3

THE CHEMISTRY OF SIZING COMPOUNDS

3.1 INTRODUCTION

Up until the development and commercial use of manmade fibers, the sizing materials employed in the textile industry had to meet the needs of the natural fiber weaving industry. The sizing material used primarily in the cotton manufacturing industry used natural starches. The natural starches such as corn, wheat, tapioca, and the like have a tendency to form very stiff films. To overcome the stiffness of the natural starches, weaving was carried out at very high humidities. Nevertheless, natural starches performed a useful function, and they still do in the cotton industry. Because the starches have a chemical nature that is similar to that of cotton, the starches adhere very well to cotton as well as to rayon—the first commercially made manmade fiber which has a chemical structure similar to cotton.

The desizing of starch can be carried out by enzymatic treatment and making the degraded product water soluble. The starch materials are relatively inexpensive and they still find widespread use in the textile industry. The starches need to be cooked and applied at a relatively high temperature, which poses some processing problems for rayon. For sizing of rayon a gelatin type natural protein sizing material derived from hides and skins of animals was developed. This material could be applied at temperatures lower than that used for natural starches. This material proved adequate for sizing rayon without causing any ''hot-wet'' damage. A protein-digesting protein is employed to

desize the material. This state of affairs prevailed until the 1940s when the first truly synthetic fibers appeared on the scene.

In 1938 nylon fiber, which is thermoplastic in nature, appeared on the scene, requiring the development of sizing material that could be applied at lower temperatures and also adhered to the hydrophobic surface of the fibers. The new types of sizing materials included such chemical compounds as carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA), copolymers of acrylic acids, and other such water-soluble materials that did not require cooking before use. The chemistry of these materials made the desizing simpler and easier. By controlling the degree of polymerization of these compounds, sizes with considerably different physical and solubility properties have been made. Some of these sizes are also blended with starches to balance the cost of sizing while at the same time improving the processing properties of yarns during weaving.

Another class of materials called ''binders'' has also been developed to improve adhesion and properties of size films formed by synthetic materials. The chemical sizing materials available in the market offer the textile technologists to engineer the sizing ingredients to meet the processing requirements of various types of fibers and high speed weaving. In this chapter, the chemical nature and the various chemical and physical properties of the sizing ingredients will be discussed.

3.2 PROPERTIES OF SIZE MATERIALS

There are a number of desirable properties which a warp size should possess. These are summarized in Table 3.1. A good sizing material should have most if not all of these properties; however, sizes that are deficient in some of these properties still may be used. For example, starch is a useful sizing material even though it has a high biological oxygen demand (BOD), lacks bacterial resistance, and is sensitive to overdrying; cannot be recovered; and must be cooked to achieve uniform properties besides other disadvantages. Yet it is a useful size material primarily because it is inexpensive, is easily desized, is a renewable resource, has good adhesion to cellulosic fibers, and can be modified and/or derivatized to yield a wide range of size film properties. In other words the usefulness of a size material for a specific application will depend upon the nature of the fibers of yarns being sized (e.g., cellulosic, nylon, polyester, etc.), the type of yarn (ring-spun, open-end, air-jet), the type of weaving machine being employed (shuttle, air-jet, rapier, projectile, etc.), and the characteristics of the fabric being woven (style, construction, weave, twist, yarn count, etc.) [1]. For example, what may be a suitable size for a ring-spun yarn

Table 3.1 Properties of a Good Sizing Material

Environmentally safe (nonpolluting)	Recoverable and reusable (or treatable)
Good film former	Low static propensity
Reasonable use economics	No skimming tendency
Penetration of yarn bundle	Easily removed (desized)
Elasticity	Easily prepared
Good film flexibility	Lack of odor
Good specific adhesion	No beam blocking
Good frictional properties (lubricity)	Compatible with other ingredients
Transparency	Good abrasion resistance
Bacterial resistance (mildew)	Neutral pH
Reasonable strength	High fold endurance
Controllable viscosity (fluidity)	Insensitive to high heat (overdrying)
Water soluble or water dispersible	Low BOD
Good hygroscopicity characteristics	No build-up on dry cans
Uniformity	Reduced shedding
Clean split at bust rods	Rapid drying
Improves weaving efficiencies	No redeposition of size
No effect on drying	Insensitive to changes in relative humidity
Reasonable extensibility	

may not work for an open-end or an air-jet spun yarn, especially if a yarn is made from blends of dissimilar fibers.

The primary size materials that act as ''film formers'' are

Starch (modified and unmodified)
Polyvinyl alcohol
Carboxymethyl cellulose
Acrylic (various addition polymers)

The properties of these materials are discussed in subsequent sections. Other sizing agents are utilized as binders to improve the adhesion aspects of the film-forming sizing agents.

3.3 STARCH

Starch was at one time the primary sizing agent for textiles, and it is still used extensively either alone or in blends with other sizing agents. Large quantities are also used by the paper and food processing industries, for medicinal and adhesive applications, in the fermentation of alcoholic beverages, and even as

explosives. It is one of the most abundant agricultural ''renewable'' resources found in nature. Starch occurs widely in plants but is found in its purest form in the seeds (such as in wheat, corn, rice, and sorghum), in the roots and tubers (such as in potato, tapioca, and arrowroot), or in the stem pith of plants (such as in sago). These sources constitute the bulk of the world's supply of commercial starches. In the United States, the endosperm portion of the kernels of the hybrid yellow dent corn (which is about 90% starch) provides the major source of starch used in textile applications.

3.3.1   Chemical Structure of Starch

Cellulose and starch have identical chemical constitution. They are both polymers of glucose, a sugar found in its pure form in grapes and often referred to as grape sugar. Glucose is only one of a family of ringed six carbon sugars that are referred to as carbohydrates because each carbon is associated with a molecule of water and have the empirical formula $[C_6H_{12}O_6 = C_6(H_2O)_6]$. The glucose molecule can exist in two structural (anomeric) forms dictated by the location of the hydroxyl group located on the C1 carbon of the pyranose ring, as shown in Fig. 3.1. This carbon is actually part of a cyclic hemiacetal involving the ring oxygen. It is possible for the hydroxyl group on C1 to be above or below the ring through an interconversion with the ring oxygen, a phenomenon called mutarotation. All of the other hydroxyl groups on the pyranose ring, at C2, C3, and C4, are fixed at the up or down position. In fact, exchanging the location of say the #4 hydroxyl from the down position (as on the glucose molecule) to the upper bond position (exchange the hydrogen and hydroxyl groups) gives a different sugar galactose, similar to one of the sugars found in milk (Fig. 3.1).
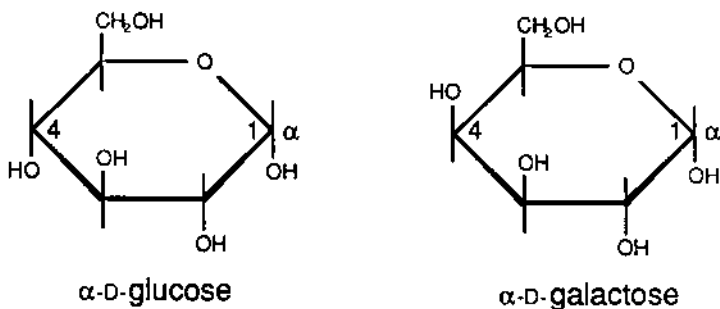

Fig. 3.1   The sugars glucose and galactose differ only in the position of the hydroxyl on the C4 of the pyranose ring.

The two anomers of glucose are normally labeled α and β. Condensation of glucose to form linear starch chains occurs between the C1 and the C4 hydroxyls through elimination of a water molecule. For starch (α form) both of these hydroxyls are down with respect to the next glucose molecule; hence no change in the orientation of the glucose units is necessary for the condensation to occur. In the β form—cellulose—the hydroxyl group is up at C1 and down at C4; therefore, every other glucose unit must flip over before the 1,4 hydroxyls can match up for condensation, as shown in Fig. 3.2. Once condensation has occured to yield the polymer chain of cellulose or starch the bond at C1 can no longer interconvert.
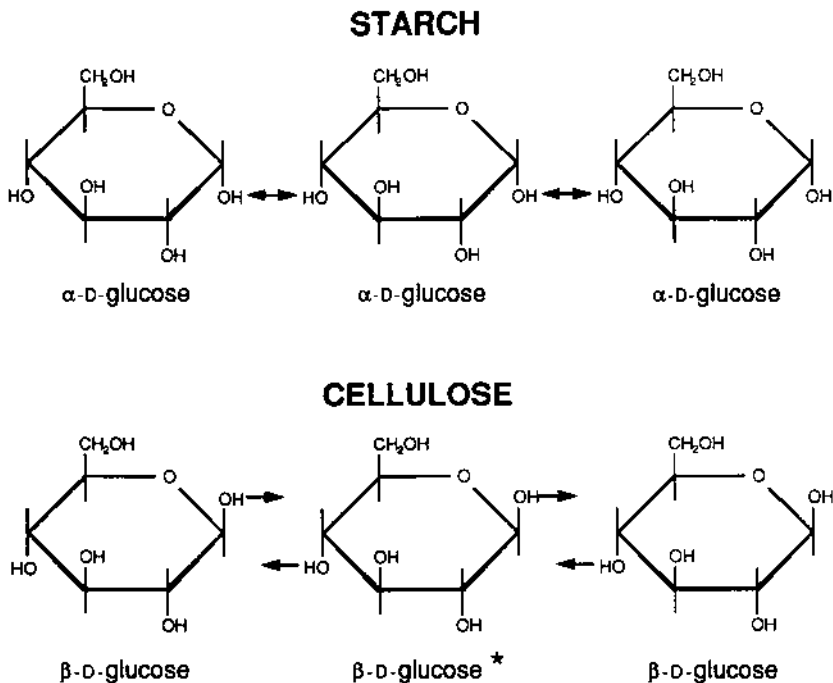

Fig. 3.2 Reactions of the alpha and beta anomers of glucose to form starch and cellulose. (*)Note that unlike the α−D−glucoses, every other β−D−glucose must rotate 180° before the 1−4 hydroxyls can condense to form the cellulose chain.

The glucose units in cellulose and starch do not actually exist in the plant, as shown in Fig. 3.2 (often used for structural simplicity), but instead exist in the more stable chain form. Comparison of the accepted conformations for the linear chain structures for cellulose and starch are shown in Fig. 3.3. It should be noted that due to their physical and chemical similarity they will have high adhesion for each other. As a result, starches are excellent size candidates for cellulosic fibers such as cotton and rayon.

In addition to the linear form of the starch polymer chain, called amylose, produced by the plant, there are also highly branched chain forms, called amylopectin containing several thousand glucose units. The branched points involve condensation at the C1 through the C6 hydroxyls (alpha) while the linear chains are α – 1,4 linkages, as shown in Fig. 3.4. Starches from various sources differ in the amount of amylose and amylopectin found within the granule, as shown in Table 3.2 [2,3]. Amylopectin, because of the high branching which occurs every 9–20 glucose units of the molecule [4], prevents rapid gelling, i.e., retrogradation or microcrystallization of starch pastes, of the cooled size. And amylose, because of its linear nature, contributes significantly to the size film strength. Genetic plant breeding has allowed the development of plant variants that produce starches approaching virtually 100% of either
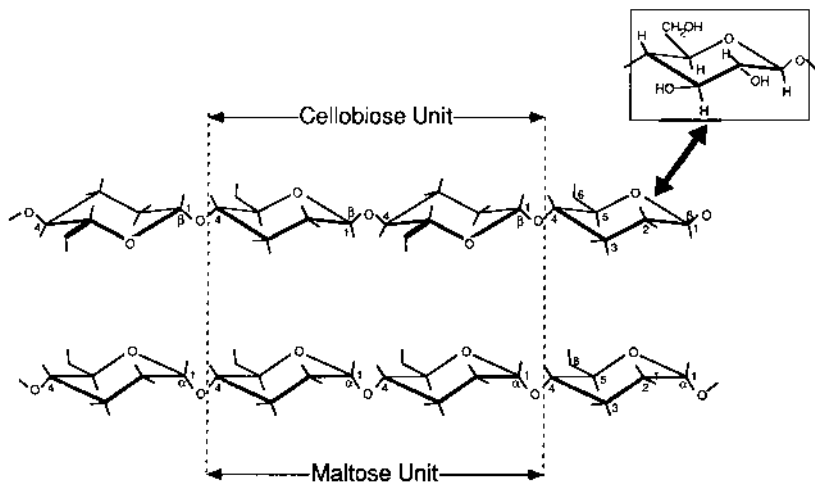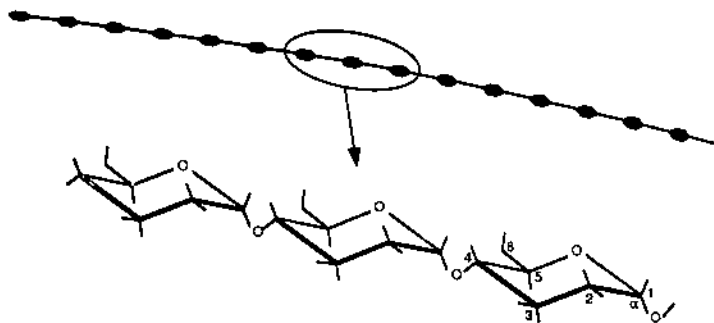

Fig. 3.3 Comparison of the glucosidic chain structures of cellulose (β) and starch (α). See insert for locations of hydrogens (H) and hydroxyls (OH).

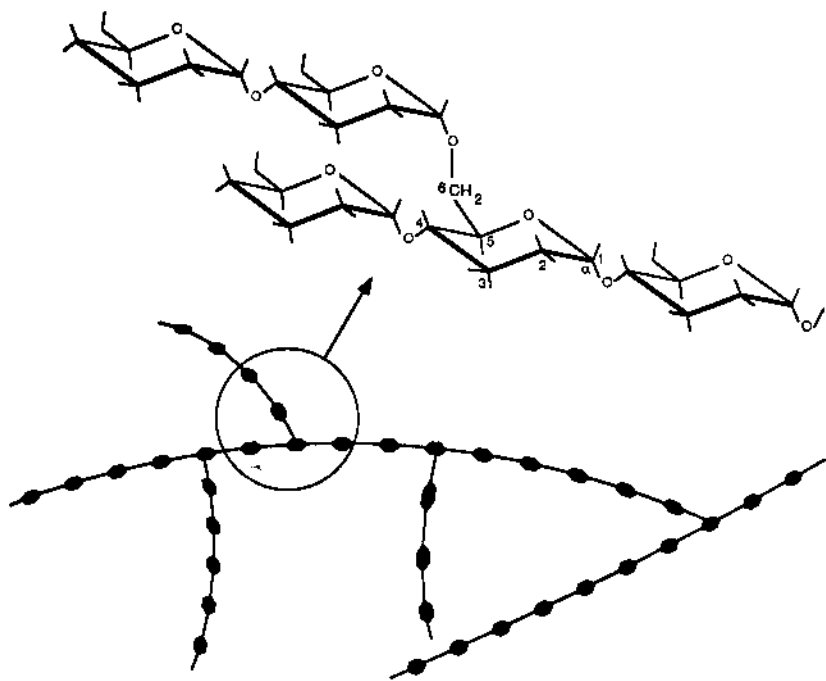# Linear Starch – Amylose

Branched Starch – Amylopectin

Fig. 3.4 Linear starch, amylose, and branched starch, amylopectin.

Table 3.2 Amylose/Amylopectin Content, Granule Size and Gelatinization Temperatures of Starches

Starch source	Starch type	Amylose/ amylopectin (%)[a]	Size diameter (μ)[b]	Gelatinization temperature (°C)[c]
Corn	Cereal			
Pearl		27/83	5–26 (15)	62
Waxy		0/100	5–26 (15)	63
High amylose		55–85/15–45	3–24 (12)	67
Oxidized				
Low conversion				52
High conversion				55
Hydroxyethyl				
DS = 0.05				58
DS = 0.09				55
Cationic (DS = 0.046)				52
Crosslinked				62
Acid modified				
40F				62
60F				63
80F				68
Potato	Tuber	20/80	15–100 (33)	59
Wheat	Cereal	25/75	2–35	58
Tapioca[d]	Root	17/83	5–25 (20)	49
Sago	Pith	26/74	15–65	
Rice	Cereal	18.5/81.5	3–8 (5)	68
Sorghum	Cereal	22/78	5–25	68
Sweet potato	Tuber	18/82		

[a]From Refs. 2, 15, and 21.
[b]Number in parenthesis is average size. From Refs. 48 and 21.
[c]Temperature when swelling begins. From Refs. 14 and 76.
[d]Brazilian origin.

amylose or amylopectin chain structures. High amylose starches require cooking temperatures of greater than 150°C for dissolution but retrogrades (gels) rapidly if cooled [5,6]. The proof of structure for amylose and amylopectin has been extensively reviewed by Peters [7]. Current knowledge of starch architecture and structure differs considerably from the earlier ideas and theories [8,9]. The starch granules produced by the various plants are actually

spherocrystals with limited crystalline order in which the two types of chain structures are compacted into stratified layers formed around a nucleus [10]. The amylose and amylopectin chains are compressed into a parallel array of double helices with the 1–6 branch points being located in the amorphous regions [4]. Each plant produces a starch granule having features specific to that starch source, e.g., corn, sago, potato, etc. Typical examples of starch granules from various sources are illustrated in Fig. 3.5. Under polarized light each granule type gives a specific birefringence pattern, as shown in Fig. 3.6. The shape and birefringence pattern is useful in starch identification [11–13].

The starch granules are not materially changed by the wet milling or mechanical/chemical processes required for separation, recovery, or modification of the starch from the seeds, tubers, or piths of various plants. Raw, unmodified starch is designated as pearl starch and can be marketed as fine or coarse, dustless powders. Like cellulose, the starch can absorb/desorb water depending upon the ambient temperature and relative humidity. When sold, the starch must be controlled to the limits of commercial acceptance of approximately 12% moisture.

Unmodified (pearl) starch has high water bonding or thickening power when cooked. Cooking provides the thermal energy necessary to permit water molecules to penetrate the compacted stratified layers, as shown in Fig. 3.7. The temperature at which enough thermal energy is available to overcome hydrogen bonding within the chain structure is called the gelatinization, or pasting, temperature. More precisely, the gelatinization temperature is taken as the point where birefringence in the granule disappears [14]. This temperature will depend upon the ratio of amylose/amylopectin and the arrangement of these molecules within the starch granule structure. The gelatinization temperatures for various starches are given in Table 3.2 [2,15].

Profound changes in starches occur as the water begins to enter and swell the granule. The viscosity of the solution shows a marked increase, as most of the provided water is absorbed by the continuously swelling granule. This process is summarized in Fig. 3.8. The granule continues to swell as the temperature increases beyond the gelatinization point, as marked by point A in Fig. 3.8. That is, the increase in thermal energy overcomes the intermolecular bonding resisting hydration of the amylose and amylopectin chains. As the granules swell to point B along the curve, the viscosity of the mixture continues to increase to a maximal level up to point C. Finally the super-swollen granule, under the influence of the shear force applied during cooking, bursts like a balloon, dispersing the swollen amylose and amylopectin chains into the size mixture, thus lowering the viscosity of the size solution [16]. With continued heating and agitation the viscosity finally levels off as all of the granules
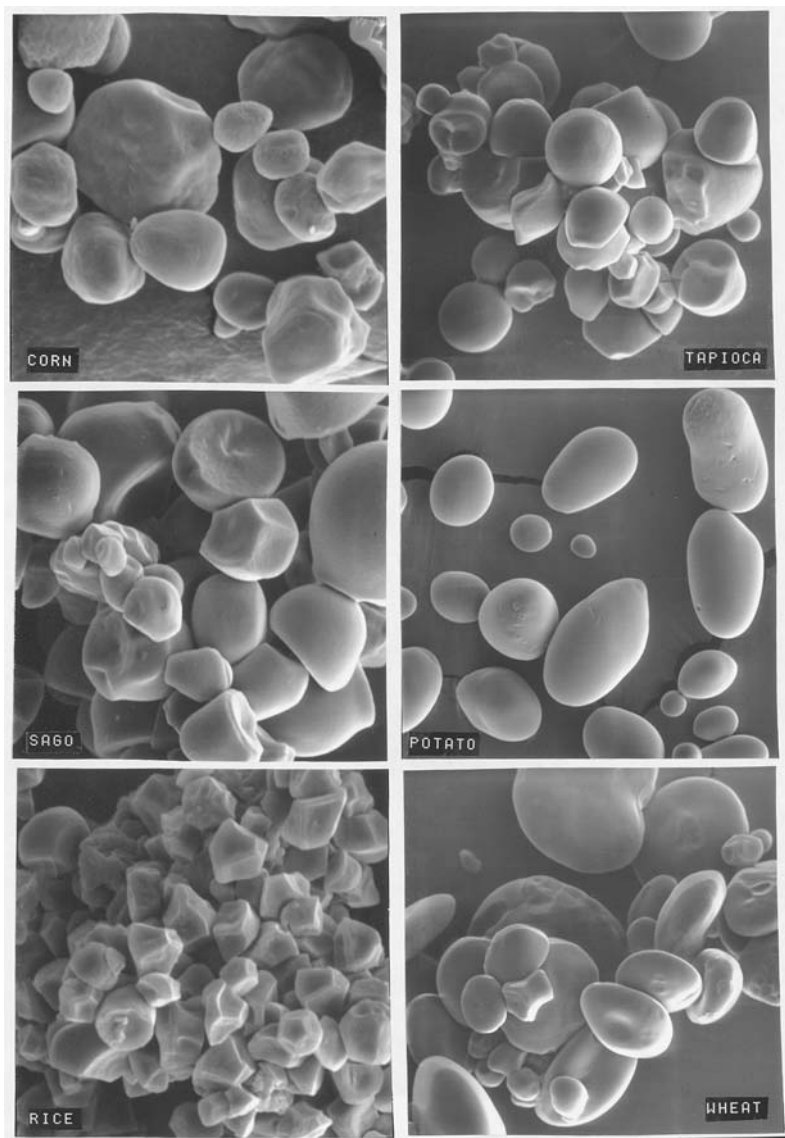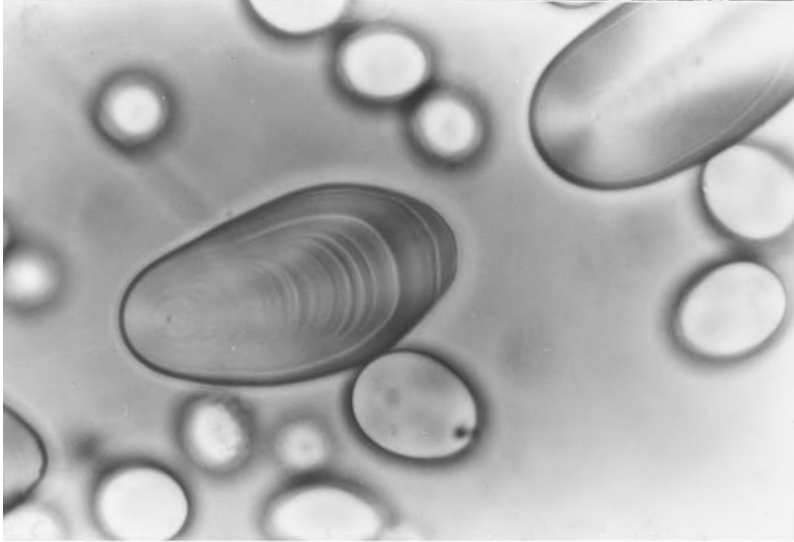
Fig. 3.5 Scanning electron photomicrographs of starch granules: corn (1000×) tapioca (1000×), sago (1600×), potato (500×), rice (2000×), and wheat (1000×). (Courtesy of Seydel Woolley & Co. for supplying the starches and M.E. Miller for the SEM work.)
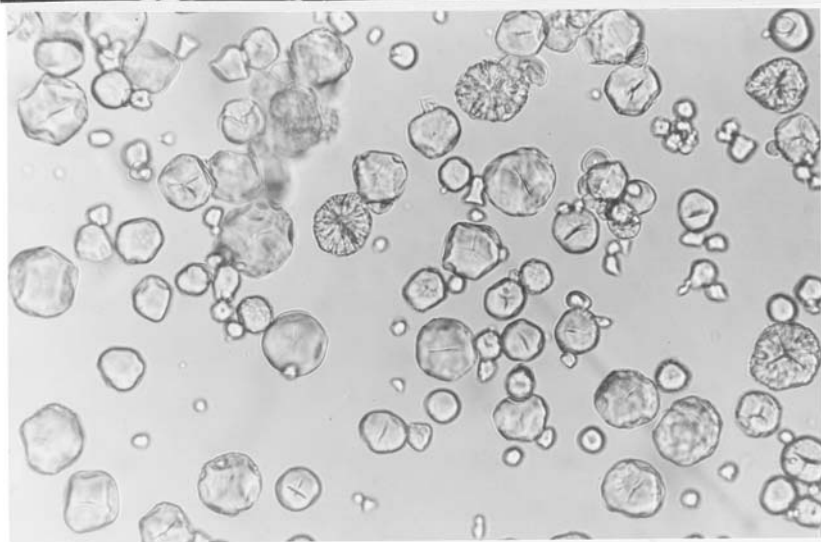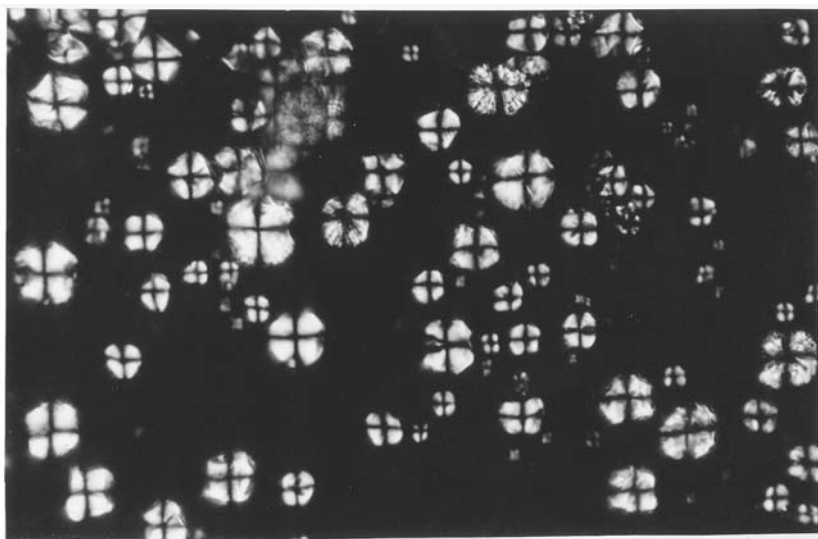
Fig. 3.6 Under polarized light, starch gives birefringence patterns that are specific to the starch genera. Shown are the birefringence patterns for potato (a), canna (b), and tapioca (c). Upper photograph is polarized light, and lower is incandescent light.
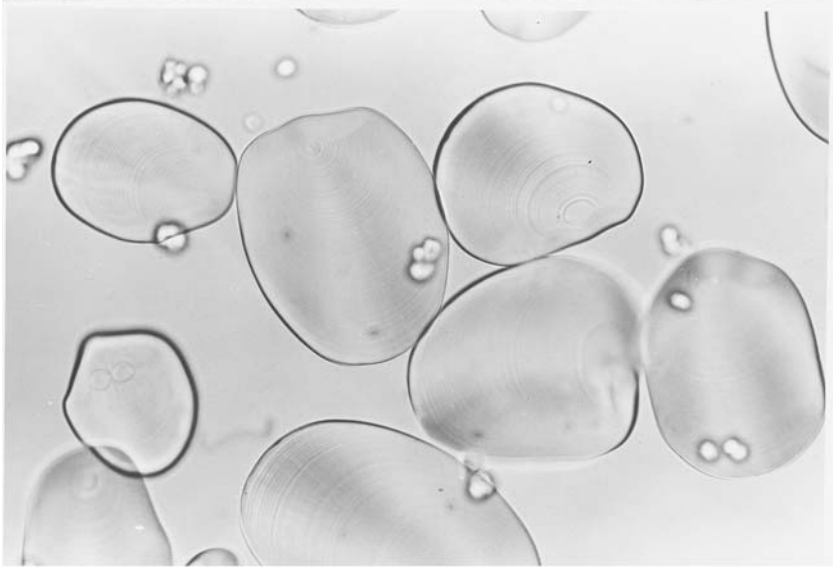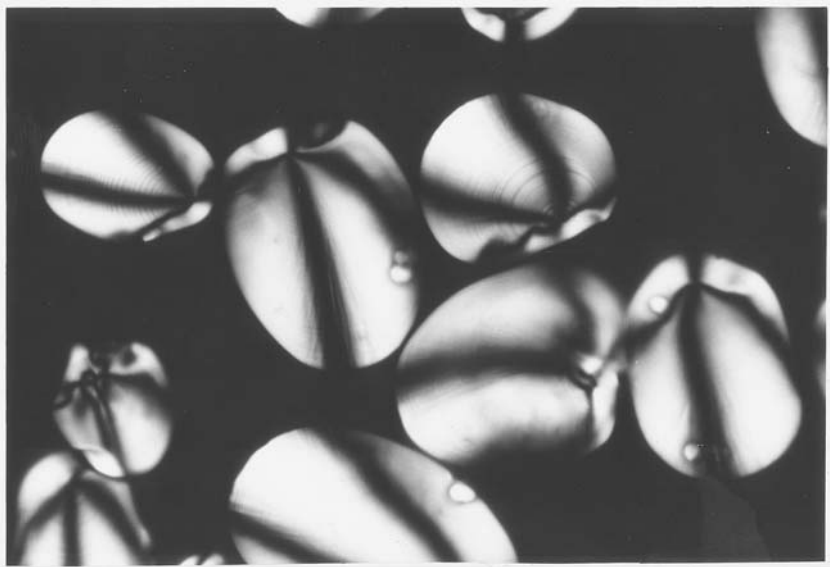
(b)

Fig. 3.6 Continued.
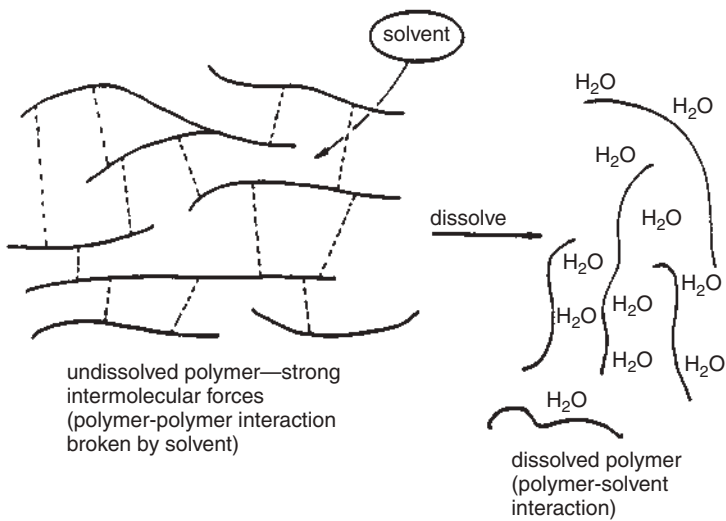
(c)

Fig. 3.6 Continued.

Fig. 3.7 In order to dissolve, the solvent must break all the polymer–polymer interactions and replace them by polymer–solvent interactions. Chains are totally surrounded by solvent.

rupture, marked by point E in Fig. 3.8). At this point a stable ''leveling-off viscosity'' is obtained and the starch size mixture is ready for use in sizing.

If the kinetic energy is removed from the cooked (swollen) size, such as when the solution is cooled, the possibilities for multiple points for intermolecular chain contacts occur, and a rigid interlocked chain structure composed of a microcrystalline, micellelike structure having hydrogen bonding networks is formed, and the starch mixture gels. When size of this gel structure is applied to the yarns, the gel dries and forms a film around the yarn. At high starch concentrations this network causes the cooled paste viscosities to be too high to be effectively handled for sizing purposes (point F in Fig. 3.8). When the hot gel structure is applied to the yarns followed by drying, a protective film is formed around the fiber bundle. The sizing process for starch is shown schematically in Fig. 3.9.

The propensity of raw (pearl) starches to produce high viscosities can be reduced or eliminated by modifying the starch by any one of the following processes:
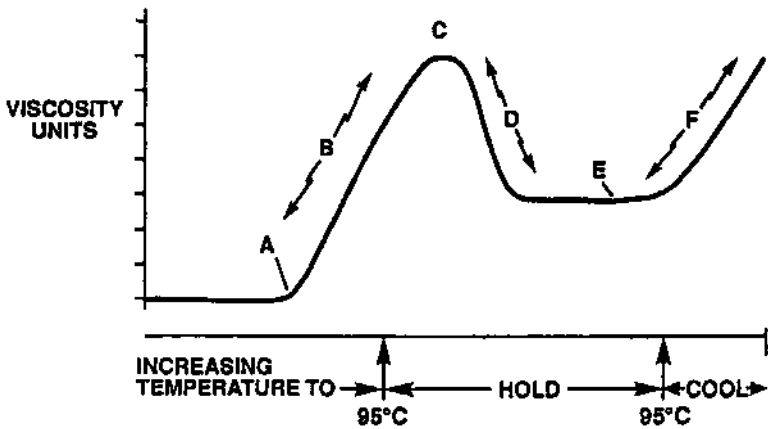
Fig. 3.8 Typical cooking (viscosity) curve for starch. (A) Gelatinization temperature; (B) granules hydrate and swell; (C) peak viscosity (granules rupture); (D) continued rupture of starch granules; (E) leveling off (use) viscosity; (F) effects of cooling (retrogradation).

Acid modification
Conversion to gums
Enzyme treatments
Derivatization (chemical modification), e.g., oxidation

3.3.2 Modification of Starch

Acid Modification

In acid modification, an aqueous suspension of the starch granules are reacted under varying conditions of time, temperature (below the gelatinization point), and hydrochloric acid concentration to reduce the molecular weight of the starch chains, while no apparent change occurs in the granule when viewed microscopically [13]. By reducing the chain lengths the viscosity of the cooked starch solution can be substantially lowered (Fig. 3.10). In addition to reducing the viscosity, such a modification provides the textile mill with size solutions having a high solids content, (i.e., high-solids, low-viscosity size; Fig. 3.11. Such sizes are ideal for loading up the woven fabric with a high size content for loom finished goods such as denim. Weaving efficiencies may also be improved. For example, the lower viscosity sizes can provide for a more con-
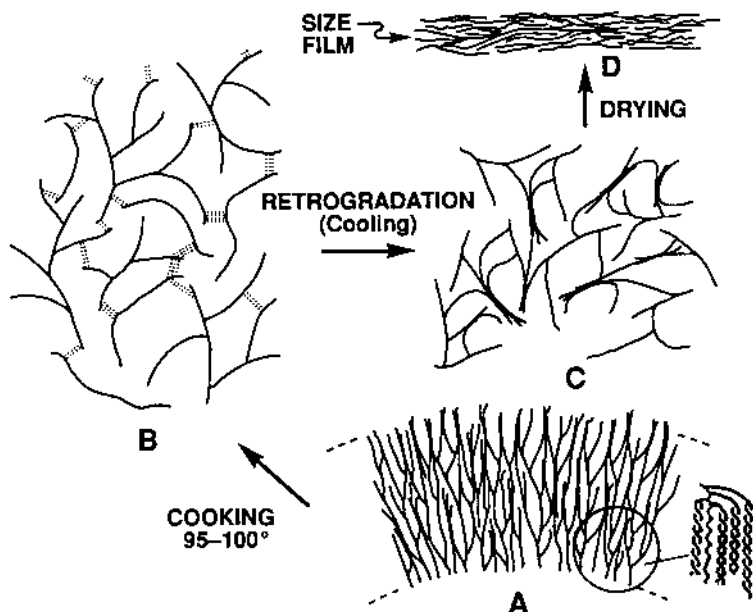
Fig. 3.9 Mechanics of starch sizing. (A) Raw starch: the amylose and amylopectin chains are thought to be compressed as double helices into layered growth rings within the starch granule. (B) High temperature hydration (cooking) swells the granules, ultimately releasing the chains to give a cooked paste with weak attractions between the molecules (represented by the dotted lines). (C) Removing the energy (cooling) causes retrogradation (chains collapses and gels) due to the formation of micelles (represented by the thickened areas). (D) Upon drying, the gel chain structures totally collapse to give a protective size film around the yarn.

trolled penetration into the warp threads. A moderate reduction in the degree of polymerization (DP), or chain length of the starch, only slightly reduces the strength of the film, as shown in Table 3.3, but offers an easier break, or separation of adjacent yarns, of the ''dry'' size during leasing on the slasher. Such materials may be conveniently added to other size formulations and may help in reducing the energy required to separate the yarn sheets at the lease rods. It may also help in attaining lower yarn hairiness, less size shedding at the loom, and eventually easier and more efficient desizing operation. Depending upon the amount of starch hydrolysis that is allowed to occur, a wide range
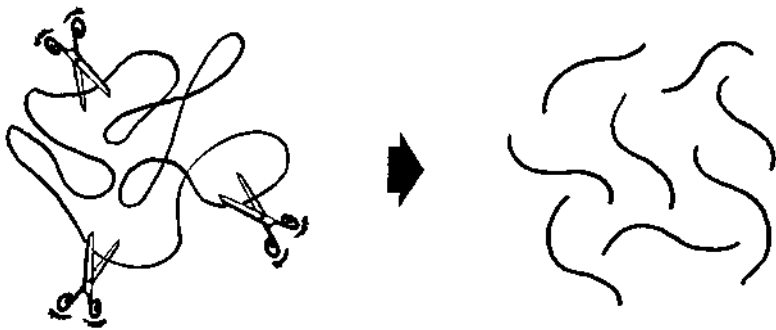
Fig. 3.10 Effect of acids, enzymes, or oxidizing agents on the length of cellulose or starch chains. The viscosity of the solutions are decreased.

of fluidities result. Starch viscosity, η, is defined by textile mills in terms of fluidity, which is defined as the reciprocal of viscosity, i.e., fluidity $= 1/\eta$. A high fluidity means a low viscosity and vice versa (Fig. 3.12).

The higher the fluidity number, which for acid-modified starches ranges from 20 to 90 g/dl, the greater the acid modification and lower the viscosity of the cooked mixture. Thus more 90 fluidity starch can be added to the size cooking

Fig. 3.11 Effect of the chain length of the size molecule on obtaining high solids low viscosity size formulas.

Table 3.3 Strength, Elongation and Viscosity Properties of Some Starches

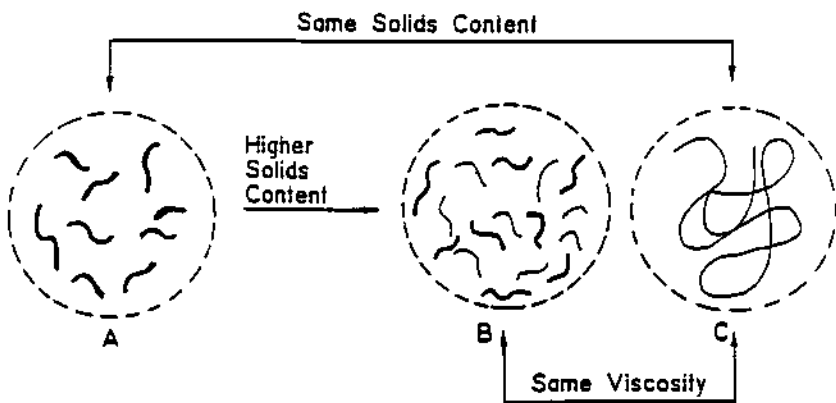| Starch	Strength (kg/mm^2)	Elongation (%)	Viscosity [η] (dl/g)
Corn			
(unmodified)	4.67	3.2	1.73
Acid Modified			
15F	4.67	2.7	1.21
34F	4.45	2.6	1.06
50F	4.94	2.7	0.88
71F	4.57	2.9	0.67
89F	4.58	2.2	0.32
Chlorine oxidized			
low	4.87	3.0	0.47
high	4.50	2.3	0.25
Hydroxyethylated			
Unmodified (DS = 0.05)	4.74	2.5	1.66
Acid modified (DS=0.05)	4.18	2.6	0.38
Waxy maize (Amioca)	3.49	1.7	1.50
Tapioca	4.40	3.4	2.03
Potato	4.42	3.1	2.20
Wheat	2.00	2.9	2.00
High amylose	5.03	2.5	1.35

kettle than a 40 fluidity; yet the final solution viscosities of the two size mixtures could be the same (Fig. 3.11). Because of the reduction in viscosity with increasing modification these types of starches are sometimes referred to as ''thin boiling'' starches. Fig. 3.13 shows a comparison of the various starches and modified derivatives in terms of parts of water required to achieve comparable viscosities. For example, a 40 fluidity starch cooked in 8 parts of water has the same viscosity as the pearl corn starch cooked in 14–15 parts water.

$$fluidity= \frac{1}{viscosity} \ or \ \frac{1}{η}$$

Fig. 3.12 Relationship between fluidity and viscosity. When viscosity is large (high number), fluidity is small (low number, $1/η = 0$). When viscosity is small (low number, 0.0000001), fluidity is large (high number).
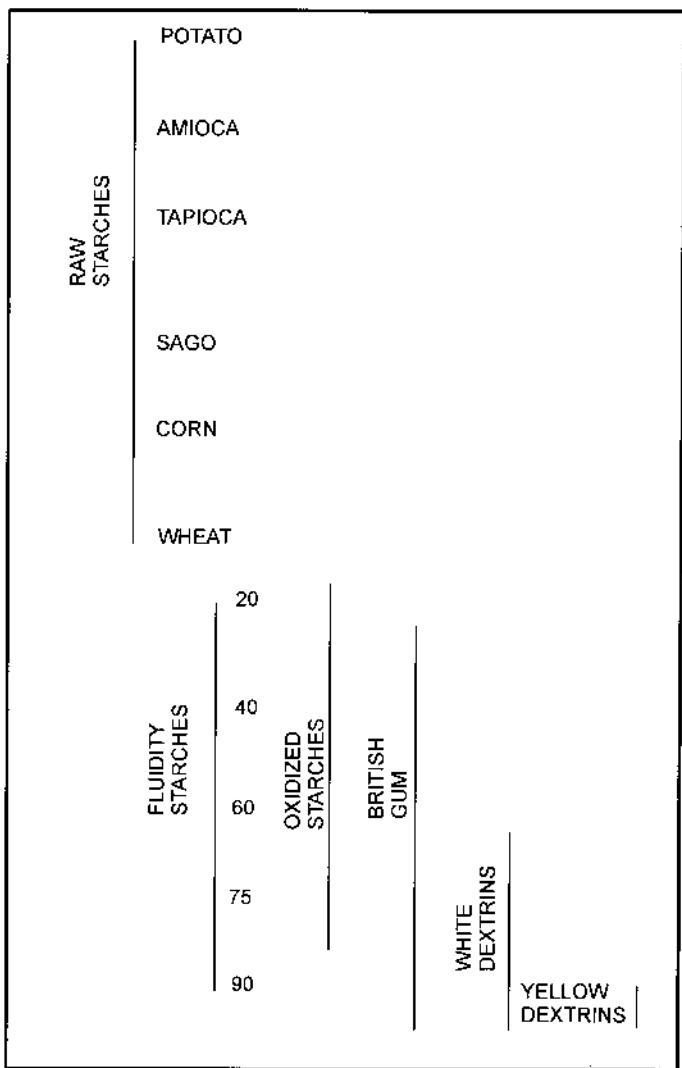
Fig. 3.13 Parts of water required to achieve comparable viscosities of various starches.

Gums

If the starch granules are roasted, often in the presence of acid, the DP of the starch chains is reduced but recombine to form highly branched systems that are soluble in cold water, as shown in Fig. 3.14. These operations are not performed by the textile mill but are carried out by the starch suppliers. Most gums have low film strengths; nevertheless, they are used in modifying the characteristics of stronger size materials and to provide high solids/low viscosity sizes for a more efficient slashing processing. Further thermal degradation gives dextrins that do not have any sizing uses. Gums are easily desized in warm water.

In addition to the starch gums there are a number of natural gums that at one time were used as binders and starch film modifiers. For the most part these products have been virtually supplanted in their sizing applications by the synthetic binders. The chemistry and sizing applications of the natural gums (gum arabic, tragacanth, locust bean, algin-alginic acids, guar, carra-
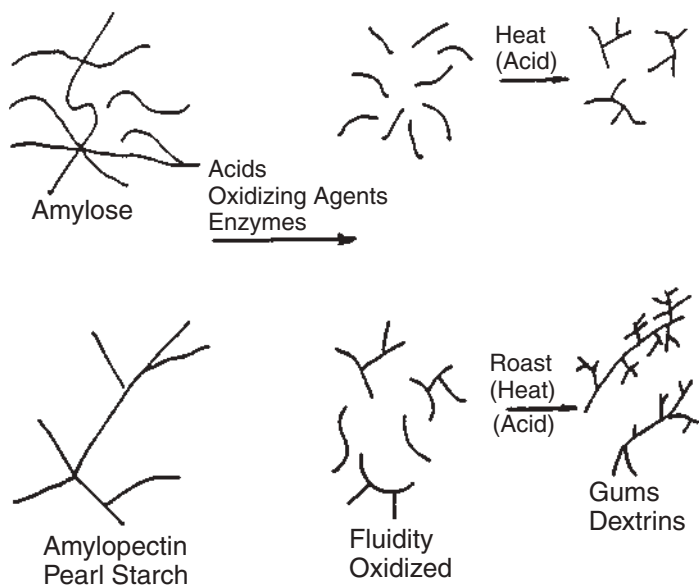

Fig. 3.14 Effect of starch breakdown using heat and acid on the properties of starch gums.

geenan, karaya, tamarind, xanthan) have been reviewed and are available in the published literature [8,17].

Enzyme Modification

Some mills start with inexpensive pearl corn starch and modify the starch themselves during the cooking cycle. This can be conveniently done by adding heat-resistant fungal or bacterial enzyme to the cooking kettle. As the size is heated, the enzyme breaks down the starch chain structure to give a higher fluidity size. Care must be taken to program the cook cycle to provide the same rate of temperature rise from batch to batch in order to achieve reproducible results. At temperatures near boiling the enzyme activity is destroyed and the chain scissions stop to prevent continuing breakdown during storage and use.

Derivatized Starches

The starch molecule has three hydroxyl groups per glucose unit that can undergo reactions analogous to those in cellulose. In fact, many of the derivatization reactions which can be successfully made for cellulose can be repeated with starch. Although numerous starch derivatives are known, only a few have practical application for sizing. The advantages offered by derivatization include

Lower gelatinization and cook temperature
Rapid attainment of a stable use viscosity
Reduced gelling (congealing or retrograde)
Lower viscosity upon cooling
Improved water holding ability
Increased paste cohesiveness
Improved film-forming characteristics
Clearer films
Compatibility with other size materials
Facilitated desized

The pendant groups derivatized onto the starch chains act as if they were wedges and prevent the coalescing or association of the starch chains either in the cooked pastes or when cooled, as shown in Figs. 3.15 and 3.16. Their retrogradation and gelling tendencies are minimized or eliminated. The chain structure can be more easily penetrated by water, reducing the gelatinization temperature, improving the water holding ability, and providing an easier desize. Water holding ability can be considered an advantage as it can help lower the humidity in the weave room. Also the films do not tend to shrink
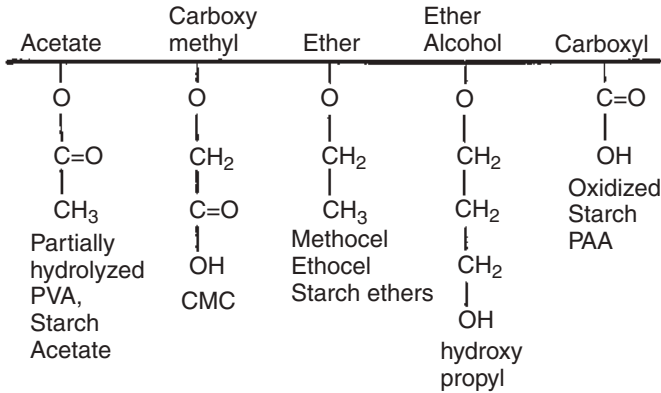
Typical Pendant Groups in Textile Size Materials

Acetate	Carboxy methyl	Ether	Ether Alcohol	Carboxyl
O	O	O	O	C=O
C=O	CH$_2$	CH$_2$	CH$_2$	OH
CH$_3$	C=O	CH$_3$	CH$_2$	Oxidized Starch PAA
Partially hydrolyzed PVA, Starch Acetate	OH CMC	Methocel Ethocel Starch ethers	CH$_2$ OH hydroxy propyl	

Fig. 3.15 Types of pendant groups (derivatives) which can be attached to the size polymer chain.

upon drying, thus cracking and shedding of the size film is reduced. Typical derivatives used for sizing include oxidation, esterification, cross-linking, and cationic starches. A brief discussion of some of the derivatives follows.

Oxidized Starch. The starch derivatives made by oxidative processes find limited use in textile sizing because they are more expensive to produce as compared to the other starch modifications which can give essentially similar properties to high solids/low viscosity cooks [5]. Instead of using acid to reduce the starch chain length, sodium hypochlorite, an oxidizing agent, is employed. In addition to chain scission, some of the primary hydroxyls at C6 are oxidized to a carboxylic acid, while carbonyls are produced at C2 and C3 hydroxyls [18]. The resulting carboxylic acid group at C6 is highly polar and larger than the original primary hydroxyl; thus sufficient wedging action occurs to prevent congealing, resulting in clear cooked pastes. During oxidation, the starch granule does not undergo any apparent structural change [19] and maintains its cold water insolubility. Further, high oxidative conversions can produce size solutions with very high solids at low viscosities [19]. Yet, because of the significant scission of the starch chains that occurs during the oxidative reactions, the granules disrupt easily upon heating so that they have short cook times. These properties of oxidized starches are more useful in the food industry [20]. The oxidized starch films are transparent and stronger. The lower fluidity oxidized starches find use in textile applications on dyed cotton yarns
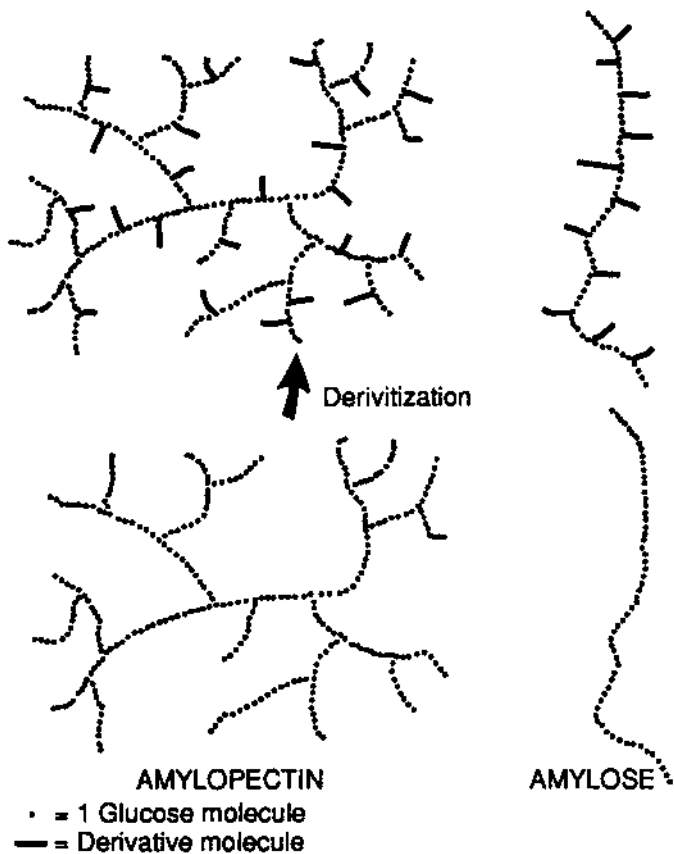
Fig. 3.16 The effect of derivatization on the chain structure of amylose and amylopectin starches.

where the transparent films do not mask the brightly colored yarns on certain styles of fabrics.

Starch Acetates (*Esters*).   Starch acetates can be thought of as the starch equivalent of partially hydrolyzed polyvinyl alcohol (PVA). Instead of removing the acetate groups, as occurs in the manufacture of PVA, they are added to the starch chains by one of several chemical routes [21]. Starch acetates used for warp size applications have a low degree of substitution (DS), the

average number of acetate groups per glucose molecule of the starch. Starch acetates are available in a wide range of fluidities and possess the characteristics expected of derivatized starches; that is, the wedging effect of the acetyl groups ($-O-C=O-CH_3$) decreases the chain association (Fig. 3.16) and thus prevents congealing or gelling, etc. Depending upon the number of acetyl groups on the starch chain, the adhesion to materials such as polyester and hydrophobic sizes improves. The acetate derivatives give good viscosity stability, lower pasting temperatures, and strong flexible films.

Starch Ethers.   Starch ethers are also used in sizing applications. For example, hydroxypropyl potato starches of low DS are soluble in hot water and thus are easily desized. This advantage has found particular use in the desizing of denim fabrics during garment laundering processes to provide prewashed jeans without having to use an enzyme wash cycle [22].

Cross-Linked Starch.   Corn starch is cross-linked to suppress swelling in hot water swelling and to provide stronger size films over a wide range of weave room humidity conditions. During conventional cooking, a high viscosity-to-solids ratio is obtained that makes this size variant well suited for low size add-ons with the heavier weight fabrics.

The cross-linking reaction must be precisely controlled. Only a few cross-links can have a significant effect on the size viscosity. Thus small changes in the reaction condition could mean large differences in the final viscosity of the size mixture. This problem resulted in a slow growth for the textile uses of cross-linked starches. The starch cross-linking reactions are summarized in Fig. 3.17.

The reagents of choice which give good results for cross linking starch are phosphorous oxychloride and sodium trimetaphosphate. Small amounts of these reagents have a marked effect upon the behavior of cooked starch [23].

Cationic Starches.   The cationic starches are relatively more expensive than the other starch derivatives; consequently they do not find widespread use in sizing. The positive charge of the cationic group on the starch gives it excellent adhesive characteristics due to its high affinity for the negative charge on textile fibers. The higher adhesion provides for greater abrasion resistance and decrease size usage [24]. Static electricity in the sized yarns is eliminated, and the sized fabric has better softness. The more useful cationic starches are those containing tertiary amino or quaternary ammonium salts [20]. These starches are primarily used to size glass filaments and other fibers having low adhesion for traditional sizes.

Genetic Variations.   Amylose and amylopectin have properties which are uniquely different, but they are both useful in slashing. Amylose provides
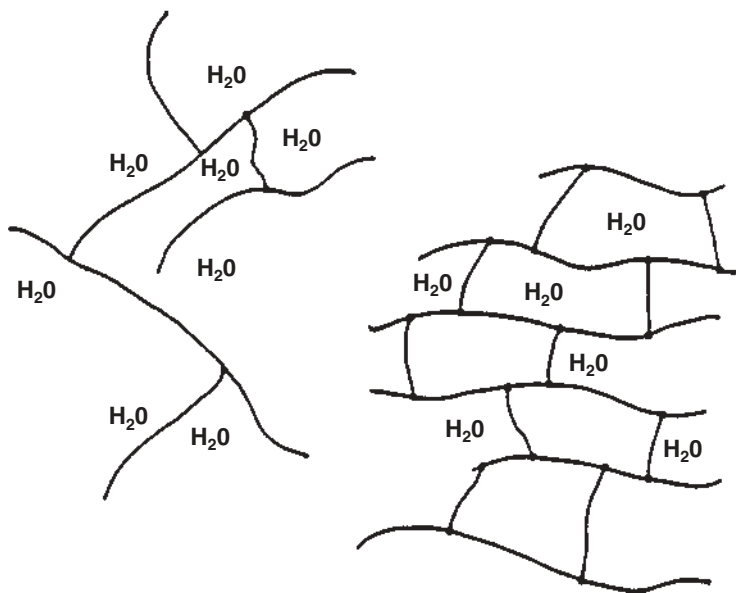
Fig. 3.17 In a highly cross-linked polymer it is not possible to surround individual chains and solubilize them.

most of the properties of strength and flexibility of the film in the starch. Amylopectin is responsible for increased viscosity and noncongealing aspects of the size mixture. The need for an amylopectin type starch as a replacement for tapioca, a starch having a high amylopectin content as shown in Table 3.2, led to the development of a hybrid genetic mutant from a waxy corn variety found in China that contained essentially 100% amylopectin [25].

Although primarily used in the food industry, this starch finds application in textile sizing because of its ease of cooking. Further, it provides pastes that set to a soft gel upon cooling and is more easily desized. As expected for a highly branched chain configuration, amylopectin films have low strength. Amylopectin sizes are used in modifying the properties of sizes containing stronger film formers or to increase the paste viscosity without greatly increasing the solids content of the size mixture.

There are two high amylose genetic mutants available commercially. They contain either 55 or 70% amylose, although one variety containing 85% has been cited [26]. It is also possible to obtain chemically fractionated amylose

starch. Pure amylose starches cannot be cooked using conventional starch cooking equipment even for long periods at the boil. Instead, high temperature and pressure cookers, such as jet cookers, are required to give useful dispersions. Even then, the starch has little application for sizing because of the high propensity of amylose starches to rapidly retrograde with cooling. Modifications by derivatization, however, provide starches having lower gelatinization temperatures than regular corn starches with no retrogradation problems [6]. The derivatized amylose starches have good film strengths, have acceptable viscosities, and are easily desized.

3.4 POLYVINYL ALCOHOL

3.4.1 Introduction

Polyvinyl alcohol (PVA) has been one of the most versatile size materials available for warp sizing formulations since it was commercialized as a textile warp sizing agent sometime around 1965. A review of the discovery and uses of PVA as a textile warp size is available in the published literature [27]. The versatility of PVA arises from the fact that it can be manufactured into a variety of modified forms and can be utilized alone or in combination with other size materials, e.g., starch, polyester resins, acrylic copolymers, and CMC, or as a binder with numerous fiber substrates, e.g., glass, acrylic, polyester, cellulose acetate, nylon, and numerous styles, as shown in Table 3.4 [28,29]. High-speed looms require yarns with strong flexible films, which makes the use of some grade of PVA in the size mixture a virtual necessity.

3.4.2 Chemistry and Manufacturing of PVA

Polyvinyl alcohol is manufactured by the process of addition polymerization of vinyl acetate rather than the highly stable vinyl alcohol [30]. The resulting vinyl acetate polymer is hydrolyzed under varying conditions of catalyst, time, and temperature to remove varying amounts of the acetate (ester) radical ($-O-C=O-CH_3$) and replace them with the hydroxyl groups ($—OH$), as shown in Fig. 3.18. By controlling the length of the PVA chain—DP or n in Fig. 3.18—and the degree of hydrolysis of the acetate groups, a family of PVA warp sizing grades can be manufactured, thus allowing the size to be tailored for specific sizing needs. For example, by allowing some of the acetate groups to remain on the PVA backbone chains, they can act as wedges to prevent other neighboring chains from the close associations that would allow for intramolecular hydrogen bonding that would prevent easy water penetra-

Table 3.4 Typical Uses for PVA Sizes

100% PVA	PVA blends
Cotton fabrics	Twill fabrics
Corduroy	Muslin sheeting
Percale sheeting	Batiste styles
Fine broadcloth	Print cloth
Tight poplin	Heavyweight apparel fabric
Rayon (100% spun and filament)	Denim
Triacetate (filament)	Lightweight 100% cotton
Polyester	
100% industrial	
100% spun	
Polyester/cotton (fabrics and towelling)	
Polyester/rayon	
Glass (filament and fabrics)	

Source: Ref. 29.

tion needed for rapid dissolution. In other words, the hydroxyl groups that are left are too far apart to achieve much intrachain hydrogen bonding, as explained in Fig. 3.19.

Another factor that assists the ready dissolution of PVA in hot water is the fact that the polymerization of vinyl acetate produces mostly an atatic chain structure [30]. The acetate or the hydroxyl groups, after saponification, are randomly distributed left or right on the carbon polymer backbone chain thus substantially reducing molecular order which would allow for greater hydrogen bonding, as shown in Figs. 3.20 and 3.21. As a result only a few nonhydrolyzed acetyl wedges remaining on the PVA chain can have a considerable effect on the properties of the size.

The chain disrupting effect of a properly selected comonomer polymerized into the PVA structure was recognized by the Du Pont company about l972 [31]. Du Pont began to produce a PVA grade used exclusively for warp sizing in which a comonomer was introduced into the PVA chain structure [32]. The comonomer not only reduced the molecular fit between the chains even further, but additionally provided a nonhydrolyzable wedge that improved water solubility and resolubility needed for easier desizing as well as greater specific adhesion to polyester and other hydrophobic fibers.

Physical properties of the copolymer size are similar to the intermediate hydrolyzed (IH) grades [32,33]. The methacrylate comonomer appears to meet
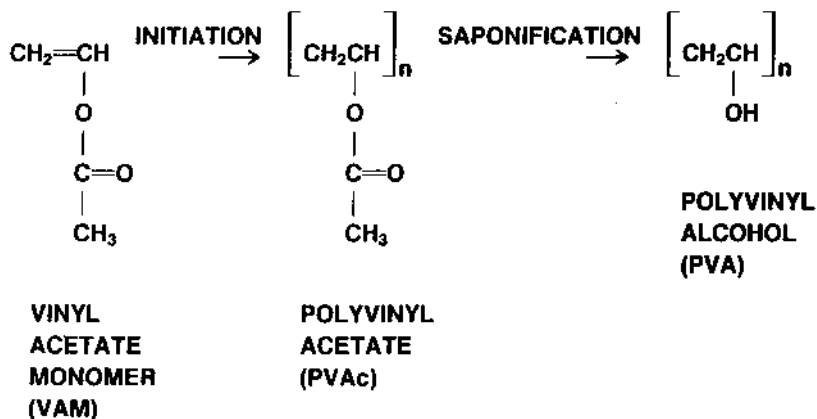
Fig. 3.18 Chemistry of polyvinyl alcohol manufacture.
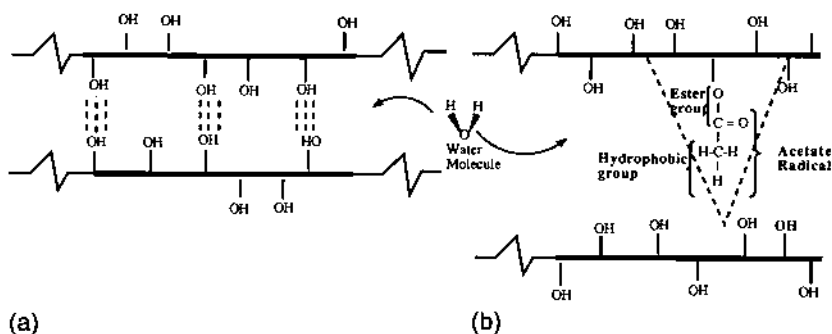
Fig. 3.19 Effect of degree of hydrolysis on the ease of dissolving (redissolving) and humidity sensitivity of polyvinyl alcohol. (a) Segment of fully hydrolyzed PVA chain. Water must break intrachain hydrogen bonding. (b) Segment of a partially hydrolyzed chain. Acetate radical forces neighboring chains to exist further apart, facilitating water penetration and dissolving (redissolving), thus lowering the strength but improving adhesion to hydrophobic fibers.
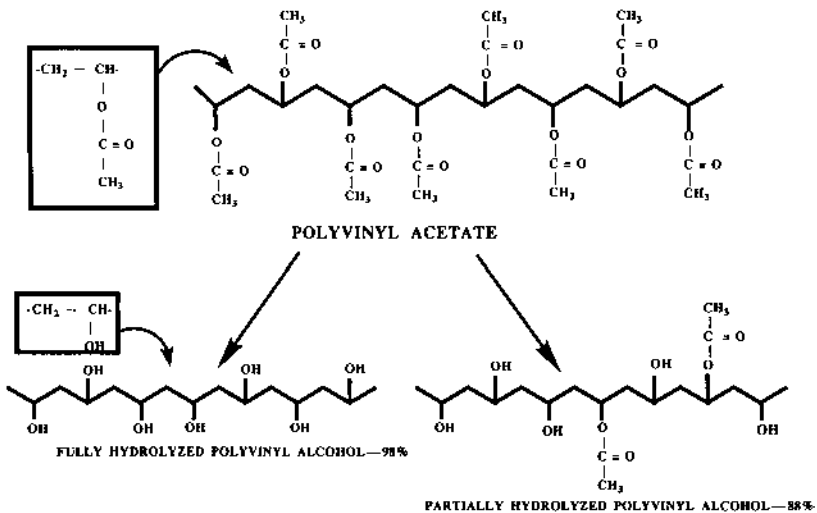
Fig. 3.20 Hydrolysis of polyvinyl acetate. Carbon and hydrogen atoms on the backbone chain omitted for clarity (see insets).

these requirements quite well [34]. For example, methacrylate copolymers are resistant to, possibly due to steric hindrance of the pendant methyl group, the hydrolytic conditions necessary for saponification of the acetate groups of PVAc [35,36] as well as having the correct reactivity ratios necessary for random atmospheric copolymerization with PVAc [36]. The latter comonomer appears ideal because it has an additional interchain disrupting group (methyl wedge) associated with the acrylate ester (—C—O—R). A few mole percent of such a comonomer may produce its maximal effect on the sizing properties of the PVA copolymer. Regardless of the comonomer employed, it must

Be stable to the hydrolysis reaction which converts PVAc to PVA
Not hinder the purification steps
Be as compatible as regular PVA to other size ingredients
Not be labile to the high temperatures employed (cooking, size box, dry cans, etc.) in sizing
Not be chemically altered by recovery (ultrafiltration) processes
Not cause size preparation problems (foaming, sticking to dry cans, etc.)
Be consistent in properties from batch to batch (i.e., be reproducible)
Have good water dispersibility and desizeability
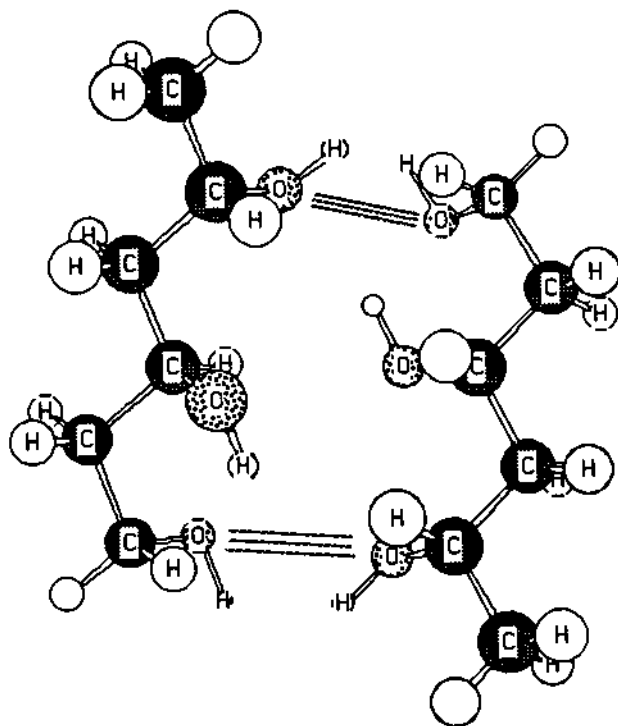
Fig. 3.21 Three-dimensional structure of atatic PVA. Hydroxyls must match up to achieve any hydrogen bonding in the molecule.

The grades of PVA with respect to chain length (molecular weight), degree of hydrolysis, and viscosities for warp sizing are given in Tables 3.5 and 3.6. A superhydrolyzed grade of PVA will have only four of every 1000 original acetate groups still remaining on the PVA chain; fully hydrolyzed, 12–20 acetyl groups, etc. This could be visualized as only 12 acetyl groups remaining along a superhydrolyzed chain (36–60 for a FHA grade) that had a DP of 3000. These small amounts of remaining acetyls have essentially no practical effect on the overall properties of PVA. It should be noted that copolymer type PVA will also have a high degree of hydrolysis of acetyl groups. A small number of residual acetyl groups will still be present on the copolymer chain; however, most of the acetyls will have been replaced by the comonomer. The comonomer group will not be saponified under the mild conditions employed

Table 3.5 PVA Grade and Percent Saponification (Hydrolysis) of Acetyl Groups

PVA grade type	Abbreviation	Acetyl removal (%)	Acetyls remaining per 1000 originals
Superhydrolyzed	SH	99.6	4
Fully hydrolyzed	FH	98–98.8	12–20
Intermediate hydrolyzed	IH	95.5–96.5	35–45
Partially hydrolyzed	PH	87.0–89.0	110–130
Copolymer	None	98–98.8	30–40[a]

[a]Includes both residual acetyl and comonomer groups.

for acetate groups. Further, the comonomer radical is more effective at achieving solubility characteristics than the acetates due to its size, reactivity, and randomness of the distribution on the PVA backbone chain.

Polyvinyl alcohol grades are normally available in viscosities ranging from a low of 5 cp to intermediate ~14 cp, medium ~25 cp, and high ~40 cp, approximately. For practical reasons most of the PVA used for warp size applications will consist primarily of the intermediate and medium viscosity grades since they are the only ones that have the proper viscosity range necessary for most sizing applications. Usually it is a practice to blend the low viscosity grades with the high viscosity types. The low viscosity types are not used alone for sizing since they provide too thin a size mixture that can result in excessive penetration of the size into the yarn bundle. On the other hand, high viscosity types are more difficult to process and mostly result in surface sizing without sufficient penetration in the yarn bundle to achieve proper anchoring of the resulting size film.

Table 3.6 Effect of Chain Length (DP) of PVA on Viscosity

Viscosity type	DP (n in Fig. 3.18)	Molecular weight (viscosity average)	Viscosity (CP) of 4% solution
Low	500–900	22,000–31,000	4–8
Intermediate[a]	1200–1800	50,000–65,000	13–16
Medium	2200–2500	77,000–79,000	21–32
High	2800–3000	106,000–110,000	40–65

[a]Not a usual textile grade after about 1985.
Source: Ref. 2.

The most important properties of a size necessary for textile processing and weaving are tensile strength, extensibility, recovery from extension, abrasion resistance, and ease of removal [37]. Addition of PVA significantly enhances these size properties.

The tensile strengths of the PVA film increases as the chain length (DP) of each grade increases and as the percentage of acetyl removal increases. Intermediate hydrolyzed (IH) grades are 7–10% weaker, while partially hydrolyzed (PH) grades are 20–25% weaker, than the fully hydrolyzed (FH) grades [38]. Nonetheless, the PH grades are significantly stronger than other size materials, as shown in Table 3.7. Thus PVA can be added to weaker sizes such as starch to improve the performance of these size products. A plot of tensile strengths as a function of the degree of acetyl hydrolysis of the various grades is shown in Fig. 3.22. One of the added advantages of PVA is its compatibility with most of the other film formers employed in sizing (see Section 3.7.8 on polyvinyl acetate binders and Fig. 3.43). Because PH grades are weaker than FH grades, they can actually decrease the energy to break at the bust and lease rods. This could result in a measurable decrease in yarn hairiness and clinging in the loom, key requirements in air-jet weaving [39].

Adhesion of PVA

The adhesion of PVA to various substrates depends primarily upon the number of acetyl groups and the fiber substrate to which it is being applied. For example, on hydrophilic fibers such as cotton and rayon, FH and IH grades exhibit good adhesion. This is because these PVA grades will have a higher number of hydroxyl groups still remaining on the polymer chain. Consequently the size will have better specific adhesion because of the potential for hydrogen bonding at the size–fiber interface. On the other hand, hydrophobic fibers

Table 3.7 Comparison of Properties of Film-Forming Sizes

| Size | Tensile strength (psi) | Elongation (%) | Moisture Content at | | |
			50% RH	65% RH	80% RH
PVA[a]	7,000–15,000	100–150		8–9[b]	16–17[b]
Starch	600–900	8–12		15–20	19
CMC	2,000–4,000	10–15	14	15–20	30.5
Acrylic	1,000–2,000	100–600			17–21

[a]At 70 °F and 65% relative humidity.
[b]Depending upon the degree of hydrolysis.
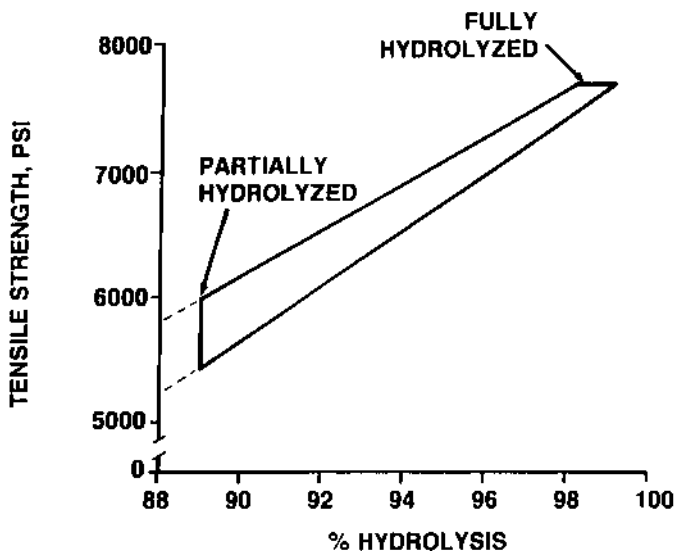
Fig. 3.22 Tensile properties of polyvinyl alcohol film as a function of hydrolysis. (1.7 mm dry film thickness equilibrated to 73°F at 50% RH, determined by Instron.)

exhibit poor wetting characteristics toward water-based sizing agents, resulting in lack of adhesion to the FH and IH grades.

Fig. 3.18 shows that the acetyl units remaining on the PVA chain contain ester groups. Thus, the PH grades should have a corresponding greater affinity for polyester fibers and other hydrophobic fibers, as well as have greater resistance to the force required to peel the size film away from the yarn at the bust rods, as shown in Fig. 3.23. This factor, coupled with the lower tensile strength of the PH grades, provides for a lower breaking energy and thus less shedding and yarn hairiness, but not at a sacrifice of ''yarn'' strength. Since the PH grade has better adhesion to polyester fibers, they can actually improve the sized yarn strength (Table 3.8) [39].

A comparison of the adhesion of CMC versus various grades of PVA to typical hydrophobic fibers is given in Table 3.9. The PH grades show excellent adhesion, while the copolymer types are better than the FH grades. All PVA grades are superior in their adhesion to hydrophobic fibers than the CMC. The superior adhesion and strength of PVA films may cause problems
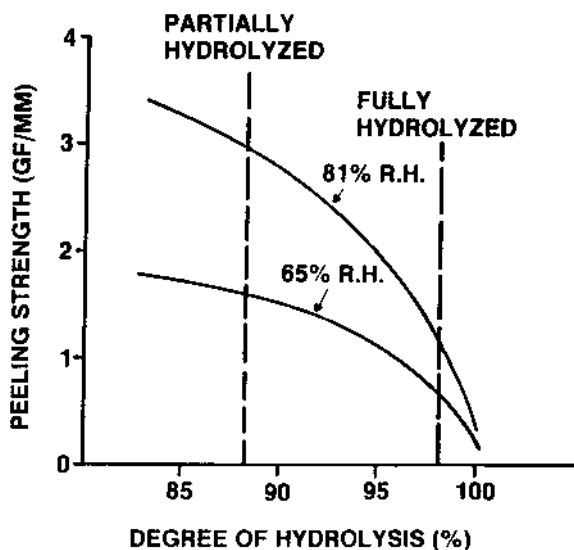
Fig. 3.23 Adhesion expressed as peeling strength of polyvinyl alcohol film from polyester film.

such as increased hairiness when the sized yarns are separated at the bust rods. Fig. 3.24 shows a comparison of the ease of sheet separation at the bust rods for the three major film formers used in sizing. Thus, PVA size formulas may need to be modified if a softer sheet separation is required. Alternatively, greater yarn spacing in the size box and on the drying cans should be employed.

Table 3.8 Breaking Strength and Elongation of Sized Yarns at 70°F and 65% relative humidity

PVA grade	Breaking strength (g)	Elongation (%)
Partially hydrolyzed	263.8	10.5
Fully hydrolyzed	252.1	12.3

Note: 65/35 polyester/cotton; yarn count 37's, 14% add-on.

Table 3.9 Adhesion of Medium Viscosity Polyvinyl Alcohol and CMC to Synthetic Films

	Adhesion strength (g/mm^2)	
Film	CMC	Partially hydrolyzed PVA
Acetate	0.5	10.0
Nylon 6	2.0	11.0
Acrylic	1.5	9.0
Polyester	0.5	7.0

Note: Conditions: 65% relative humidity, 20°C.
Source: Ref. 40.
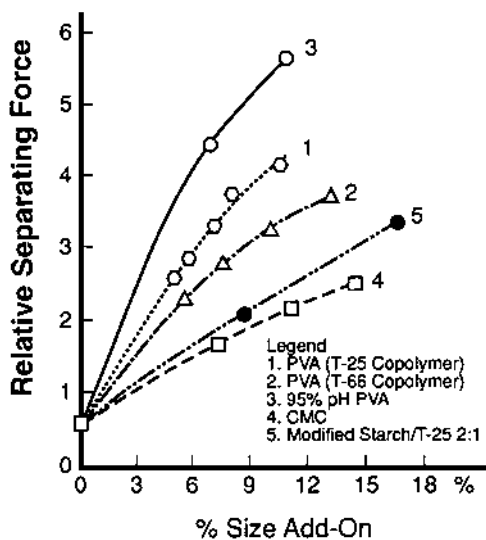
Fig. 3.24 Separating force (bust and lease rods).

Water Solubility and Resolubility of PVA

Polyvinyl alcohol with less than 88% hydrolysis, i.e., the PH grade, is not 100% soluble in cold water (~70°F). As the percent hydrolysis increases, however, the water solubility decreases such that the fully hydrolyzed PVA have high water resistance, as shown in Fig. 3.25. In hot water (~140°F), all grades of PVA above 88% hydrolysis are water soluble (see Fig. 3.26). Heat setting of PVA in the greige cloth can reduce the resolubility of FH grades and will require a higher temperature for solubility in water in order to achieve acceptable desizing, as shown in Figs. 3.27 and 3.28. The copolymer sizes can be considered comparable to the partially hydrolyzed grades as far as resolubility is concerned (Tables 3.10 and 3.11). Generally, temperatures in the range of 170 to 190°F are required to achieve acceptable desizing of most grades of PVA. The solubility of the FH grades of PVA can be improved by the addition of polyester resins [41].

Size Recovery

One of the major advantages of PVA is that it can be recovered by ultrafiltration techniques. Ultrafiltration is a membrane separation process that selectively filters chemicals according to the molecular size. The ultrafiltration membranes suitable for PVA recovery include carbon tubes manufactured by Gaston
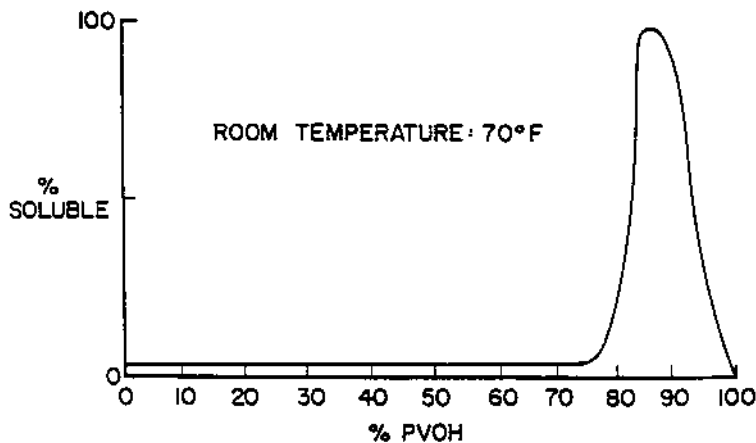
Fig. 3.25 Water solubility of PVA at 70°F.
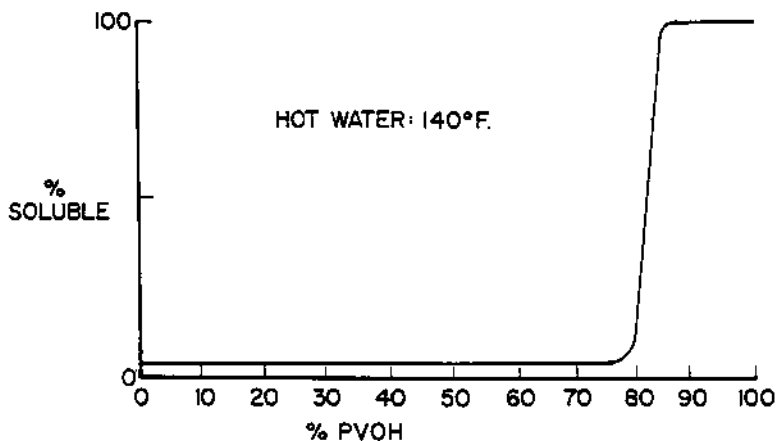
Fig. 3.26 Water solubility of PVA at 140°F.
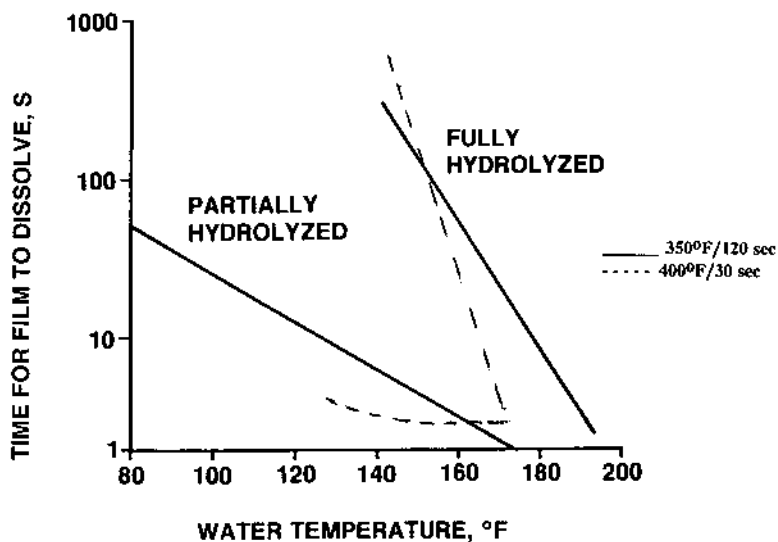
Fig. 3.27 Water solubility of heat-set films.
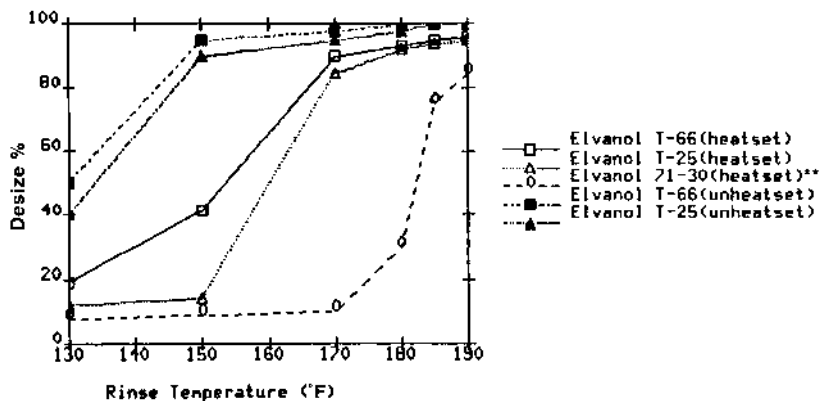
Fig. 3.28 Percent desize versus temperature for heat-set and non-heat-set PVA. (Heat-set at 392°F for 45 s. FH grade having the same DP as T25.)

County [42], stainless steel and inorganic membrane manufactured by Carre-Du Pont [43], and spiral wound polymeric types manufactured by Abcor [44,45]. These systems can recover about 94–97% of the PVA from desize liquors. PVA can be removed from the cloth with as little as 0.5–0.6 gallons of hot water per pound of fabric, allowing recovery of about 90–95% of the PVA removed by the desize operation [32]. ''Actual'' recovery is somewhat less since allowances for loom shed, desize washer efficiency, etc., must be made. Generally, 10–20% virgin PVA is added to the recovered size to make

Table 3.10 Percent Size Removal from Non-Heat-Set Fabric (Not Steamed) at 150°F

Number of washes	Homopolymer high viscosity	Homopolymer medium viscosity	Copolymer medium viscosity	Partially hydrolyzed high viscosity
1	90.1	90.9	93.5	88.0
2	93.3	94.8	94.8	92.6
3	98.7	97.6	97.3	98.1
5	100.0	99.4	100.0	100.0

Note: Percentages based on total water extractables in greige fabrics.

Table 3.11 Percent Size Removal from Heat-Set Fabric (Not Steamed)

Temperature (°F)	Number of washes	Homopolymer high viscosity	Homopolymer medium viscosity	Copolymer medium viscosity	Partially hydrolyzed high viscosity
150	1	11.2	13.3	16.1	50.4
	2	10.4	10.3	10.9	42.7
	3	18.4	18.2	37.6	70.1
	5	16.1	19.2	45.9	78.1
150	1	19.3	20.0	40.3	62.1
	2	16.9	17.6	59.6	71.2
	3	15.8	18.6	56.3	70.3
	5	16.6	20.0	60.4	80.0
170	1	18.6	29.5	80.3	71.3
	2	14.8	20.0	84.5	73.2
	3	17.8	22.6	89.6	74.9
	5	18.4	20.2	91.6	78.2
190	1	51.2	67.5	74.7	63.9
	2	60.5	78.6	88.3	70.1
	3	57.0	77.2	89.6	70.1
	5	63.9	82.7	91.5	70.9

Note: Percentage based on total water extractables in greige fabrics. Most desize temperatures range from 170 to 190°F.

up for these losses; however, the recovered size can be used directly with only wax and other additives such as defoamers, and antistats [44,45].

Polyvinyl alcohol recovery requires that special consideration be given to the total size system, including the type of PVA and other additives which will be employed in the size system. Because of their stability, copolymer type PVAs lend themselves more readily to reclamation. The size enters into the recovery system at about 180°F and at a slightly acidic pH (5.5–6.5). Such conditions could remove the more labile acetate ester groups on partially hydrolyzed PVA chains.

There are a number of textile mills that are operating units to recover PVA from desizing of sheeting, apparel, and industrial fabrics [46]. From 17 to 20 million pounds of PVA is recovered yearly, which represents 22% of the total PVA requirements in sizing [47]. Currently only PVA is being recovered in the United States, although other size materials are also recoverable. A chemical process for separating PVA from starch (Shikibo Process) and then recovering the PVA is currently being employed in Japan [48].
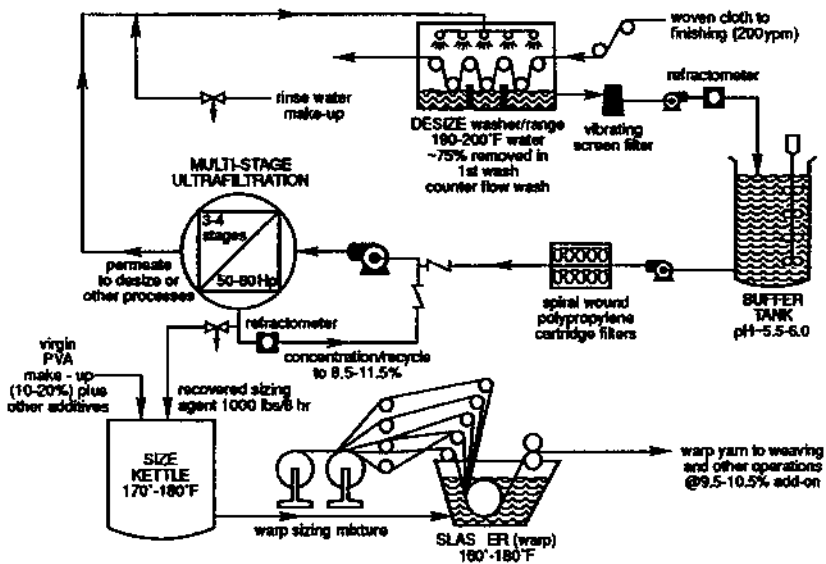
Fig. 3.29 Typical PVA size recovery by ultrafiltration.

About 65% of all chemicals entering a finishing plant effluent is size related; yet, desizing uses only 10–15% of the total water. Waste treatment plants average about 75% treatment efficiencies. One reason is that bacteria acclimated to degrade PVA are temperature dependent and are not as efficient during the colder winter months. Size reclamation can substantially reduce waste treatment loads and save water and energy during preparation. A plant using 3 million pounds of size per year (36 million pounds of woven fabric per year) can pay for the recovery equipment in less than 2 years [49]. The distance the recovered size must be transported from the recovery site to the mill is an additional consideration [50]. A typical PVA size recovery system is shown in Fig. 3.29.

3.5 CARBOXYL METHYL CELLULOSE

3.5.1 Introduction

Carboxyl methyl cellulose (CMC) is the cold water–soluble carboxymethyl (ether) derivative of cellulose. It is an excellent film former and has numerous

textile and nontextile uses. Cellulose like starch is a renewable natural product. CMC is not a major textile sizing agent in the United States. The nontextile uses have virtually supplanted its markets, primarily for price considerations. It is now used where the special properties of the size are the overriding considerations. For example, in loom finished goods, the cost of the size can be partially recovered. CMC still has considerable markets overseas, principally in Europe and the Far East, where the economics of the raw materials are somewhat different than in the United States. About 90% of the CMC produced in the United States is highly purified material used in food, pharmaceutical, and cosmetic applications. The remaining 10% is a crude grade of CMC that finds uses in detergents, anti–soil redeposition agents, oil drilling [51], etc., while a semirefined grade (90–95% CMC) is used for textile warp sizing [34].

3.5.2   Chemistry and Manufacturing of CMC

The synthesis of CMC from cellulose is shown in Fig. 3.30. The starting material for CMC manufacture is either wood pulp or cotton linters or similar cotton waste. In either case the cellulose must be purified. Cotton cellulose contains waxes and pectins among other impurities, while wood pulp contains lignin and hemicellulose. Fortunately all of these impurities are soluble in concentrated caustic soda (NaOH), which both helps in the removal of impurities and converts cellulose into its alkali cellulose or ''soda'' cellulose intermediate form. In this form soda cellulose reacts with monochloroacetic acid (MCAA) under controlled reaction conditions to form the carboxymethyl derivative.

Depending upon the DP of the cellulose source and the extent of the degree of substitution, e.g., in the DS range 0.7–1.2, of the MCAA onto the cellulose chain, a family of stable CMC products is obtained that finds wide applications in textile and nontextile uses. Most warp size grades of CMC have a DS in the 0.65–0.85 range [52]. The grades of CMC depend upon the length of the cellulose chain or molecular weight, which control the solution viscosity; the degree of substitution, which determines the solubility or insolubility and moisture sorption; and the purity, which controls the salt content, etc.

The carboxymethyl group preferentially attaches to the cellulose chain at the C6 primary hydroxyl through a stable primary ether linkage. The carboxymethyl derivative of cellulose is considerably more stable toward removal than the more labile acetate ester found on the partially hydrolyzed PVA chain.
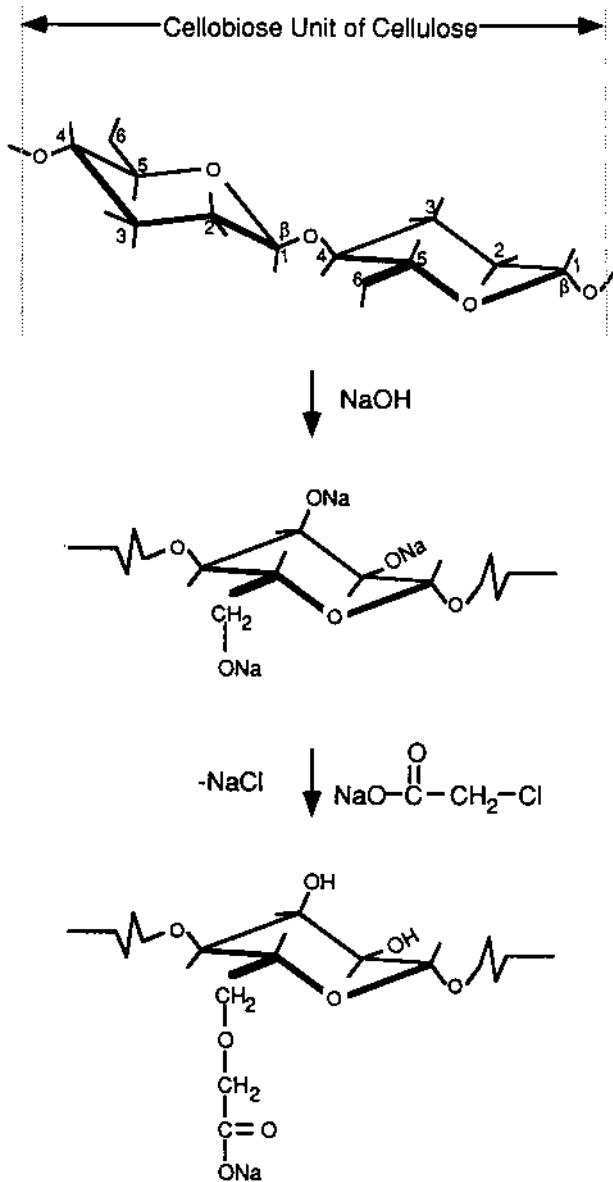
Fig. 3.30 Carboxymethyl cellulose manufacture from purified cellulose.

During the derivatization reaction, the sodium hydroxide greatly swells the cellulose destroying all of the cellulose crystalline order. Attachment of the carboxymethyl groups to the chain acts to wedge them apart, preventing the cellulose chain from recrystallizing by reforming the original ''hydrogen bonds.'' Thus, even cold water can now penetrate and surround the CMC chains, causing dissolution at low energy levels. The material now acts as if it were a ''cold water–soluble cotton.'' CMC finds advantage in the sizing and finishing of shrink-sensitive fabrics such as acetate and viscose rayons because to remove other types of sizes during the desize step in finishing it is necessary to use hot water. Hot water, enzymes, and chemical additions are not required for desizing of CMC. Further, being a natural product, CMC is biodegradable yet has a considerably lower biological oxygen demand (BOD) than does starch.

CMC is generally used in textile sizing as a more water-soluble sodium salt derivative. Occasionally the product is contaminated with considerable salt (sodium chloride) that is produced in the carboxymethylation reaction and can cause corrosion problems on slashing and weaving machines [53].

Properties of CMC

Like starch, CMC can be obtained in high solids low viscosity grades while providing the same sizing properties as conventional CMC grades [54]. The tensile strength, elongation, and moisture-related properties of CMC compared to other film forming sizes are given in Table 3.7. The tensile strength of CMC films falls somewhere between starch and PVA. When dried on the slasher, the CMC films split easily at the lease and bust rods, but after regaining the moisture lost in drying the CMC recovers its strength and abrasion resistance to protect the yarn on the loom. Its high water-binding ability makes it less sensitive to low weave room humidities (ca. <50% RH) but can give problems at high humidity conditions, especially above 80% RH employed in ''wet'' weave rooms. This can be somewhat reduced by blending 25–50% starch to give warp that has good weaveability at most weave room humidities [54]. If CMC sized warps are to be used under conditions that favor mold or mildew, a preservative (antiseptic) may be required to prevent yarn damage.

Carboxyl methyl cellulose is not heat set in the greige fabric as are some of the PVA type sizes and remains water soluble after being heated and dried. Cooked mixes are quite stable and need not be dumped at the end of a set or on weekend shutdowns. They can be cooled and reheated with no gelling or skinning [55]. The cooked size has less tendency to stick onto the hot drying cylinders compared to PVA. Thus soft waste can be minimized. CMC sized

warps are split at low energy (soft split) at the bust or lease rods (Fig. 3.24). The water solubility of CMC compared to PVA is shown in Figs. 3.31 to 3.33 [56]. The size has significant cold water solubility. Only at 180°F does the solubility of PVA approach that of the CMC.

Chemically, CMC is a hydrophilic type size that has good adhesion to polar fibers, e.g. cellulosics. As the amount of hydrophobic fibers in a blend of polar fibers increases, the adhesion of the CMC to the yarn bundle will decrease. This loss of adhesion can be somewhat mitigated by the addition of acrylic, polyester, or vinyl binders to the CMC size formula. A comparison of the adhesion of CMC versus other sizing agents and binders is given in Table 3.12. The adhesion of CMC to cotton is good but poor on the polyester fiber. Addition of binders to the CMC will improve the adhesion to the more hydrophobic fibers.

Blending with Other Sizes

Although CMC is cold water soluble, the size is generally prepared in hot water for most sizing applications. CMC is readily soluble in hot water; however, for rapid dissolution, CMC may be added to half a kettle of cold water with good agitation. Then the mixture may be heated to dissolve the size followed by
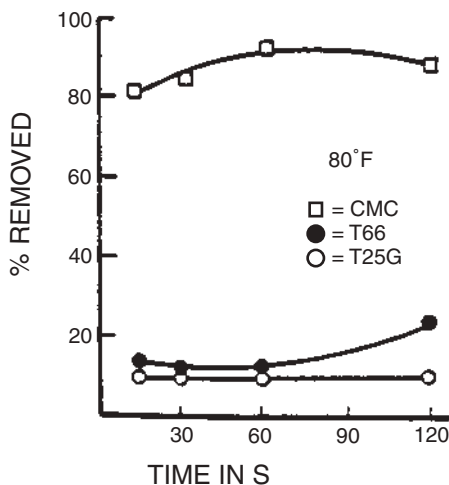

Fig. 3.31 Removal of CMC versus PVA sizes at 80°F.
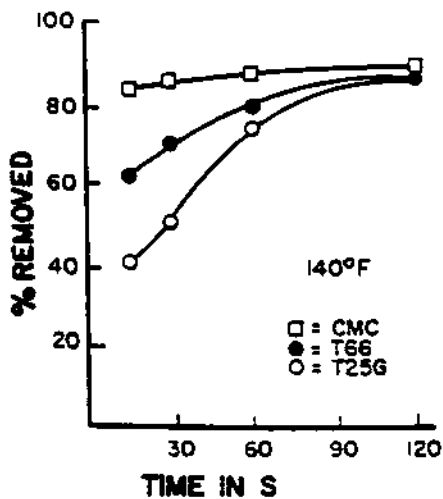
Fig. 3.32 Removal of CMC versus PVA sizes at 140°F.
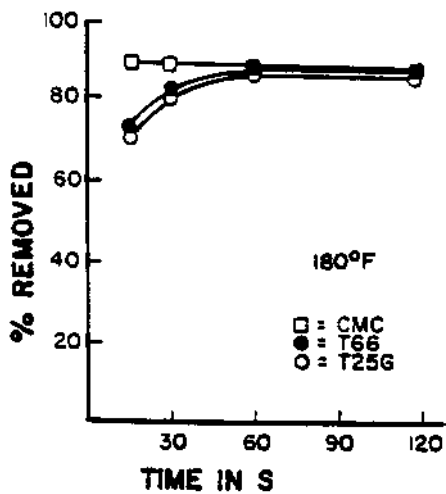
Fig. 3.33 Removal of CMC versus PVA sizes at 180°F.

Table 3.12 Ranking of Sizing Materials Based on Adhesion to Base Fibers

Adhesion to polyester		Adhesion to cotton	
Material	Force (kilopascal)	Material	Force (kilopascal)
Eastman WD	15	PVA	4.9
PVA	10	CMC	3.9
Poylacrylate	5	Starch	3.6
CMC	4	Polyacrylate	3.5
Starch	3	Eastman WD	0.8

Source: Ref. 22.

slow addition of the remaining water. For blends of CMC with other size materials such as starch, the kettle needs to be heated to ~95–98°C. This temperature has no adverse effect on CMC, which may be blended (25–50%) with the starch. CMC can be used in sizing as a viscosity builder or modifier with other size materials. For example a 4.2% solution of CMC is approximately equivalent to a 10.2% solution of a 30 fluidity corn starch [55]. CMC readily blends with PVA. Usually a 75% PVA/25% CMC blend can be used to provide a size having excellent abrasion resistance with good slashing performance.

Desizing and Recovery

Carboxyl methyl cellulose can be easily removed in cold water (~27°C) during desizing. Wax used in sizing is generally not removed at this temperature; however, it can be effectively removed in the scouring and bleaching steps at finishing. Thus a significant savings of energy used in finishing can be realized for CMC sized warps [57]. Often, such savings are overlooked by the greige mill management, as cost savings in a downstream process is not perceived as significant. CMC, being a natural product, is totally biodegradable.

Carboxyl methyl cellulose also lends itself to economical recovery by ultrafiltration techniques [55]. The cold/warm water solubility and low water volume overflows [58] used in finishing allow the total water volume used for desizing to be reduced by as much as two-thirds [56]. Flux rates for CMC recovery have been found to be 30–50% higher than for PVA [58]. The membrane and pumping costs are thereby reduced. Wax elimination from the recovered desize liquor at finishing should further increase the flux efficiency of the process.

Another method of size recovery for CMC makes use of its water insolubility at low pH. CMC is normally used for sizing as it is a highly water-soluble neutral sodium salt. Upon acidification to pH 2–3, the CMC precipitates and can be recovered by decanting the water layer and redissolving the precipitate as the sodium or ammonium salt [59].

The CMC can also be recovered by chemical coagulation. Heavy metal ions such as silver, copper, lead, or zirconium and the trivalent ion such as aluminum, iron, or chromium will cause the CMC to precipitate from solution as salts of these metals. The CMC is more tolerant toward calcium ions [60]. Aluminum ions, Alum, are the ions of choice for the recovery process using the ion precipitation method. The size is recovered and reused with only a slight loss in properties [61]. The degradation of properties are probably due to the occlusion of other metal ions normally found in water that cause hardness, which may be prevented by using deionized water in the recovery process. As with PVA, virgin CMC (ca. 5–8%) must be added to the reclaimed CMC after each cycle. The various recycling methods for warp sizes have been reviewed elsewhere [61].

3.6 ACRYLICS

3.6.1 Introduction

The term ''acrylic'' is a generic term for sizing materials that contain polyacrylic acid (PAA) and its derivatives as a homopolymer or copolymer. In some cases the acrylic size is used alone as the primary film former or as a binder component of the size to improve the adhesion between a primary base sizing agent (film former) and the yarn. Acrylics even at high molecular weight produce solutions of low viscosity and give clear, colorless, mildew- and mold-resistant thermoplastic films having good strength, in the range of 1000 to 2000 psi, elongations in the range of 100 to 600%, and flexibility. They can be made readily water soluble or insoluble and have excellent compatibility with other sizing materials and generally improve their performance.

Acrylic sizes do not require cooking but can be heated up to 100°C for dispersing wax or lubricants as well as with other sizes, e.g., starch, with which it may be blended. Perhaps its greatest advantage is the high binding strength to a number of manmade fibers under weave room conditions, yet it has low dry bonding strength on the slasher, facilitating easy splitting at the bust rods.

The acrylic sizes can be broadly divided into two classes, namely, water or alkali soluble or water insoluble. The alkali soluble types will have *acrylic acid* or its ammonia or sodium salt or other water-soluble derivative (such as

acrylamides) as a major component of the polymer chain. The insoluble size materials contain acrylic esters or acrylonitrile derivatives. The copolymers can vary widely in composition (ester, amide, nitrile, acid, etc.) to give a large family of "acrylic" polymers useful as sizing materials. Some typical comonomers useful as acrylic binder components are illustrated in Fig. 3.34.

3.6.2 Characteristics and Properties of Acrylic Sizes

The two important factors that affect the size properties are the molecular weight and the chemical composition of the size. The water-soluble size consists primarily of the sodium and ammonium salts of acrylic acid, as shown in Fig. 3.34. These are the primary film formers and are used as the primary size for nylon filament yarns. The low molecular weight materials also form excellent binders with other sizes, particularly starch. Figure 3.35 shows why the acrylic sizes, particularly the ammonia salt, are excellent for filament nylon or as binders for spun yarns containing nylon as one of the blend components.

Viscosity

The effect of molecular weight on the viscosity of sodium and ammonium salts of acrylic acid that are the water-soluble forms are shown in Fig. 3.36 [62]. As would be expected, viscosity increases with molecular weight and
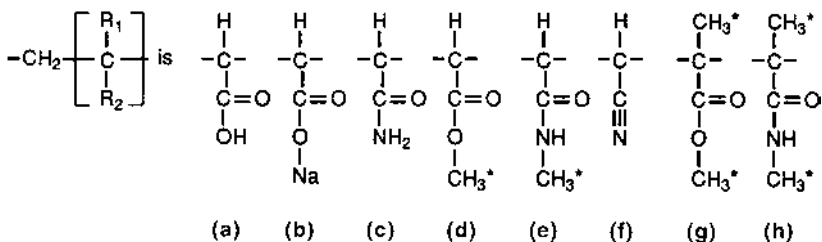
Fig. 3.34 Some of the "acrylic" family of copolymers useful in sizing. (a) Polyacrylic acid (PAA); (b) PAA sodium salt (or ammonium salt); (c) acrylamide; (d) methyl ester (methyl acrylate); (e) methyl amide (methyl acrylamide); (f) nitrile (acrylonitrile); (g) C2 substituted ester (N-methyl methacrylate); (h) C2 substituted amide (N-methyl methacrylamide). a, b, and c are water soluble; d, e, f, g, and h are water insoluble. *Derivatives other than methyl include ethyl, propyl, n-butyl, isobutyl, and 2-ethylhexyl, among others.
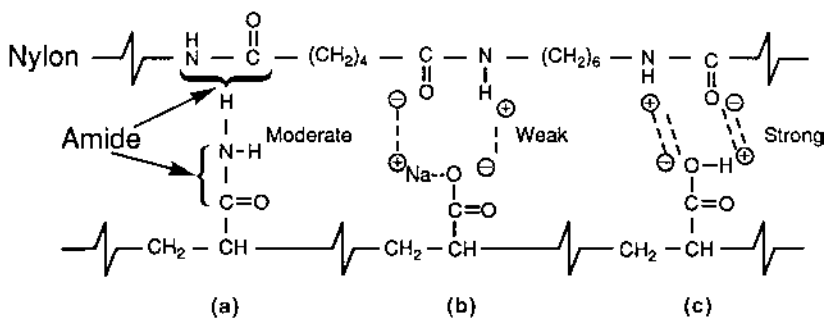
Fig. 3.35 Structural features of nylon and acrylic acid affecting adhesion of sizes to fiber. (a) Acrylamide (moderate adhesion). (b) Acrylic acid (sodium salt) (poor adhesion). (c) Acrylic acid (good adhesion).

size concentration. The ammonium salt derivatives have higher solution viscosity than the corresponding sodium forms. It can be noted that even a small amount of a high molecular weight acrylic size can have a significant effect on the solution viscosity; thus it can be utilized as a viscosity builder at low concentrations. Alternatively, a high amount of low molecular weight material as a binder or adhesion promoter can be added to the size formula without
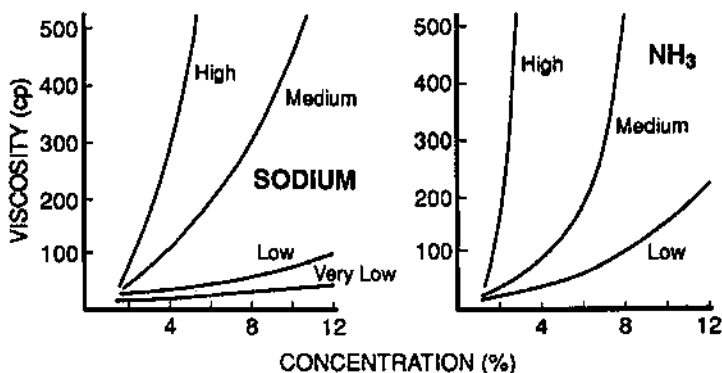
Fig. 3.36 Effect of molecular weight on the viscosities at (80°C) of polyacrylates.

any significant effect on the size viscosity. Size materials normally have viscosity in the 50–500 cps range. Thus, acrylic size materials can cover a wide variety of sizing conditions.

Solubility

The water solubility of the acrylate sizes compared to CMC or another derivatized starch, pearl starch, and PVA are given in Table 3.13. Even the high molecular weight acrylics are significantly more cold water soluble than the other size materials. At 50°C the size films have almost immediate solubility. Heat-set acrylamide films are more easily solubilized than heat-set PVA [63].

Tensile Properties

The relationship of molecular weight to strength and extensibility of acrylic sizes is given in Fig. 3.37 [62]. As the molecular weight of the acrylic sizing material increases so does the extensibility. At very high molecular weight, however, the extensibility decreases and the films become brittle and are no longer useful for sizing.

3.6.3 Sizing of Nylon Filament

Most nylon filament yarns woven on non-water-jet looms are sized almost exclusively with acrylic sizes because of high adhesion and abrasion resistance

Table 3.13 Comparison of Solubility of Acrylic Films Versus Other Sizes

	Solubility of Size Film (min/mm^2) at	
Size	25°C	50°C
Acrylics		
Low viscosity	10	<2
Medium viscosity	17	<2
High viscosity	22	<2
Sodium CMC		
Low viscosity	>25	14
Medium viscosity	>25	49
Starch		
Pearl	>25	>120
Starch ether	>25	52
PVA (partially hydrolyzed grade)	>25	14
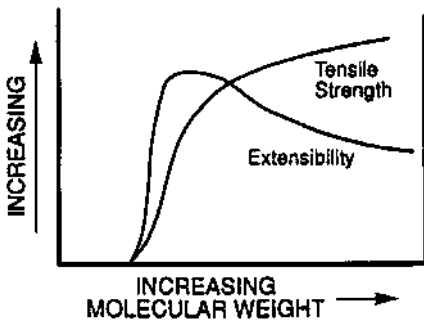
Fig. 3.37 Relationship of molecular weight to the tensile strength and extensibility of acrylic sizes.

of these sizes. Some nylon filament yarns are designed to be woven on a water-jet loom without size. Yet size applied to the warps can increase weaving efficiency by preventing any broken ends from peeling back at the heddles or reeds causing fuzz balls and eventually causing yarn breakage. Broken ends can also interfere with the path of the filling yarn, thus causing a warp related filling stop.

The ammonium salts of acrylic acid copolymers are the size of choice for water-jet weaving applications. Inevitably, the size must be water soluble and wet out the filaments during application in the size box. Yet the size must then lose its water solubility on the sized warp so that the nylon can be woven without size removal that can build up on the heddles. During weaving, the size must still bond to the nylon filaments. Then the size must be again made water soluble for desizing. The ammonium derivatives are quite suitable for this amazing task.

The ammonium salts used in sizing of nylon are designed to have high water solubility. When heated over 100°C on the drying cylinders much of the ammonia is lost, and the size is converted into the insoluble free acid copolymer form, which still has high adhesion to nylon, as shown in Fig 3.35. Ordinarily PAA is water soluble; however, by copolymerizing 10–20 mole percent of an insolubilizing monomer, such as an acrylate ester, the copolymer size becomes water insoluble after loss of ammonia. In other words, depending upon the final acrylic acid/copolymer content, surfactant system employed, and the amount of ammonia removed during drying, a water-resistant size having high adhesion to nylon remains to protect the yarn during weaving.

The most important consideration is not to have the acrylic size shed off of the yarns during weaving and build up on the loom parts. When this occurs, the deposits slough off into the water-jet system, which can cause weaving problems or dye resist spots since these small size particles are not easily resolubilized during desizing. During alkaline desizing the free acid form of the size is resolubilized as the soluble sodium salt and becomes removable. This process is shown schematically in Fig. 3.38. The ammonium PAA copolymer is also suitable for water-jet weaving of polyester filaments, although composition changes are necessary to reach optimal performance.

3.6.4 Acrylic Sizes for Spun Yarns

For spun yarns, the PAA in the molecular weight range of 200,000, which is relatively high, have been found to be the most suitable. However, acrylic acid copolymers are manufactured with molecular weights numbering in the millions for nonsizing applications, e.g. printing, while very low molecular weight PAA are employed as surfactants. The 200,000 molecular weight range provides a viscosity that gives suitable penetration into the yarn bundle while providing a soft break and the bust at lease rods.

Ordinarily the sodium salt of PAA along with polyester binders are the two types of size that are the most suitable for the dry weaving of polyester spun yarns. The advantage of the sodium salt over the ammonium form is that the size can be heated to higher temperatures during cooking and sizing or drying without loss of the sodium anion that occurs with the ammonium salt. Studies with acrylamide sizes indicate that it can replace PVA for spun yarns using PVA/starch blends [63].
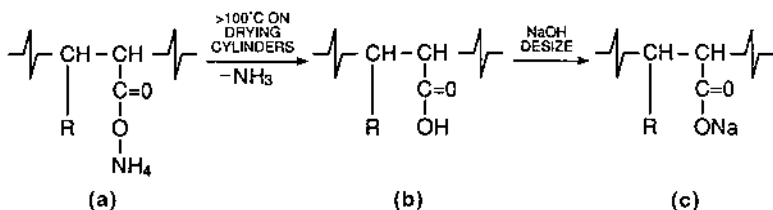
Fig. 3.38 (a) Water-soluble size having high affinity for nylon. (b) Loss of ammonia during drying provides a water-insoluble polymer usable on water-jet looms. (c) Alkaline desize removes the size as the water-soluble sodium derivative.

Generally, the selection of the grade of acrylic size will depend upon the slasher and weaving style. For example, low twist yarns will require a higher viscosity size having lower film strength in order to obtain a softer break at the bust and lease rods than will stronger yarns having a higher twist.

3.7 BINDERS

3.7.1 Introduction

There are a number of polymeric materials that can be used in sizing as binder materials. Binders are true film formers but are generally not used alone for sizing, although some sizes (e.g., acrylics) are useful as both a primary size and as a binder. Binders are typically used to increase weaveability by promoting the *adhesion* of the primary ''film-forming'' size (starch, PVA, CMC, acrylic) to a specific fiber substrate while reducing the *cohesion* between sized yarns. By judicious selection of a binder, additional sizing advantages can be realized, such as

Splitting more easily at the bust or lease rods — reduced cohesion
Greatly reduced shedding
Easier application and removal of size
Improved weaving efficiencies
Improved fabric quality
Reduced hairiness
Improved size film/solution viscosity properties, e.g., strength and elongation
Desizeability, etc.
No blocking
No sticking on the dry cans
Better warps (loom build-up, clinging, and fuzz balling eliminated)
No downstream processing problems (preparation, dyeing and finishing)
Reduced costs while improving compatibility with other size box ingredients
Improved sizing properties — no size migration or foaming; better penetration and leveling, film flexibility, and fiber lay; reduced friction; decreased moisture sensitivity; etc.

Note that some of the advantages cited transcend the weaving operation. To save money in weaving and then lose it and more because of finishing problems

does not make sense. Table 3.14 summarizes the sizes for spun yarns which function as primary sizes or as binders. In some cases the primary size components can be blended together to modify the size film properties. For example, the weaker starch sizes can be blended with PVA to reduce cost, obtain a softer yarn split at the lease rods, and improve adhesion, etc., with no reduction in weaving efficiencies.

3.7.2   Acrylics as Binders

Acrylic compounds used as binders generally consist of lower molecular weight polymers, as shown in Fig. 3.36. Also, acrylics may be copolymerized with other monomers to further modify their properties. For example, as the molecular weight of the acrylic is reduced, the strength and flexibility decreases. One of the advantages of the acrylic binders is their compatibility with most primary size and other binder materials, including the following [64,65]:

Pearl corn starch
Modified starch
Starch derivatives (ether, acetates, etc.)
Polyvinyl alcohol (all grades FH to PH, copolymer)
CMC

Table 3.14   General Classification of Size Materials as Primary Size, Binder, or Other

Primary size	Binder	Other
Spun yarns		
Starch	Acrylics	Styrene/maleic anhydride
PVA	Polyester resin	Polyamides
CMC	Vinyl acetate	
Acrylic	Starch derivative	
	Starch gums	
Filament yarns		
Poly acrylic acid		
Polyester		
Polyvinyl acetate		
PVA		

Polyesters
Vinyls
Flow (viscosity) control agents

By selection of the proper acrylic, proper adhesion, cohesion, and plastic properties can be controlled to yield films that are as stiff as glass or as soft as chewing gum. The range of properties include [62,65]

Hard/slick
Soft/tacky
Strong/weak
Brittle/flexible
Tough/elastic
Water soluble/water insoluble

There is a considerable number of acrylic binders marketed with a wide range of different sizing properties (Fig. 3.39). An understanding of these properties is necessary in order to select the correct variant for the proper sizing of the warp. For example, as the acrylic acid component of the size increases, the size adhesion and resolubility increases; however, the sensitivity to moisture also increases.
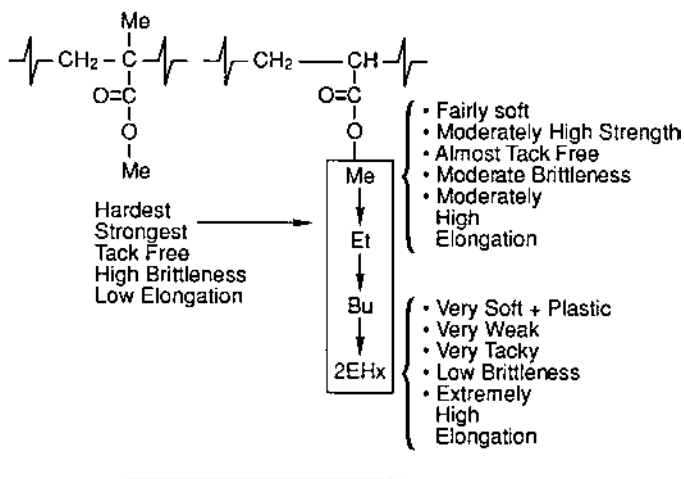
Me = Methyl, Et = Ethyl, Bu = Butyl, 2EHx = 2 Ethyl Hexyl

Fig. 3.39 Effect of the length of pendant ester group on the properties of an acrylic size.

Acrylics are marketed as both sodium and ammonium salts. The sodium salt is more water soluble and also has greater weave room moisture sensitivity. The ability to pick up water can improve the antistatic propensity of the sized synthetic fibers, but can result in tacky films at high weave room humidities. The heating of the ammonium salt in the cooking kettle or size box must be carefully monitored, especially in starch blends. Heating near the boil can cause these size materials to prematurely lose ammonia, causing potential foaming problems as well as insolubilizing the size. Agitation in the kettle or size box can break up the now-insoluble size into small ''gritlike'' particles that can build up on the yarn while sloughing off at the bust and lease rods or on loom parts to cause yarn breaks at the slasher or the loom.

Acrylic/Starch Binders

Acrylic binders are often blended with starch to promote better adhesion to the more hydrophobic fibers in a blended yarn such as polyester/cotton. Yarns sized with starch generally require high weave room humidities for good weaving results. The use of starch blended with the acrylic binder thus reduces the size sensitivity to high humidities. The sodium salts are more humidity sensitive than the ammonium salt. Other advantages of starch/acrylic blends include

> Better stability more stable than PVA blends.
> Retrogradation of the starch is reduced.
> Skinning in the size box is reduced or eliminated.
> Smash outs due to skinning are avoided.
> Weaving performance is improved.
> Size film properties are improved.
> Productivity is improved.
> Desizing is improved.

The diversity of available acrylic sizes allows the manufacturer to select the materials to achieve the desired characteristics. Tables 3.15 and 3.16 illustrate the effect of additions of low and medium molecular weight binders on the viscosity and the abrasion resistance of starch films [62].

3.7.3 Polyester Resin Binders

Polyester resins used as binders for size applications are very similar in their chemistry to the ''polyester fibers.'' Polyester as a generic class is one of the most important textile fibers that is produced worldwide. Polyester employed in fibers is synthesized from the condensation of ethylene glycol and terephthalic acid to give polyethylene terephthalate (PET) type polyester. At high

Table 3.15 Effect of the Adhesion of Acrylic Binder Size on the Viscosity of Starch

Size	PAA sodium salt, low MW (cps)	PAA sodium salt, medium MW (cps)
Starch ester	40	180
Pearl corn starch	150	600

Note: 5% Solution, 70/30 blend of starch/acrylic at 85°C.

molecular weights, this polymer can be extruded into strong hydrophobic fibers. The molecular chains comprising the polyester fibers have high stereoregularity and thus have excellent fit between themselves. Since the molecules have a rigid chain structure, much like two flat rulers, the chains align themselves to maximize their intermolecular bonding, and the fiber possesses excellent crystallinity when the chains are properly oriented, as shown in Fig. 3.40. For sizing, the polyester polymer must have a different molecular structure and orientation. For example, the polyester resin size must as a minimum be water or solvent soluble or dispersible. This is accomplished by adding to the molecular chains solubilizing groups which destroy the molecular fit and act to *wedge* open the chain structure (much like acetate groups on a PH grade of PVA) [66]. Generally aromatic sodium sulfonate (SO_3Na) groups are used to provide the water solubility, chain flexibility, and reduction in the chain ''fit'' needed to make the polyester resin useful for sizing. A typical polyester resin based upon 1,3 isoterephthalic acid which has been reacted with glycol or glycol ether units and modifiers and polymerized to a molecular weight of 5000–7000 is shown in Fig. 3.41 [66]. Oddly, the sodium salt is employed when the potassium salt would give even greater wedging and solubility char-

Table 3.16 Effect of Acrylic Size on the Abrasion Resistance of Starch Sizes

Size	Abrasion Resistance	
	NEAT	Blend (70/30)
Starch ester (7.3% add-on; 1/40's cc)	8/3000	2/3000
Pearl corn starch	8/157 (6.5% add-on)	5/3000 (6.9% add-on)
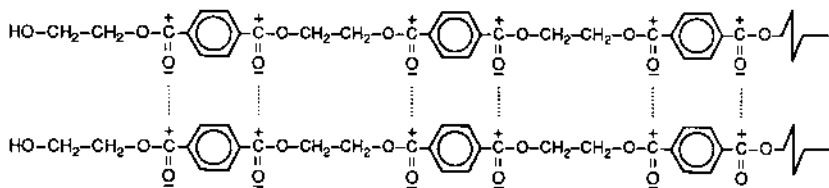
Fig. 3.40 Intermolecular bonding force in a segment of polyester (polyethylene terephthalate) fiber chain structure.

acteristics. The molecular weights of sodium and potassium are 23 and 39, respectively. Odd numbered glycol or glycol ether units are used to reduce the molecular fit inherent in fibrous polyesters (which use an even numbered glycol unit). Such comonomer arrangements produce the greatest flexibility and ease of dissolving and redissolving needed for sizing and desizing. The use of mixed glycols and/or aromatic acids reduces the polyester chain fit even further, thus lowering the second order or glass transition temperature (T_g) to give a size candidate with optimal sizing properties. The proper formulation of the base resin and knowledgeable neutralization and reduction of the polyester resin system into water can provide an excellent ''polyester'' binder that does not give the problems formerly experienced with poor desizeability or other difficulties. The more stable and useful polyester resin systems avoid the use of cosolvents in their manufacture. In fact, the resin can function as a detergent when the desize is conducted at pH above 7.0 to provide a cleaner desized fabric and assist in the dispersing of lubricants, etc., employed in sizing. This factor also assists in optimizing the size rheology [67].

As expected, *polyester* resins make excellent size ''binder'' candidates for *polyester* fiber, either spun or filament yarns. The use of polyester resins was first introduced by Tennessee Eastman. The history of polyester resins has been reviewed elsewhere [67].

Since an alkaline desize is required for the polyester resin binder system, they are not suitable for use in sizing wool or wool blends. Some polyester resins require the use of an organic cosolvent to accomplish viscosity reductions, dissolving of the polyester resin (to stabilize), and resin acid removal from the cooking kettle. Additions of polyester resins to PVA and PVA/starch blends can measurably assist the redissolving of the size during the desizing operation. As little as 10% of polyester resin added to fully hydrolyzed PVA sizes or PVA/starch blends can affect a considerable reduction in the time and temperature for redissolving the size film, as shown in Table 3.17.
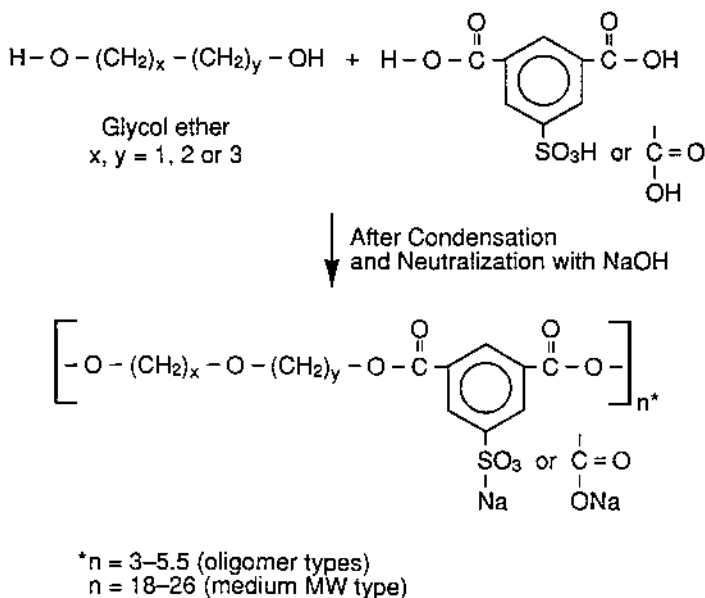
Fig. 3.41 Synthesis of a typical polyester resin.

Table 3.17 Desizeability of PVA and PVA/Starch Films Containing Polyester Resins

Film	Time(s)	Temperature (°C)
Fully hydrolyzed PVA[a]	386	85
90% fully hydrolyzed PVA/10% Polyester resin	165	72
PVA/starch film		
50% fully hydrolyzed PVA/50% modified soluble starch	75	68
45% fully hydrolyzed PVA/45% modified soluble starch/10% polyester resin	45	66

[a]Fully hydrolyzed grades are not generally used in sizing applications and are shown here to better illustrate the effect of the polyester resins toward improved desizeability.
Source: Ref. 41.

The primary advantages cited for polyester resins are [41,67,68]:

To provide high adhesion to hydrophobic fibers
To plasticize the primary film former
To provide for significant reduction in warp stops
Stabilization of size temperature/viscosity parameters
To optimize size cook rheology properties
To make compatible with other film formers and size additives
Increased abrasion resistance during weaving
Better matching of size film strength and elongation with yarn employed
Easier desizeability
Improved leasing ease (softer break at the bust and lease rods)
Reduction in yarn hairiness
Faster and more uniform drying on the slasher
Potential cost savings in blended size formulations with PVA
To make some sizes recoverable by ultrafiltration

3.7.4 Vinyl Acetate Resins

Polyvinyl acetate (PVAc) polymers are effectively utilized as binders to improve the adhesion of the primary size agent to the yarn. Structurally, the same stereochemistry considerations described for PVA are operative for the PVAc polymer. That is, the chain structure is *atatic*, and the comonomers are randomly distributed along the chain, greatly reducing chain fit regularity.

The primary advantage of vinyl polymers is that the vinyl acetate is relatively inexpensive vis a vis other polymers employed in sizing. The vinyl acetate homopolymer is not water soluble; hence, the monomers must be copolymerized with mono- or dicarboxylic acids (usually as their monoester), acrylic esters, or other vinyl monomers to achieve useful size properties [69], as shown in Fig. 3.42. If acid units are employed as comonomers in the polymerization, the resulting vinyl resin is solubilized as an alkali metal salt. Care must be exercised in the neutralization step (pH 8.0–8.5) in order to prevent the removal of the acetate groups, as is done in the hydrolysis of PVAc into PVA. If ammonia is used for neutralization, then the size finds applications in water-jet weaving, since the ammonia will be lost in a manner similar to the ammonium acrylate to give a water-insoluble size. The ammonium derivative is also usable as a permanent size for loom finished goods.

The vinyl acetate binders are useful sizing agents for both filament and spun yarns. Because of their weak film strength, PVAc polymers are used as sizing agents on acetate and polyester filament yarns and as binders for fiberglass, polyester, and blended spun yarns.

Poly Vinyl Acetate (PVAc) Copolymers

Fig. 3.42 Polyvinyl acetate copolymers. (a) Basic vinyl acetate monomer (homopolymer); (b) acrylic acid (ammonia or sodium salt); (c) monoester of a dicarboxylic acid; (d) vinyl chloride; (e) acrylate ester; (f) methyl acrylate ester; (g) vinyl alcohol.

3.7.5 Sizing of Acetate Yarns

The excellent adhesion of PVAc to secondary acetate and triacetate fibers is obvious. Both the polyvinyl *acetate* size and the *acetate textile fiber* are highly acetylated derivatives (contain $O–C=O–CH_3$ groups). The adage ''like likes like'' certainly is operative for these fibers. Acetate and triacetate fibers have relatively lower tensile strength than any other manufactured textile fibers. A 4–5% add-on of PVAc size is weak enough (i.e., has low enough cohesion) to separate the ''bone dry'' sized sheet at the front of the slasher without breaking the fragile acetate filaments or causing size separation from the fibers of the yarn. It has high adhesion properties which will prevent peel back problems if any filaments are broken during weaving. Another advantage of PVAc sizes is that they can be utilized at low size box temperatures, a must in sizing acetate yarns since they are highly sensitive to stretching under hot/wet conditions [70]. Other combinations of sizes useful for acetate fibers are blends of PVAc with either acrylic or styrene/maleic anhydride (SMA) sizes. The SMA produces a hard and brittle film which can be effectively modified by additions of PVAc to this size.

3.7.6 Sizing of Polyester Fibers

Polyvinyl acetate has also been effectively used for sizing texturized polyester filaments (again like likes like) [71]. The producer-applied finish on the polyes-

ter fibers can sometimes be removed by bleeding into the size box. This can result in modification of the PVAc size film that may cause a build-up of size on the loom parts. Other additives used with the PVAc when sizing polyester yarns include penetrants, plasticizers, lubricants, and antistatic agents. Size box temperatures in the range of 120–165°F are generally utilized.

Flat yarn polyester fibers are more difficult to size with PVAc due to the higher solution viscosity required for these types of yarns. For this reason, the acrylic and polyester type sizes have better application for these types of yarns.

When the choice is between the PVAc size or the polyester resin, the cost advantage generally will favor the PVAc sizes due to the lower costs and the easier desizeability. For economy, some size suppliers will do their own sodium or ammonium conversion. Offering the PVAc size as liquid products can reduce the costs such that they can compete favorably with other liquid binder systems.

When PVAc is added to PVA sizes, significant improvement in the adhesion to polyester fibers is obtained while also lowering the bone dry size film strength. This facilitates a softer split at the bust rods without removal of the size film from the polyester fiber. When the yarn is then conditioned in the weave room, the adhesion characteristics are recovered, providing for excellent weaving performance.

3.7.7 Sizing of Fiberglass

Blends of PVAc (ammonium salt) and PVA (50/50 to 85/15 PVA/PVAc) at 8–9% solids have been successfully used to size fiberglass. The size with a 2–3% add-on to the weight of yarns is typically removed by flame desizing. The ammonium salt provides virtually an ash-free desize.

3.7.8 Sizing of Spun Yarns

It is in the sizing of spun yarns that the PVAc sizes find their major niche as a binder. The PVAc reduces or eliminates size box skinning with starch and/or PVA on 100% polyester and their blends, especially at creep speeds. The size, because of its ester chemistry is a significant adhesion promoter for polyester (as well as other hydrophobic) fibers and their blends. The PVAc has high compatibility with the PVA, particularly the PH grades because of their similar chemistry. Further, PVAc reduces the viscosity of PVA sizes [71] (Fig. 3.43) and because of its hydrophobic nature improves the speed and uniformity of drying.
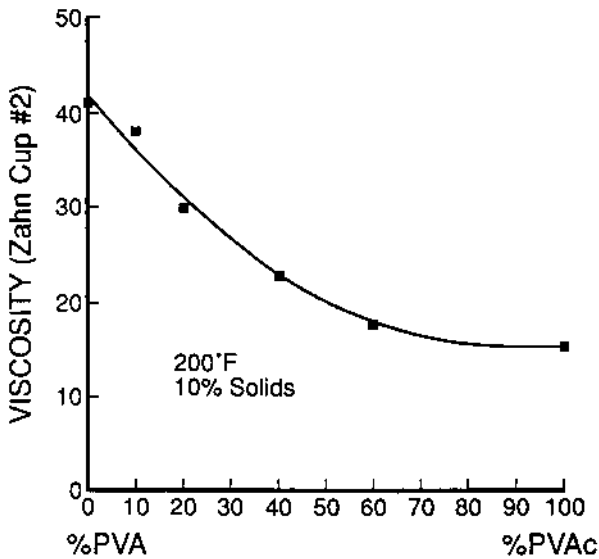
Fig. 3.43 Viscosity of size blends of PVA/PVAc.

Compatibility with other size ingredients is important because noncompatible size films are not smooth and uniform in appearance. For noncompatible size mixtures the chances of sized yarns passing unhindered through the loom without problems is decreased.

3.7.9 Drying and Size Box Skinning Considerations

High tensile strength hydrophilic size films are difficult to dry on the slasher. This is due to the fact that the size rapidly forms a dryer surface film through which the remaining trapped moisture must diffuse in order to become evaporated. This problem is mitigated by as much as 25% by the addition of PVAc to PVA sizes. Thus, up to one-quarter of the drying cylinder requirement is eliminated, giving the possibility for increasing slasher speeds.

The PVAc functions to interrupt some of the strong hydrogen bonding in the drying of the primary size, thus the surface filming cannot occur as readily. It is this same mechanism which also results in the reduction of size box skinning. During creep speeds, the exposed surface of the size in the size

box can cool down due to low agitation. This can allow the cooler size to congeal and develop a thick skin of size, which can cause roll marks and hard size spots that can often cause yarn breaks at the split rods on the slasher or at the loom.

3.7.10   Desizing and Recovery of PVAc

Ordinary desize procedures at the finishing plant readily removes the PVAc size. The size does not react or cross-link with the fibers or other size box ingredients, e.g., lubricants. Although PVAc has been shown to be recoverable by ultrafiltration techniques in the same ratio as is found in the desize liquor, it is not being presently recovered by any mills in the United States [69].

3.8   STYRENE/MALEIC ANHYDRIDE SIZES

Styrene/maleic anhydride (SMA) copolymers are the size of choice for acetate rayon continuous filament yarns. The size is the copolymer of styrene and maleic anhydride, which is employed as either the water-soluble ammonium or sodium salts, as shown in Fig. 3.44. Other terpolymers include acrylics or methacrylic acid. The optimal styrene content is about 1.8 to 4.0 mole percent [61].
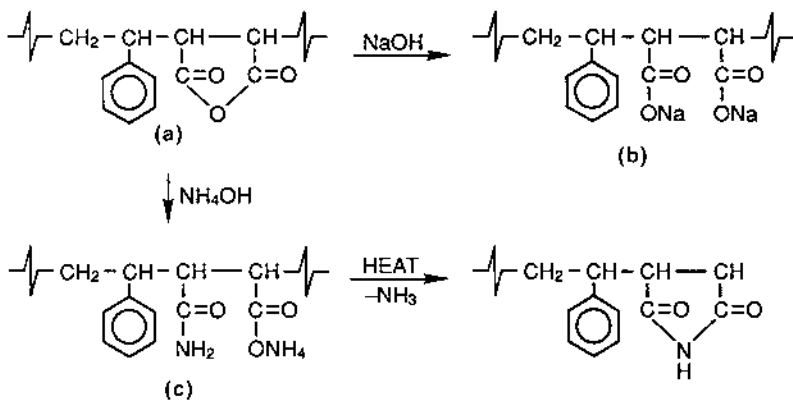

Fig. 3.44   Styrene/maleic anhydride. (a) Styrene/maleic anhydride; (b) sodium; (c) ammonium. The sodium and ammonium are water soluble.

The ammonium salt of SMA is particularly suitable for water-jet weaving because the ammonia can be lost when the yarn is heated on the drying cylinders, converting it into the water-insoluble form. The ammonium derivative is also effectively employed for loom finished goods or as a permanent stiffening agent, such as acetate taffeta.

Generally a lubricant and a plasticizer are added to the SMA size formulation [72]. A typical size formulation [72] is

Styrene/maleic anhydride 45–55 lb.
Lubricant 0–10 lb.
Urea 0–15 lb.
Finished product 100 gallons

When urea is used as a plasticizer, it can reduce static build-up at the slasher and on the loom [73].

Because of the easy stretchability of acetate under hot/wet conditions [70] the sizing of acetate must be done at 58–62°C. Liquid vinyl/maleic copolymer sizes have been effectively used to size acetate. They have been shown to give equal or better sizing parameters with the advantage of faster drying. Further, they give the mill the advantage of a one-piece product which readily lends itself to computer automation of sizing [72].

Styrene/maleic copolymer sizes are easily desized using mildly alkaline detergent at 70–80°C. More severe desize conditions can result in damage to the acetate fabric or affect the fabric dyeability. For example, increasing the alkalinity of desizing can remove some of the acetate groups on the backbone polymer chain, causing it to become regenerated cellulose having a different dyeability or nondyeability with certain dyestuffs.

3.9 SIZE RECOVERY AND DESIZE WASTEWATER TREATMENT

3.9.1 Other Size Recovery Methods

The most efficient method of size recovery is by ultrafiltration or some similar techniques. However, any method to recover size prior to desizing can reduce the amount of size in the effluent, thereby reducing treatment costs. Perkins [74] has shown that the use of a vacuum slot extractor can reclaim approximately 50% of low viscosity PH grade PVA at 10–15 in. of mercury vacuum. The recovered size is lower in viscosity than the original size, indicating that only the low molecular weight fractions are preferentially removed. Fabric

structural parameters such as type of fiber yarn and weave have an effect on recovery efficiencies.

Approximately 10–15% of size can be removed by merely beating the dry sized fabric with hexagonal beater bars followed by vacuuming the fabric [75]. Some size materials, notably hydroxypropyl cellulose (HCP), are cold water soluble but precipitate in hot water, leading to a novel sizing and recovery system [76]. Other cellulose ethers have similar properties. The use of solvent systems other than water for sizing and desizing has been shown them to be economical alternatives to water-based systems [52]. The most viable system uses chlorinated hydrocarbons, which must meet present day environmental concerns [52].

3.9.2 Treatment of Desize Wastewater

There was a time when desize wastewater could be dumped directly into the nation's rivers and streams. This practice was no longer possible after the Clean Water Act of l972, which placed stringent government regulations on mill effluent discharges. Desized waste constitutes the bulk (at least 65%) of the discharge effluent (solids) of a finishing plant yet constitutes only 10–20% of the total water usage [49]. The typical BOD contributions of various textile processes are provided in Table 3.18. To meet the present-day zero discharge requirements a plant may

1. Upgrade the treatment facility of the plant to an advanced tertiary type. This requires a considerable capital outlay with no return on investment. Further, waste treatment involves considerable operating costs.

2. Employ size materials that are less polluting or use no size at all. The pounds of oxygen requirement of one pound of various warp sizes are given in Table 3.19. There is a significant difference in the five-day biological oxygen demand (BOD_5) requirements of size materials, with starch having the greatest BOD_5. Some of the latest works in this area consider the three-day BOD (BOD_3) along with the ultimate BOD requirements.

   This must be considered, however, along with the chemical oxygen demand (COD) loading. PVA is the highest in this regard. It is the total oxygen demand (TOD), which is the sum of the BOD and COD, that a mill must be concerned with. In this regard, PVA has the greatest TOD. Most size materials can be effectively broken down using bacteria in an activated sludge that has been acclimated under conditions attainable in mill treatment facilities. These mi-

Table 3.18 Typical Biological Oxygen Demand
Contributions of Various Textile Processes

Process	BOD produced per 100 lb fabric (lb)
Singe	None
Desize (woven only)	
Enzyme/starch	67
Starch/CMC mix	20
PVOH or CMC only	0–5
Scouring	40–50
Bleaching	
Peroxide	3–4
Hypochlorite	8
Mercerizing	
No caustic recovery	15
With caustic recovery	6
Heat-setting	0
Dyeing	50–100
Finishing	0–50

Source: Ref. 78.

Table 3.19 Waste Treatment Requirements for Various Sizes

Size material	BOD_5 (ppm)
Starch	
Pearl corn	500,000
B2 gum (starch dextrins)	610,000
Keofilm No. 40	550,000
Penford gum 300 (starch ether)	360,000
Wheat starch	550,000
Polyvinyl alcohol (PVA)	10,000–16,000
Carboxymethyl cellulose (CMC)	30,000
Polyvinyl acetate (PVAc)	10,000
Hydroxymethyl cellulose (HEC)	30,000
Sodium alginate	360,000
Acrylic	205,800

Source: Ref. 78.

crobes are temperature sensitive, however, and are not as effective during the cold winter months. In addition to the oxygen demand required by the size materials and the other additives in the size mix such as lubricants, humectants, antistats, defoamers, etc., must also be considered.

3. Use a lower add-on of the size. By substitution of sizes and adjusting formulations, it may be possible to reduce the amount of size, thus reducing the waste treatment requirements. However, other factors such as the effects on weaving efficiencies must be considered. Trials necessary to properly evaluate sizing formulations are expensive and time consuming. For example, 24,000 loom hours are required to properly evaluate a size candidate if only warp stops are considered (55,000 h for all stops) [77]. In order to cut down on the time requirements, several looms may need to be dedicated for a trial. Thus, development of alternative low TOD formulas that can still give high weaving efficiencies are time consuming and expensive and provides little economic incentive for a textile mill.

4. The size can be reclaimed and reused. This is the only practical option for a textile mill. Today, only PVA is being recovered and reused by the U.S. textile industry, although all sizes except for starch (e.g., acrylic, polyester, vinyl acetate, etc.) have been shown to be recoverable and reusable either alone or along with blends of PVA. Starch products are enzymatically or chemically broken down during desizing in order to solubilize them for removal from the fabric. Since this degradation is time, temperature, and process related, it is not possible to achieve a desized product that is useful for recycling. Even the highly water-soluble starches that do not require enzyme or chemical desizing are not usable since they break down or change in composition during the ultrafiltration process.

   By recovering and reusing the size, the plant reduces the cost of the sizing process as well as reduces the wastewater treatment requirements. As a consequence, the payback for a reclamation system can be less than 2 years [49]. Weaving results have shown that the recovered sizes perform at equal or better efficiencies as the virgin sizes on most fabrics [78].

REFERENCES

1. Hall, D.M. Some factors affecting the application of size to textiles. Text. Inst. Ind. 1976, 14, 197–201.

2. Encyclopedia of Polymer Science and Technology; Interscience: New York, 1972; Vol. 12, 800.

3. Langlois, D.P.; Wagoner, J.A. Production and uses of amylose, Starch Chemistry and Technology. Whistler R.L., Paschall E.F., Eds.; Academic Press: New York, 1967; Vol. II, 456.

4. Imberty, A.; Buleon, A.; Tran, V.; Perez, S. Recent advances in the knowledge of starch structures. Starke. 1991, 43(10), 375–384.

5. Yahl, K.R. Cooking characteristics of starch and laboratory development of potential sizing ingredients. Textile Slashing Short Course Proceedings; Auburn University: Auburn: AL, 1984, 58–83.

6. Langlois, D.P.; Wagoner, J.A. Production and uses of amylose, Starch Chemistry and Technology. Whistler R.L., Paschall E.F., Eds.; Academic Press: New York, 1967; Vol. II, 490.

7. Peters, R.H. Textile Chemistry; Elsevier Publications: New York, 1967; Vol. 2, 106–113.

8. Peters, R.H. Textile Chemistry; Elsevier Publications: New York, 1967; Vol. 2, 116–119.

9. La Pianna, F.G. Sizing, Chapter 11, Chemistry and Technology of Cotton. Ward K., Ed.; Interscience: New York, 1955.

10. French, D. Organization of starch granules, Starch Chemistry and Technology . Whistler R.L., et al., Ed.; Academic Press: New York, 1984, 230–232.

11. Hall, D.M.; Sayre, J.G. Internal architecture of potato and canna starch. Part I: Crushing studies. Text. Res. J. 1971, 41, 147–157.

12. Hall, D.M.; Sayre, J.G. A scanning electron microscope study of starch.

12a. Part I: Root and tuber starches. Text. Res. J. 1969, 39, 1044–1052.

12b. Part II: Cereal starches. Text. Res. J. 1970, 40, 256–266.

12c. Part III: Miscellaneous starches. Text. Res. J. 1971, 41, 880–895.

13. Schock, T.J.; Maywald, E.C. Industrial microscopy of starches, Starch Chemistry and Technology. Whistler R.L., Paschall E.F., Eds.; Academic Press: New York, 1967; Vol. II, 643.

14. Schoch, T.J.; Maywald, E.C. Starch and Its Derivatives. Radney J.A., Ed.; John Wiley & Sons: New York, 1954, 637 and 643.

15. Snyder, E.M. in Starch Chemistry and Technology. 2nd. Edition. Whistler R.L., et al., Eds.; Academic Press: New York, 1984, 668.

16. Hall, D.M.; Sayre, J.G. Internal architecture of potato and canna starch. Part II: Swelling studies. Text. Res. J. 1971, 41, 404–414.

17. Nettles, J.E. Warp sizing, in Handbook of Chemical Specialities; John Wiley and Sons: New York, 1971, 29–64.

18. Rutenberg, M.W.; Solanek, D. in Starch Chemistry and Technology. 2nd. Edition. Whistler R.L., et al., Ed.; Academic Press: New York, 1984, 315–321.

19. Hall, D.M.; VanPatten, E.; Brown, J.L.; Harmon, G.R.; Nix, G.H. Yellow Dent corn starches: effects of chlorine oxidation. Ind. Eng. Prod. Res. Dev. 1971, 10, 171–175.

20. Rutenberg, M.W.; Solanek, D. In Starch Chemistry and Technology. 2nd. Edition. Whistler R.L., et al., Ed.; Academic Press: New York, 1984, 354–364.

21. Rutenburg, M.W. Starch and its modification, Handbook of Water Soluble Gums and Resins. Davidson R.L., Ed.; McGraw-Hill: New York, 1980, 7.

22. Green, D. Easily removed size materials for pre-washed denim. Textile Slashing Short Course Proceedings; Auburn University: AL, 1987, 54–59.

23. Corn Starch. 7th. ed.; Corn Refiners Association, Inc.: Washington: D.C., 1986.

24. Olsen, H.C. Starch with a positive change. Text. Ind. 1959, 123(9), 104–106.

25. The Story of Starches; National Starch and Chemical Corporation, 1953.

26. Whistler, R.L. History and future expectations of starch use, Starch Chemistry and Technology. 2nd. edition; Academic Press: New York, 1984, 7.

27. Lindermann, M.K. Vinyl acetate and the textile industry. Textile Chemist and Colorists. 1989, 21(1), 6.

28. Nehrenberg, D.L. Application of polyvinyl alcohol in warp sizing. Textile Slashing Short Course Proceedings; Auburn University: AL, 1988, 91–100.

29. Nehrenberg, D.L. Application of polyvinyl alcohol in warp sizing. Textile Slashing Short Course Proceedings; Auburn University: AL, 1989, 36–46.

30. Kirk-Othmer, D.L. Enclopedia of Chemical Technology. 3rd ed.; John Wiley and Sons: New York, 1983; Vol. 23.

31. Inskip, H.K.; Adelman, R.L. Copolymer of vinyl alcohol and methyl methacrylate and uses thereof US Patent 3,689,469, September 5, 1972.

32. Nehrenberg, D.L. Application of polyvinyl alcohol in warp sizing. Textile Slashing Short Course Proceedings; Auburn University: AL, 1987.

33. Robinson, G.D. An overview of spun yarn size formulations. Textile Slashing Short Course Proceedings; Auburn University: AL, 1991, 14–62.

34. Selzer, G.I.; Klug, E.D. Carboxymethyl cellulose, Handbook of Water Soluble Gums and Resins. Davidson R.L., Ed.; McGraw-Hill: New York, 1980, 7.

35. Tincher, W.T. Solid on solid sizing. Textile Slashing Short Course Proceedings; Auburn University: AL, 1986, 71–83.

36. Fox, C.J. CMC warp size. Textile Slashing Short Course Proceedings; Auburn University: AL, 1980, 46–49.

37. Compton, J.; Martin, W.H. Starch in the textile industry, Starch Chemistry and Technology. Whistler R.L., Paschall E.F., Eds.; Academic Press: New York, 1967; Vol. II, 151–152.

38. The chemical and physical properties of PVA as they relate to sizing. Textile Slashing Short Course Proceedings; Auburn University: AL, 1981, 84–96.

39. Geary, M.A. Advantage of partially hydrolyzed PVA for sizing and desizing. Textile Slashing Short Course Proceedings; Auburn University: AL, 1985, 21–39.

40. Tsunemitsu, K.; Kishomoto, H. The use of PVA in warp sizing and processing of textiles, in Alcohol, Properties and Applications. Finch C.A., Ed.; John Wiley and Sons: London, 1973, 234–275.

41. Seydell, S.O. The contribution of synthetic polymer used in warp sizing. Textile Slashing Short Course Proceedings; Auburn University: AL, 1989, 1–10.

42. Cacho, J.W. AATCC Warp Sizing Symposium; Belmont: NC, November 27, 1979.

43. Buyers Guide. Textile World. 1991, 141(7), 145, 72, 86, and 164.
44. Ragin, J.J. PVA recovery. Textile Slashing Short Course Proceedings; Auburn University: AL, 1976, 22–26.
45. Ragin, J.J. Procedures (used at Springs Mills) for concentrating solutions of PVA. Textile Slashing Short Course Proceedings; Auburn University: AL, 1977, 75–79.
46. Robinson, G.D. New developments in size reclaimation using ultra filtration. Textile Slashing Short Course Proceedings; Auburn University: AL, 1990, 88–89.
47. Flukinger, W.T. Recycling Elvanol PVA for spun woven sizing, Paper presented to Southern Textile Association. October 22, 1991.
48. Kerr, R.W. Chemistry and Industry of Starch. 2nd ed.; Academic Press: New York, 1950, 14–17, 133–134.
49. Combs, J.S. Warp size receevery. Textile Slashing Short Course Proceedings; Auburn University: AL, 1985, 103.
50. Allera, J. Economics of PVOH recovery in textile applications, Paper presented at the Spring 1982 AATCC Committee RA-73. Warp Sizing Technology Symposium; Research Triangle Park: NC, 1985.
51. Ulmans Encyclopedia of Industrial Chemistry. 5th. ed.; 1986; Vol. 5, 468.
52. Klug, E.D. Sodium carboxymethyl cellulose, Enclyopedia of Science and Technology; Interscience: New York, 1965; Vol. 3, 528.
53. Seydel, P.V.; Hunt, J.R. Textile Warp Sizing; Phoenix Printing: Atlanta: GA, 1981, 285–288.
54. Noro, N. Preparation of modified polyvinyl alcohols from copolymer. Finch C.A., Ed. Polyvinyl Alcohol: Properties and Applications; John Wiley and Sons: New York, 1973, 56.
55. Griffiths, A.L. CMC warp size, Textile Slashing Short Course Proceedings ; Auburn University: AL, 1977, 68–74.
56. Thorp, S.N. Procedure for energy efficient desizing. Textile Slashing Short Course Proceedings; Auburn University: AL, 1980, 91–96.
57. Livengood, C.D.; Tomasino, C. How much energy should it take to remove water soluble sizes. Text. Chem. and Colorist. 1980, 12(No. 4), 67–70.
58. Griffiths, A.L. CMC warp size. Textile Slashing Short Course Proceedings; Auburn University: AL, 1978, 38–49.
59. Diekman, S.F.; Jarell, J.G.; Voris, S.R. Carboxymethyl cellulose in the free acid form. Ind. Eng. Chem. 1953, 45, 2287–2290.
60. Klug, E.D. Sodium carboxymethyl cellulose, Enclyopedia of Science and Technology; Interscience: New York, 1965; Vol. 3, 521.
61. Drexler, P.G.; Tesoro, G.C. Materials and processes for textile warp sizing, Handbook of Fiber Science and Technology: Vol. 1 Chemical Processing of Fibers and Fabrics (Part B: Fundamentals and Preparation); Marcel Dekker: New York, 1984, 1–89.
62. Heap, V.; Seddon, R. Power grade acrylic sizes for staple yarns. Textile Slashing Short Course Proceedings; Auburn University: AL, 1987, 79–94.
63. Rutledge, B.L. Slashing research at Clemson, Proceedings of Slashing Today and Tomorrow; Clemson University, Nov. 18–19, 1986.

64. Hunt, J.R. Size additives. Textile Slashing Short Course Proceedings; Auburn University: AL, 1983, 142–152.
65. Shramm, C.K. Acrylic binder for warp sizing. Textile Slashing Short Course Proceedings; Auburn University: AL, 1983, 108–116.
66. Lark, J.C. Polyester resin composition, US Patent 4,268,645, May 19, 1981.
67. Lark, J.C. The Development of polyester resin binder for spun yarn size formulations, Warp Sizing Handbook; Livengood C.D., Ed.; AATCC Committee RA 73: Raleigh: NC.
68. Salsman, K. The scientific approach to sizing with polyester resins. Textile Slashing Short Course Proceedings; Auburn University: AL, 1991, 63–70.
69. Caloway, B.C. Vinyl acetate copolymer, Warp Sizing Handbook; Livengood C.D., Ed.; AATCC Committee RA 73: Raleigh, NC.
70. Farrow, J.C.; Hall, D.M.; Perkins, W.S. Theory and Practice of Textile Slashing (ATOE Monograph No. 1); Auburn University: AL, 1972, Chapter 8:227, Chapter 9:226–267.
71. McAllister, I. How to make those sizing calculations. Textile World 130(8), 99–102.
72. Fleicher, P.F. Liquid size for acetate filament yarn, Paper presented at Slashing Today and Tomorrow Symposium; Clemson University: Clemson: SC, November 18–19, 1986.
73. Gibbons, T. Sizes for cotton blends and filament yarns. Textile Slashing Short Course Proceedings; Auburn University: AL, 1983, 136–141.
74. Perkins, W.S. Size reclaimation using vacuum extraction. Textile Slashing Short Course Proceedings; Auburn University: AL, 1986, 84–90.
75. Hall, D.M.; Perkins, W.S. Water conservation by mechanized/chemical treatments to desize textile fabrics, Water Resources Research Institute Bulletin, 49; Auburn University: AL, Sept. 1985.
76. Glicksman, R. Gum Technology in the Food Industry; Academic Press: New York, 1969, 287.
77. Seydel, P.V.; Hunt, J.R. Textile Warp Sizing; Phoenix Printing: Atlanta: GA, 1981, 269.
78. Smith, B. Sizing: the total perspective, Paper presented at the AATCC Warp Sizing Symposium: Raleigh: NC; March 13–14, 1991.