrinkage process proceeded at a maximum rate after an induction period which was believed to be associated with diffusion of the solvent into the fibre structure. The temperature-depen-dence of the maximum shrinkage rate followed the Arhenius relationship.

Desai (62) studied the crystallization of polyester by organic solvents and reported that this process might be considered as involving the following steps: The solvent was imbided in the polymer by diffusion. The solvent-polymer interaction caused enhanced mobility of the polymeric segments by interrupting the inter-segmental

forces. If the polymer-solvent system was strong enough, then the polymer macro-molecules might be capable of re-arranging into a more thermodynamically lower energy state, generally the crystal state.

Lemons *et al.* (63) showed that the mechanism by which a compound induced crystallization was a plasticization of its amorphous regions. Finally, these liquids such as nitrobenzene, acrylonitrile, dimethyl form amide, cyclohexanone, dimethyl-o-phthalate, benzyl alcohol, m-cresol, acetonitrile, etc., which plasticize the polymer had the cohesive energy density close enough to that of the polymer and interacted with it through generalized non-specific forces.

Moore and Sheldon (64) observed that the nature, polarity type, solubility parameter, and molecular size of a solvent were the governing factors for both the equilibrium swelling and crystallinity. It was further suggested by them that the non-polar hexane and carbon tetrachloride did not induce crystallinity and so also ethanol and n-butanol. The polarizable aromatic hydrocarbons for example benzene, toluene did so however, and so did benzyl alcohol. They concluded that swelling might be considered as a measure of the interaction between the polymer and the organic liquid and the development of crystallinity might depend on such interaction.

It was shown by Watanabe (65) that the degree of swelling of polyester fibres treated with benzyl alcohol, benzene, tetrachloro-ethylene and chloroform increased with a rise of treatment temperature. On the other hand, the degree of swelling of the polyester fibres treated with dimethyl form amide, dimethyl acetamide and nitrobenzene at -10 to 75°C increased with a lowering of the temperature. The degree of crystallinity after the solvent treatment increased with the rise in the temperature in every case, the crystallization was almost complete at 10°C in dimethyl form amide and benzene. Acceleration of the crystallization in an organic solvent might be attributed to the fact that the Tg of polyester was lowered in the organic solvent.

Weigmann and co-workers (66) studied the effect of the thermal history of the polyester-solvent interactions, because the thermal history of a polyester fibre was of considerable importance to the ability of a subsequent dimethyl form amide treatment at 140°C to swell the fibre structure and produce voids upon removal of the swelling solvent. They suggested that the stabilization of the fibre structure against solvent treatments became effective only at a thermal pretreatment temperature of approximately 180°C-200°C. In this relatively narrow temperature range, crystallites of a sufficient size and stability were formed to resist the action of the solvent. Structural changes produced by the thermal pretreatments below this temperature range, on the other hand could be over-come by the solvent treatment. If the thermal pretreatment exceeded the apparently critical temperature range, a destabilization of the resulting structure by the subsequent dimethyl form amide treatment was again possible and led to the formation of voids and increased dye uptake values.

Knox and co-workers (67) measured the structural and physical properties of an oriented semi crystalline polyester yarn as a function in time after the treatment with an aqueous-dodecylsulphate solution buffered to pH 5 at 100°C. Four major structural events were observed: 1) longitudinal shrinkage, 2) crystallization leading to structural stabilization, 3) surface stress concentration, and 4) rapid hydrolysis and decline in molecular weight following surface cracking of the fibres to relieve surface stress concentrations. Knox and co-workers also observed that a comparison of the effects of aqueous, thermal, and dimethyl form amide treatments of polyester suggested that the molecular mechanisms and kinetics of aqueous and of thermally induced changes were similar. Solvent-induced changes were to a large extent controlled by diffusion processes. Aqueous and solvent-treated polyester were similar in that there was an increase in structural porosity as a result of crystallization in the swollen state.

Vicini *et al.* (68) treated amorphous polyester filaments in acetone water mixtures by soaking for differing periods of time at 25°C under unrestrained conditions and gentle stirring. The treated filaments were found to retain the amorphous properties. The Tg's and Tc's were lowered well below the usual values and at the time the structure became swollen. Ageing the treated polymer freed from acetone resulted in a reversible process that gave transition values close to the values for the untreated sample; but the polymeric remained swollen.

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