CHAPTER 1

# Polymeric Materials for Coating

## 1.1 RUBBER—NATURAL AND SYNTHETIC [1–4]

### 1.1.1 INTRODUCTION

IN ancient times, Mayan Indians waterproofed articles of clothing and footwear by applying (coating) gum from a tree (rubber tree) and drying it over smoke fires. Modern day history of coating rubber on fabrics dates to 1823, when the Scotsman Macintosh patented the first raincoat by sandwiching a layer of rubber between two layers of cloth [3].

Since then, there have been great advances in rubber-coated fabric technology. Coated fabrics are now used for diverse applications. Almost all types of rubbers are used for coating, but the discussion here will be restricted to the more popular kinds.

Rubber is a macromolecular material that is amorphous at room temperature and has a glass transition temperature, $T_g$, considerably below ambient. Raw rubber deforms in a plastic-like manner, because it does not have a rigid network structure. It can be cross-linked by vulcanization to form an elastomer with the unique ability to undergo large elastic deformations, that is, to stretch and return to its original shape. For natural and most synthetic rubbers, vulcanization is accomplished with sulfur.

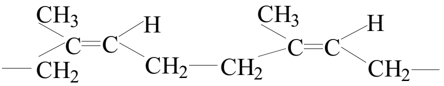
Elastomers that have stereoregular configuration and do not have bulky side groups or branching undergo crystallization. Crystallization cannot occur above melt transition, $T_m$. The rate of crystallization is greatest at about halfway between $T_g$ and $T_m$. For natural rubber, for example, this is about $-25°$C. The crystallites embedded in the elastomeric matrix act as physical cross-links, like reinforcing fillers. Most importantly, crystallinity can be induced by stress. Formation of crystallites enhances the strength of the rubber.

Vulcanization lowers the crystallinity as three-dimensional networks create obstacles in segments entering the crystal lattice. Lower crystallinity is also observed in random copolymers.

## 1.1.2 PRODUCTION, STRUCTURE, AND PROPERTIES

### 1.1.2.1 Natural Rubber (NR)

NR is obtained from the exudation of the rubber plant, *Hevea brasiliensis.* The rubber is obtained from the latex by coagulation, sheeting, drying, and baling. There are various internationally recognized market grades, common among them are ribbed smoked sheets and pale crepe. Natural rubber contains about 90% rubber hydrocarbon as *cis*-1,4-polyisoprene along with naturally occurring resins, proteins, sugars, etc., that precipitate during latex coagulation. The average molecular weight of polyisoprene in natural rubber ranges from 200,000 to 500,000, with a relatively broad molecular weight distribution. As a result of its broad molecular weight distribution, NR has excellent processing behavior.

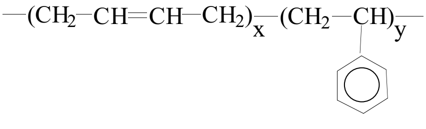


*cis*-1,4-Polyisoprene unit

The $\alpha$-methylene group of the polyisoprene units is reactive for vulcanization with sulfur. NR vulcanizates combine a range of properties that are of great technological interest. The individual property can be improved by the use of synthetic rubber, but a combination of high tensile strength, resilience, dynamic properties, and good low temperature flexibility make NR indispensable for several applications. The high tensile strength and tear resistance of NR vulcanizates is due to strain crystallization. Being nonpolar, NR swells in nonpolar solvents. Reaction of the double bond in the polyisoprene unit with oxygen or ozone results in degradation of the polymer.

### 1.1.2.2 Styrene-Butadiene Rubber (SBR)

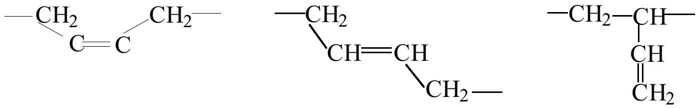
SBR is a copolymer of styrene and butadiene. The styrene content ranges from about 25 to 30 wt.%. The structure is given as



SBR

SBR is mainly prepared by emulsion polymerization, The monomers are randomly arranged in the chain, and the butadiene part is mainly in the *trans* configuration (~75%). Some 1,2-addition products are also formed. Depending on the temperature of polymerization, SBR may be classified into hot-polymerized and cold-polymerized grades. The hot grades are highly branched compared to the cold grades.

SBR can also be copolymerized in a solution process using alkyl lithium catalysts in a nonpolar solvent. These rubbers have much higher *cis*-1,4-butadiene content (50–55%), less chain branching, and narrower molecular weight distribution.



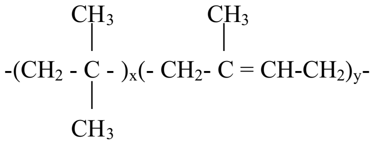
cis *trans*

1,4-Butadiene 1,2-Addition product

SBR does not crystallize even on stretching their vulcanizates, therefore, pure gum strength is generally low. It has better heat and aging resistance than NR and is usually used in combination with NR and other rubbers.

### 1.1.2.3 Isoprene-Isobutylene Rubber, Butyl Rubber (IIR)

Butyl rubber is a copolymer of 97 to 99.5 mole % of isobutylene and 0.5 to 3 mole % isoprene. The isoprene unit provides the double bond required for sulfur vulcanization.



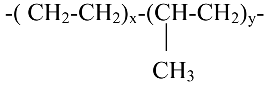
$$-(CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-)_x(-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_2)_y-$$

IIR, Butyl rubber

It is produced by cationic polymerization in methylene chloride with $AlCl_3$ as catalyst, at subzero temperatures (−90°C to −100°C). The isobutylene monomer units polymerize mainly in head-to-tail arrangements, and the isoprene units in the polymer chains polymerize in *trans* 1,4-configuration. The molecular weight ranges between 300,000 to 500,000. On halogenation of IIR in an inert organic solvent, a rapid electrophilic substitution takes place, and one halogen atom is substituted per isoprene unit, mainly in the allylic position. Thus, a small number of halogen atoms are incorporated into the polymer chain. These are known as chlorobutyl rubber (CIIR) or bromobutyl rubber (BIIR) depending on the halogen substituted. The polymer chains are highly saturated and have a very regular structure due to the symmetrical nature of the monomer. As a result, butyl rubber exhibits very low gas permeability, ozone, heat, weathering, and chemical resistance. Butyl rubbers are self-reinforcing with a high gum tensile strength. The halobutyl rubbers cure faster than butyl rubber. Bromobutyl has much lower gas permeability and better resistance to aging, weathering, and heat than butyl rubber. Butyl and bromobutyl rubbers are especially used where low gas permeability is required.

### 1.1.2.4 Ethylene Propylene Polymers (EPM) and Terpolymers (EPDM)

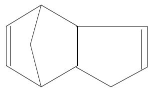
Copolymers of ethylene and propylene EPM are made by solution polymerization using vanadium containing alkyl aluminum, Ziegler-type catalyst. These are elastomers, but they do not contain any double bonds.



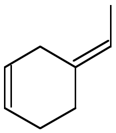
$$-(\ CH_2-CH_2)_x-(\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_2)_y-$$

EPM

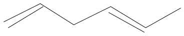
For good elastomeric properties, the ethylene propylene ratio ranges from 45–60 wt.%, and the monomers are arranged randomly. Consequently, these polymers are predominantly amorphous, and the pure gum strength is low. The molecular weight ranges between 200,000 to 300,000. Because EPM is saturated, the polymeric chain is cured by peroxides. The terpolymer EPDM contains, in addition to the olefin monomers, a nonconjugated diene as the third monomer, which renders EPDM able to be vulcanized by sulfur. The common third monomers are dicyclopentadiene, ethylidene norbornene, and 1,4-hexadiene. In these dienes, one double bond is capable of polymerizing with the olefins, but the other is not a part of the main chain.



Dicyclopentadiene



Ethylidene norbornene



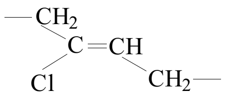
*trans*-1,4-Hexadiene

Both EPM and EPDM have excellent resistance to oxygen, ozone, heat, and UV radiation.

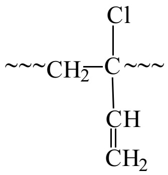
### 1.1.2.5 Polychloroprene Rubber (CR)

These rubbers are produced by the emulsion polymerization process of 2-chloro-1,3-butadiene. The polymer chains consists of approximately 98%

1,4-addition products which are mostly *trans* in configuration, and the rest are 1,2-addition products. The 1,2-addition product contains a chlorine atom attached to a tertiary allylic carbon atom that is highly activated and thus becomes the curing site in the polymer chain.



*trans*-Polychloroprene unit



$$\sim\sim\sim CH_2{-}\overset{\displaystyle Cl}{\underset{\displaystyle CH{=}CH_2}{C}}\sim\sim\sim$$

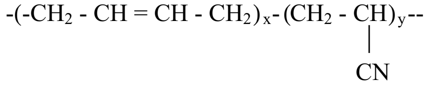
1,2-Addition product

The temperature of polymerization has an important bearing on the polymer structure. At higher temperatures, there is less uniformity in the chain due to large proportions of 1,2 and 3,4 moieties and other isomers in the monomeric sequences. On the other hand, at lower temperatures, the polymeric chain is more regular. The CR is also available in sulfur-modified grades. The polymer chains have Sx groups, and this aids processing due to easy depolymerization. Unlike the diene rubbers, CRs are not vulcanized by sulfur but are vulcanized by metal oxides—a combination of MgO and ZnO.

Polychloroprene stiffens at low temperatures. This is due to second-order transition and crystallization. The rate of crystallization is most rapid at −10°C. Though the stiffening is reversible, it is detrimental for the production of certain goods. Incorporation of low temperature plasticizers like butyloleate can lower the stiffening temperature of CR compounds. CR produced by high temperature polymerization has a much lower rate of crystallization than that produced at a low temperature. The high crystallizable grades are useful as adhesives. For production of coated fabrics, materials with long crystallization times are chosen, as softness and flexibility are more important than ability to withstand heavy stress. The gum vulcanizates of CR show high tensile strength because of strain crystallization, but the resilience is lower. Polychloroprene rubbers are resistant to oxidation, ozone degradation, and flex cracking, and, because of the chlorine atom in the molecule, are inherently flame resistant. Because of its polar nature, the rubber is resistant to hydrocarbons, fats, oils, and most chemicals. It is used for applications requiring weather, oil, ozone, and flame resistance.

### 1.1.2.6 Nitrile Rubber (NBR)

NBR is a copolymer of acrylonitrile and butadiene obtained by emulsion polymerization. The acrylonitrile content varies from 18–50%, depending on the properties desired. The molecular weight ranges from 20,000 to 100,000.



$$-(-CH_2 - CH = CH - CH_2)_x - (CH_2 - \underset{CN}{\underset{|}{CH}})_y--$$

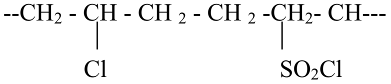
NBR

Like SBR, varying temperatures of polymerization produce different grades of NBR. NBR produced at low temperatures shows less branching than hot rubbers. The steric configuration, i.e., *cis*-1,4, *trans*-1,4, and *trans*-1,2 structures are also influenced by polymerization temperature. The lack of compositional uniformity along the polymer chains prevents formation of crystallites on extension. This results in poor tensile properties of NBR gum vulcanizates.

Nitrile rubbers are of special interest because of their high degree of resistance to fuels, oils, and fats. An increase in acrylonitrile (AN) content increases its oil resistance because of enhancement of polarity of the rubber. NBR has a low gas permeability. Increase of AN percentage in NBR lowers its gas permeability but adversely affects its low temperature flexibility and resilience. NBR is extensively used where oil resistance is required.

### 1.1.2.7 Chlorosulfonated Polyethylene Rubber (CSM)

CSM is produced by reaction of polyethylene solution with chlorine and sulfur dioxide in the presence of UV radiation.



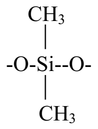
$$--CH_2 - \underset{Cl}{\underset{|}{CH}} - CH_2 - CH_2 - \underset{SO_2Cl}{\underset{|}{CH_2}} - CH---$$

CSM unit

Commercial grades contain 25–40 wt.% of chlorine and about 1% of S. The chlorine and sulfur are randomly distributed along the polymer chain. It is cross-linked by metal oxides through chlorine atom and chlorosulfonyl group. These rubbers are characterized by a unique combination of special properties like ozone resistance, flame retardance and resistance to corrosive chemicals and oxidizing agents.

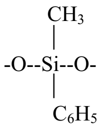
### 1.1.2.8 Silicone Rubber

Silicone rubber is obtained from silicones. Chemically, silicones are polysiloxanes containing Si-O- bonds. The most important polymers are polydimethyl siloxane, polymethyl phenyl siloxane, and vinyl methyl siloxane. They are manufactured by the hydrolysis of the appropriate dichlorosilane $R_2SiCl_2$. Silicones are available in a wide range of molecular weights and viscosities, from fluids to gums.



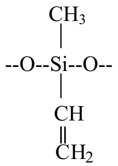
$$-\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}--\mathrm{O}-$$

Dimethyl siloxane unit



$$-\mathrm{O}--\overset{\mathrm{CH_3}}{\underset{\mathrm{C_6H_5}}{\mathrm{Si}}}--\mathrm{O}-$$

Methyl phenyl siloxane unit

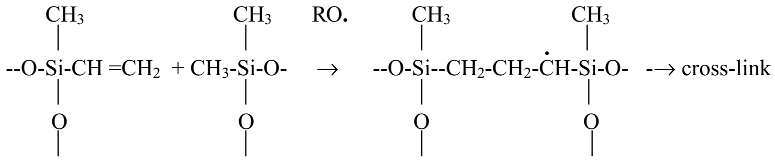


$$--\mathrm{O}--\overset{\mathrm{CH_3}}{\underset{\mathrm{CH}=\mathrm{CH_2}}{\mathrm{Si}}}--\mathrm{O}--$$

Vinyl methyl siloxane unit

There are three major ways of curing silicone rubbers, viz., peroxide cure, hydrosilation, and condensation cure [5,6].

(1) Peroxide initiated cure: $ROOR \xrightarrow{\Delta} 2R\dot{O}$

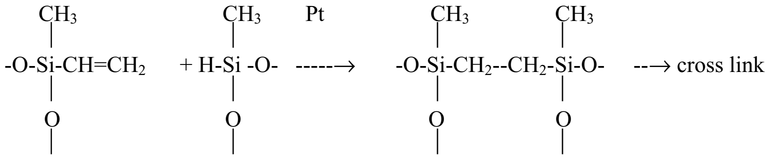


$$--\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{O}}{\mathrm{Si}}}-\mathrm{CH}=\mathrm{CH_2} + \mathrm{CH_3}-\overset{\mathrm{CH_3}}{\underset{\mathrm{O}}{\mathrm{Si}}}-\mathrm{O}- \xrightarrow{\mathrm{RO.}} --\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{O}}{\mathrm{Si}}}--\mathrm{CH_2}-\mathrm{CH_2}-\dot{\mathrm{C}}\mathrm{H}-\overset{\mathrm{CH_3}}{\underset{\mathrm{O}}{\mathrm{Si}}}-\mathrm{O}- \longrightarrow \text{cross-link}$$

(1)

This is a one-part system where the peroxide is activated on heating above 100°C. The vinyl group facilitates free radical reaction with the formation of vinyl to methyl and methyl to methyl bonds.

(2) Hydrosilation: an addition reaction occurs between vinyl siloxane and siloxane containing Si-H group catalyzed by Pt (chloroplatinic acid). The cross-link occurs due to multiple functionality of both reactants. This is a two-part reaction with one part containing vinyl siloxane with Pt catalyst and the other containing silicone with Si-H functionality. The two liquid parts permit direct processing including coating without solvent and are known as liquid silicone rubber LSR.

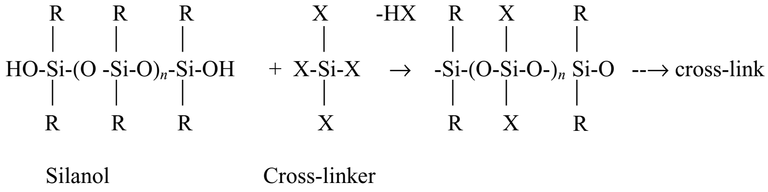


$$-\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{O}}{\mathrm{Si}}}-\mathrm{CH}=\mathrm{CH_2} + \mathrm{H}-\overset{\mathrm{CH_3}}{\underset{\mathrm{O}}{\mathrm{Si}}}-\mathrm{O}- \xrightarrow{\mathrm{Pt}} -\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{O}}{\mathrm{Si}}}-\mathrm{CH_2}--\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{O}}{\mathrm{Si}}}-\mathrm{O}- \longrightarrow \text{cross link}$$

PDMS with Si-H group

(2)

(3) Condensation cure: condensation reaction between siloxanes with terminal hydroxyl groups, -silanols, and a cross-linker,–tri or tetra functional organo silicon compound, leads to cross-linking/cure.



$$\text{HO-}\underset{R}{\overset{R}{\text{Si}}}\text{-(O -}\underset{R}{\overset{R}{\text{Si}}}\text{-O)}_n\text{-}\underset{R}{\overset{R}{\text{Si}}}\text{-OH} + \text{X-}\underset{X}{\overset{X}{\text{Si}}}\text{-X} \xrightarrow{\text{-HX}} \text{-}\underset{R}{\overset{R}{\text{Si}}}\text{-(O-}\underset{X}{\overset{X}{\text{Si}}}\text{-O-)}_n\ \underset{R}{\overset{R}{\text{Si}}}\text{-O} \dashrightarrow \text{cross-link} \qquad (3)$$

Common cross-linking agents are tetraethyl ortho silicate ($X$ = OEt), triacetoxy silane ($X$ = OAc ), etc. Condensation occurs at room temperature in the presence of metal soap catalysts, typically, stannous octoate and moisture. The rubbers are known as room temperature vulcanizates (RTV). The RTVs may be two-part systems or one-part systems. In a one-part system, the common cross-linker is methyl triacetoxy silane, and the reactants are stored in anhydrous condition.

The molecular weights of hot vulcanizates range from 300,000 to 1,000,000. The Si-O bond energy is higher than that of the C-C bond, as such, the polysiloxane chain is thermally and oxidatively much more stable than organic hydrocarbon chains. Silicone rubbers can also retain their flexibility to as low as $-100°$C. The stability of silicones over a wide range of temperatures is outstanding and is not found in any other rubber. Silicones are extraordinarily resistant to aging, weathering, and ozone. They have, however, lower mechanical properties, but they do not change much with temperature. The vulcanizates are hydrophobic and are resistant to chemicals. They form transparent/translucent coatings. Because of their unique properties, they find specialized applications, for example, gaskets, O-rings, wire cable, etc.

### 1.1.3 RUBBER ADDITIVES

Various chemicals, fillers, accelerators, and cross-linking agents are added to rubber to facilitate processing and vulcanization. The properties of the end product can be significantly altered by proper choice and amount of the compounding ingredients to meet the diverse end-use requirements.

Typical ingredients of a rubber formulation are as follows:

- raw rubber
- cross-linking agents
- accelerators
- accelerator activators

- antidegradants
- fillers, reinforcing, diluents
- processing aids
- pigments and dyes
- special additives, e.g., flame retardants, fungicides

The cross-linking agent for natural rubber is sulfur along with organic accelerators. Zinc oxide and stearic acid are used as activators of the accelerator. The synthetic olefin rubbers like SBR, NBR, butyl, and EPDM can also be cured by sulfur system. For butyl and EPDM rubbers having low unsaturation, more active accelerators are used with a higher temperature of cure. Apart from elemental sulfur, organic compunds that liberate sulfur at the temperature of vulcanization can also be used for vulcanization, e.g., dithiodimorpholine and 2-morpholine-dithio benzothiazole.

The nonolefin rubbers, polychloroprene and chlorosulfonated polyethylenes are cured by metal oxides. In the case of polychloroprene, the curing is done by zinc oxide and magnesium oxide, because sulfur cure is not possible as the double bond is hindered by the neighboring chlorine atom. The zinc oxide reacts with chlorine atoms of the 1,2 units present in the chain after an allylic shift. Magnesia also acts as scavenger of the chlorine atom. More rapid cure is achieved by the use of organic accelerators like ethylene thiourea. Chlorosulfonated polyethylene is cured by litharge and magnesia, along with accelerators. The curing occurs by ionic and covalent bond formation through sulfonyl chloride groups.

In the case of ethylene propylene rubber (EPM) and silicones, peroxides are the cross-linking agents. In EPM, the tertiary carbon atom at the point of branching is attacked by peroxides with H abstraction, generation of a tertiary free radical, followed by termination, forming a cross-link. The cross-linking of polydimethyl siloxane by peroxides, as discussed earlier, occurs through abstraction of H from the methyl group with the formation of free radical followed by termination. More rapid vulcanization is achieved when vinyl groups are present in the chain. Some common peroxides are benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, dicumyl peroxide, etc.

The accelerators used for sulfur vulcanization of olefin rubbers are of various types depending on the rate of cure, i.e., medium, semi-ultra, and ultra accelerators. The chemical types are aldehyde amine, guanidines, thiazoles, sulfenamides, dithiocarbamates, thiuram sulfides, and xanthates. The action of the accelerator is further enhanced by activators. Zinc oxide and stearic acid system for sulfur vulcanized rubbers is most common, but other zinc salts of fatty acids like zinc laurate can be used. Most of the rubber formulations contain antidegradants, antioxidants, and antiozonants. They function by either capturing the free radical formed during the degradation process or by decomposing the peroxides and hydroperoxides produced into nonreactive fragments. The majority of the commercially available inhibitors belong to two main chemical classes: amines and phenolics. Fillers are incorporated into a rubber formulation for reinforcement, i.e., for enhancement of tensile strength, abrasion resistance, and tear resistance, or as diluent to reduce cost. The most common reinforcing filler is carbon black. Among the nonblack reinforcing fillers, common are precipitated silica, fume silica, calcium silicate, hydrated aluminium silicate (clay), etc. Barytes, whitings, talc, chalk, kaolin, and kieselguhr are some of the other fillers used. Plasticizers and softeners are added to rubber compounds to aid various processing operations of mixing, calendering, extruding, and molding. These include a wide range of chemicals such as petroleum products, oils, jelly, wax, coal tar products, pine tar, fatty acid salts, factice (reaction product of vegetable oil and sulfur), and esters of organic acids. Peptizers are also added to increase the efficiency of molecular breakdown, facilitating the mastication process. Pentachlorophenol, its zinc salt, and di-(*o*-benzamido phenyl) disulfide, are common peptizing agents. For noncarbon black rubber compounds, coloring materials are used, which are generally colored inorganic compounds. Sometimes, special purpose additives are added to obtain specific properties, like blowing agents for cellular rubber, flame retardants, like chlorinated paraffins, zinc borate, etc.

### 1.1.4 COMPOUNDING AND PROCESSING OF RUBBER

For coating of rubber on fabric, it has to be properly processed. The steps involved are as follows:

- mastication or milling
- compounding
- coating by calendering
- preparing dough and spread coating
- vulcanizing the coated fabric

The processing and machinery required for rubber are different from those required for coating other polymers. A brief account of the processing steps are discussed here.

#### 1.1.4.1 Mastication and Compounding

Raw rubber is masticated to decrease its viscosity to a desired level for incorporation of the compounding ingredients and their proper dispersion. A proper adjustment of viscosity is also required for various processing operations. When rubber has all of the ingredients needed, it is known as a “compound.” If some ingredients have been deliberately withheld, particularly curing agents, the partially completed compound is known as the master batch. Mastication is done generally in mixing mills or in internal mixers.

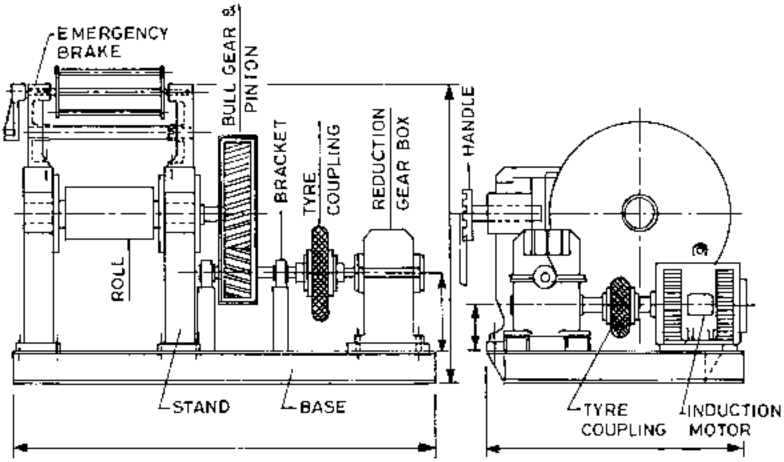


**Figure 1.1** Line diagram of a two-roll mixing mill. Courtesy M/s Slach Hydratecs Equipment, New Delhi, India.

Mixing mills are used for small-size compounds and as a follow-up to internal mixers. They consist of two horizontal and parallel rolls made from hard castings, that are supported through strong bearings in the mill frame. The distance between the rolls is adjustable. The two rolls move in opposite directions at different speeds, the back roll running faster than the front (Figure 1.1). The ratio of the two speeds is known as the friction ratio, which is about 1:1.25 for natural rubber. Frictioning promotes tearing, kneading, and mixing of the rubber mass and the ingredients in the roll nip. Side guides are provided to prevent rubber from flowing to the bearings. The rolls can be cooled or heated with water or steam by circulating water through a drilled core or through peripheral holes. Raw rubber is first placed between the rolls, the elastomer is torn, and then it wraps around the front roll. After several passages, a continuous band is formed. The degree of mastication is controlled by the temperature of the roll, the size of the nip, and the number of passes. The compounds are then added in a well-defined sequence, such as accelerators, antioxidants, factice, pigments, fillers, and sulfur. If peptizers are used, they are added first. At the end, the compounded layer is cut off repeatedly in order to homogenize it.

The mixing in an internal mixer is done in a closed chamber by rotating kneading rolls. The mixer can handle larger batches. The internal mixer consists of a mixing chamber shaped in the form of a horizontal figure of eight. Two rotors are fitted into the chamber that rotate at different speeds to maintain a high friction ratio. The walls of the mixing chamber and the rotors are equipped with cavities for cooling or heating. The mixing chamber has a filling device at the top, which is used for adding ingredients.

The chamber is closed by a pneumatically operated ram to ensure that the rubber and ingredients are in proper contact. A ram pressure of about 2–12 kg/cm$^2$

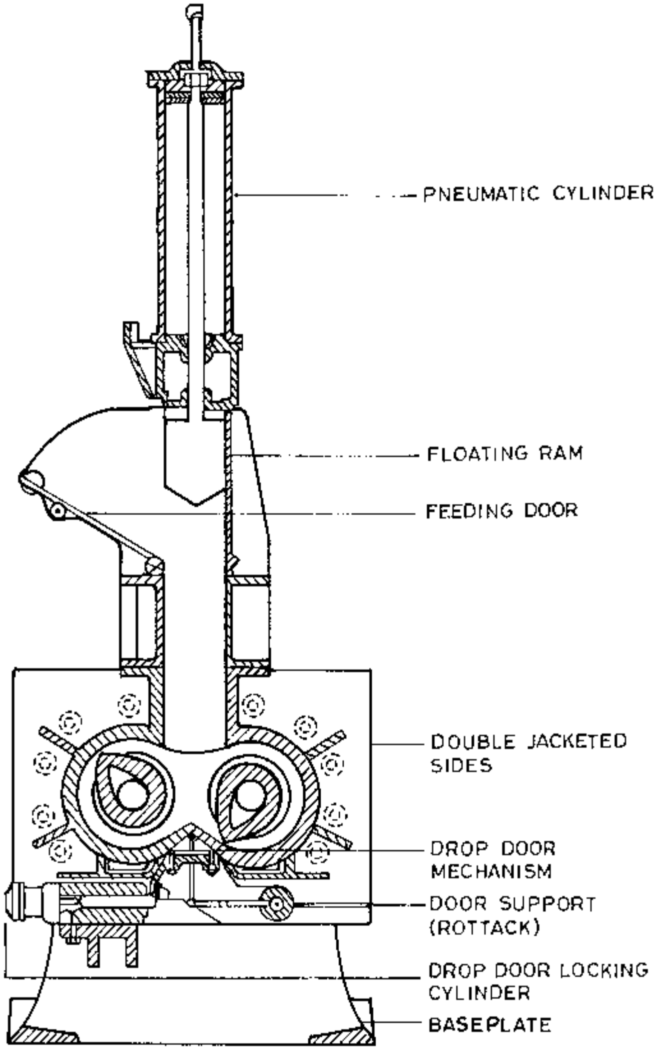


**Figure 1.2** Line diagram of a drop door type internal mixer. Courtesy M/s Slach Hydratecs Equipment, New Delhi, India.

is applied for this purpose. Higher ram thrust results in better mixing efficiency. The design of the rotors may be (1) tangential type, where the kneading action is between the rotors and the jacket or (2) intermeshing type, where the kneading occurs between the rotors. A drop door type internal mixer is shown in Figure 1.2.

The rotor speed varies between 20–60 rpm. The capacity of the internal mixer can vary widely, but mixers of 200 kg batch size are quite popular. The operation of the mixer consists of adding rubber in split or pelletized forms. After a short mastication, the compounding ingredients are added. The incorporation of rubber and other ingredients can be partly or fully automated. Normally, complete mixing is not done in an internal mixer because of the scorch problem. Master batch is initially prepared and the remaining ingredients are added to it afterwards in a mixing mill. The compound coming out of the internal mixer is in the form of lumps and has to be cooled and homogenized in sheeting mills. Mixing can be done continuously in a single- or twin-screw extruder, however, extruders are not very popular for mixing rubbers.

### 1.1.4.2 Spreading Dough

Preparation of dough of the right consistency is of great importance for spread coating. The compounded rubber is cut thinly in narrow strips or pieces and soaked in a proper solvent for a few hours. Organic solvents capable of dissolving the elastomers are selected for the purpose, keeping the cost factor in view. Mixed solvents are also used quite often for better solvating properties, enabling preparation of a more concentrated solution. Toluene, aromatic and chlorinated hydrocarbons, and esters are common solvents used. For natural rubber, toluene is usually used. The soaked mass is then transferred into solution kneaders for preparation of a homogenous dough. The solution kneaders consist of a semicircular trough with a lid and two kneading paddles in the shape of Z or sigma. The paddles turn with a differential speed, the forward one is 1.5 to 2 times faster than the back. The trough is double walled to permit cooling and is closed by a movable lid. The rotating paddles disintegrate the swollen mass while continuously wetting the rubber. The agitation is continued until a dough of the right consistency is produced; this may take up to 12 hrs. The dough is emptied from the trough either by tilting or by discharge screws as per the design of the kneader. However, high speed Ross mixers do this job in 30 min to 1 h.

### 1.1.4.3 Vulcanization of Rubberized Fabrics

Vulcanization can be carried out as a batch process in a steam autoclave using saturated steam. An autoclave is a cylindrical pressure vessel, normally used in the horizontal position. Curing can also be done by hot air under pressure. However, because the heat transfer coefficient of air is lower than steam, air curing requires higher curing time, needing a change in formulation. Moreover, the oxygen of air can oxidize the elastomer. In steam curing, on the other hand, formation of condensed water can lead to unsightly water spots, and local undercuring. This problem is solved by coating the uncured article with a wetting agent.

Continuous drum cure, also known as rotocure, is also used. In this process, the curing of the coated fabric is achieved by placing the fabric in contact with a rotating steam-heated drum (Figure 1.3).

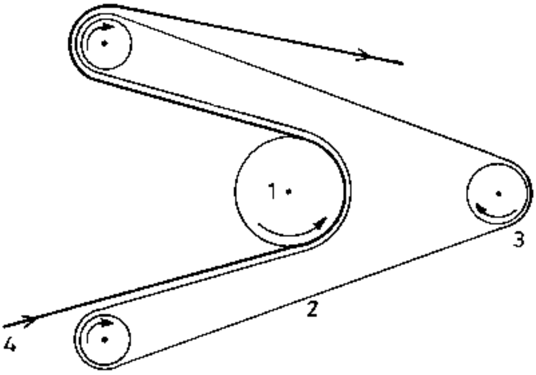


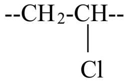
**Figure 1.3** Rotocure process: (1) steel drum, (2) steel belt, (3) tension roll, and (4) fabric.

A steel band runs over about two-thirds of the circumference of a slowly rotating steam-heated steel drum. The steel band is pressed against the drum. The sheet to be vulcanized runs between the drum and the steel band and is pressed firmly against the drum with a pressure of about 5–6 kg/cm$^2$. The sheet slowly moves with the rotation of the drum. Vulcanization occurs because of the temperature of the drum and the pressure on the sheet created by the steel band.

## 1.2 POLYVINYL CHLORIDE [7–11]

### 1.2.1 INTRODUCTION

Polyvinyl chloride (PVC) is one of the few synthetic polymers that has found wide industrial application. The popularity of PVC is due its low cost, excellent physical properties, unique ability to be compounded with additives, and usefulness for a wide range of applications and processability by a wide variety of techniques. The repeat unit of PVC is



$$\text{--}CH_2\text{-}\underset{\displaystyle Cl}{\underset{|}{CH}}\text{--}$$

The units are linked mainly head to tail, with very few head to head links. PVC is considered to be an amorphous polymer. The crystallinity is only about 10%. This is attributed to the nonregular position of the chlorine atoms around the carbon chain. Branching is low in PVC. Lower polymerization temperature favors more linear structure. The molecular weight ($\bar{M}_n$) of commercial resins, ranges from 50,000 to 100,000.

It is produced by the addition polymerization of vinyl chloride, $CH_2{=}CH\text{-}Cl$. The methods of polymerization are suspension, emulsion, mass, and solution processes. Among these, suspension is the most favored commercial process, contributing to about 80% of total polymer production. The emulsion and mass processes contribute to about 10% each. The resins obtained from suspension and mass polymerization are porous and absorb plasticizer rapidly. Polymer obtained by the emulsion process is nonporous, with very fine particle size. It quickly and reversibly absorbs plasticizer once heated at temperatures above 80°C. The main use of emulsion PVC is in plastisol and organosol preparations, which are extensively used in coating and slush molding. The solution process is almost exclusively restricted to the manufacture of PVC copolymers for use in surface coatings.

### 1.2.2 RESIN CHARACTERISTICS

The physical forms of PVC resins are diverse which permits a wide range of processing techniques. The resins are classified on the basis of important properties required for processing. The specifications of the resins have been standardized by ASTM and ISO; and a nomenclature system to designate the properties evolved. The characteristics of general purpose resins (G) and dispersion resins (D) are different.

The important characteristics of general purpose resins are as follows:

(1) Molecular weight: in industrial practice, dilute solution viscosity is normally determined as an index of molecular weight. The results are commonly expressed in terms of $K$ value or viscosity number. The $\bar{M}_v$ can be determined from the Mark-Houwink equation. A high $K$ value denotes high molecular weight, a high melt viscosity of the unplasticized PVC requiring higher processing temperature.

(2) Particle size: particle size and particle size distribution influence compounding and processing properties.

(3) Bulk density

(4) Dry flow: this property is a measure of the ease of handling of granular resins.

(5) Plasticizer absorption: it is a measure of the capacity of the resin to absorb plasticizer, yet remain a free-flowing powder. It is dependent on surface properties of the resin powder.

(6) Electrical conductivity: this test is intended to distinguish between electrical and nonelectrical grades.

Important characteristics for dispersion resins are as follows:

(1) Molecular weight

(2) Particle size

(3) Settling

(4) Plastisol viscosity: usually determined by viscometer at specified shear rates with a specified concentration of plasticizer (dioctyl phathalate)

(5) Plastisol fusion: it denotes the complete solvation of the resin by the plasticizer and is a function of solvating power of plasticizer, temperature, and time. Determination of clear point and measurement of rate of increase of viscosity at a constant temperature are some of the methods of determination of fusion.

### 1.2.3 ADDITIVES FOR PVC

For processing and imparting properties for special applications, PVC is compounded with a variety of additives. Some of the important additives are as follows:

- plasticizers
- heat stabilizers
- fillers
- lubricants
- colorants
- flame retardants

### 1.2.3.1 Plasticizers

Plasticizers are an important additive of PVC resin, because the majority of PVC products are plasticized. These are liquids of low or negligible volatility or low molecular weight solids, which when incorporated into the polymer, improve its processability and impart end product softness, flexibility, and extensibility. The other concomitant effects of plasticization are lowering of $T_g$ and softening temperature, reduction of strength, and increased impact resistance. The plasticizer acts by lowering the intermolecular forces between the polymer chains. The plasticizer should be compatible with the polymer, or exudation will occur. Those plasticizers that are highly compatible with PVC are known as primary plasticizers, while plasticizers that have limited compatibility are known as secondary plasticizers. Secondary plasticizers are added to impart special properties or to reduce cost.

#### *1.2.3.1.1 Plasticizer Characteristics*

The main parameters for ascertaining the effectiveness of a plasticizer are compatibility, efficiency, and permanence.

(1) Compatibility: this can be determined from solubility parameter $\delta$ and Flory Huggins interaction parameter $\chi$. The PVC-plasticizer system is considered

compatible if its solubility parameters are nearly equal. Again, if the $\chi$ value is low ($<0.3$), the system is considered compatible. Compatibility can also be determined from clear point, which is the temperature at which the PVC-plasticizer mixture becomes clear. The lower the clear point temperature, the greater the compatibility.

(2) Efficiency: technologically, it is the amount of plasticizer required to produce a selected property of practical interest, like hardness, flexibility, or modulus. The efficiency of plasticizer can also be gauged by the lowering of $T_g$, and changes in dynamic mechanical properties.

(3) Permanence: the plasticizer may be lost from the compounded resin by vaporization into the atmosphere, extraction in contact with a liquid, or migration into a solid in intimate contact with the plasticized PVC. Permanence can be determined by weight loss measurements on exposure to the extraction media.

### *1.2.3.1.2 Plasticizer Types*

(1) Phthalates: these are the largest and most widely used group of plasticizers. The esterifying alchohol ranges from methyl to tridecyl. The lower chain length esters have high solvating power but suffer from high volatility and poor low temperature properties. Medium chain $C_8$ phthalates possess optimum properties. The longer chain $C_{10}$–$C_{13}$ esters have reduced solvating power and efficiency, though low volatility. Di-2-ethylhexyl phthalate (DOP) and diisoctyl phthalate (DIOP) are extensively used in industry because of their better balance of properties.

(2) Phosphates: these are organic esters of phosphoric acids. The triaryl phosphates, like tricresyl (TCP) and trixylyl (TXP), are by far the most important phosphate plasticizers.The triaryl phosphates offer excellent flame retardance, good solvating power, and good compatibility, but poorer low temperature properties.

(3) Aliphatic diesters: in this category are esters of adipic, azelaic, and sebacic acids of branched chain alcohols such as isooctanol, 2-ethylhexanol, or isodecanol. These impart low temperature flexibility to PVC compositions. Their compatibility is, however, low, and they are categorized as secondary plasticizers.

(4) Epoxies: epoxidized soybean oil and linseed oil exhibit good plasticizing and stabilizing actions. They possess low volatility and good resistance to extraction.

(5) Polymeric plasticizers: the majority of commercial plasticizers of this class are saturated polyesters, synthesized by the reaction of a diol and dicarboxylic acid along with an end capping agent, which may be a monohydric alcohol or monocarboxylic acid. An increase in molecular weight results

in improved permanence and lower volatility, but it adversely affects low temperature properties and compatibilty.

### 1.2.3.2 Heat Stabilizers

Unless suitably protected, PVC undergoes degradation at the processing temperatures. The manifestations of the degradation include the evolution of hydrogen chloride, development of color from light yellow to reddish brown, and deterioration of mechanical properties. The degradation occurs due to the progressive dehydrochlorination of the polymer chains with the formation of conjugated double-bond polyenes, possibly by a free radical mechanism. The site of initiation could be a chlorine atom attached to a tertiary carbon atom at the site of branching. As shown in Figure 1.4, the first step is the formation of an allylic group, whose Cl atom is strongly activated by the neighboring double bond favoring further elimination of HCl. The HCl acts as an autocatalyst.

In addition to the polyene formation, the polymer undergoes chain scission, oxidation, cross-linking, and some cyclization. The Diels Alder reaction between polyene moieties of neighboring chains is believed to be responsible for much of the cross-linking. PVC also undergoes photodegradation on exposure to light in the presence as well as in the absence of oxygen. The manifestations and degradation products are similar to those of thermal degradation. In plasticized PVC, exudation of plasticizers from PVC occurs on weathering, which has been attributed to their partial exclusion from the areas where cross-linking has occurred. A heat stabilizer should prevent the reaction responsible for degradation of PVC. It should bind the liberated hydrogen chloride, deactivate potential initiation sites by substituting stable groups for labile chlorine, disrupt formation of polyene sequence, and deactivate the free radicals. Morever, the stabilizer should be compatible with the polymer and other additives in the compound.

The heat stabilizers may be classified as lead compounds, organo tin compounds, compounds of other metals like barium, cadmium, and zinc, and organic

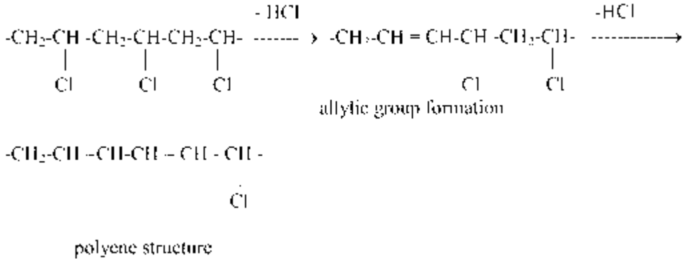


**Figure 1.4** Formation of polyene structure.

compounds. Common lead and tin compounds are lead phosphate, dibasic lead stearate, dibutyl tin laurate, dibutyl tin maleate, etc. Barium, cadmium, and zinc salts, when used in combination, impart excellent stability and show synergistic effect. The compounds are salts of fatty acids, like laurates, stearates, and octoates. These compounds are used in calendered goods, plastisols, floorings, and coated fabrics. Organic stabilizers are epoxidized oils, phosphites, and polyhydric alcohols. They are normally regarded as secondary stabilizers in conjunction with Ba-Cd-Zn stabilizers.

For some special applications antioxidants are added to the PVC compound. They are usually phenolics like 2,6-di-t-butyl-4-methyl phenol and 3-(3,5-di-t-butyl-4-hydroxy phenyl) octadecyl propionate. The degradation of PVC by UV radiation can be prevented by incorporation of UV absorbers like derivatives of 2-hydroxy bezophenone, benzo triazoles, etc., or by addition of inorganic particulate screening agents like carbon black and titanium dioxide.

#### 1.2.3.3 Other Additives

(1) Fillers: the primary role of a filler in PVC is to reducte cost, but they can play a functional role by improving processing and properties of the end product. The common fillers are (1) calcium carbonate fillers—whiting, and marble dust, (2) silicates—clay, talc, and asbestos, and (3) barytes.

(2) Lubricants: the role of a lubricant is to facilitate processing and control the processing rate. Mineral oil, silicone oils, vegetable oils, and waxes are common lubricants. Metal stearates of Pb, Ba, Cd, and Ca may be used for the dual purpose of stabilizing and lubricating. The compatibility of lubricants is low, resulting in their exudation at processing conditions.

(3) Colorants: the colorants of PVC are inorganic and organic pigments. The inorganic pigments include titanium dioxide, chromium oxide, ultramarine blue, molybdate orange, etc. The organic pigments are phthalocyanines, quinacridines, and benzidines. The inorganic pigments have excellent heat resistance, light stability, and opacity.

(4) Flame retardants: the inherent flame retardant property of PVC due to the presence of a chlorine atom is affected by the addition of flammable plasticizers. Antimony trioxide and borates of zinc and barium are widely used for this purpose. Chlorinated paraffins and phosphate ester-plasticizers also act as flame retardants.

### 1.2.4 PLASTISOLS AND ORGANOSOLS

These are fluids in which fine PVC particles are dispersed in plasticizers. Plastisol or pastes (used synonymously) do not contain any solvent/volatile components. An organosol is a plastisol containing volatile organic solvents.

The viscosity of plastisols varies from pourable liquids to heavy pastes. PVC pastes have two important characteristics.

(1) They are liquids and can be processed in that condition. The processing conditions are determined by the property of the paste at ambient temperature.
(2) On application of heat, when required, they fuse to viscous solutions of polymer in plasticizer, and on cooling, they result in familiar plasticized PVC.

A typical formulation consists of resin, plasticizer, stabilizer, fillers, pigments, and viscosity modifiers. Unlike solid formulations, lubricants and polymeric modifiers are not added in pastes. The natures and roles of various ingredients are discussed below.

### 1.2.4.1 Resins

The requirements of paste polymers are rather conflicting. They should have the following:

*a.* Resistance at room temperature to the plasticizer for stability
*b.* Good affinity for plasticizer to rapidly dissolve in it at an appropriate temperature for proper gelation and fusion

Resins made by mass or suspension are porous granules and will absorb a high level of plasticizer to form a sticky agglomerate. They are not used for making plastisols. Paste resins are made by emulsion or microsuspension polymerization and are finished by spray-drying techniques. They have high sphericity and a fairly dense surface, so that penetration of plasticizer at room temperature is low. Particle size ranges from 0.1 $\mu$m to 3 $\mu$m. Particle size and particle size distribution profoundly influence the viscosity of the paste. Extender resins of particle size 80–140 $\mu$m having a nonabsorbent surface are generally added to lower the viscosity of the paste. Because emulsion-grade resins are expensive, incorporation of extender resins lowers the cost. Paste resins are usually homopolymers, but copolymers with vinyl acetate (3–10%) are used to lower the fusion temperature. Although paste resins are resistant to swelling or solution by plasticizer at ambient temperature, slow solvation still occurs, otherwise settling of the resin will take place. The slow solvation results in an increase in viscosity of the paste on storage, known as aging. Higher molecular weight resins give products with superior physical properties, but the fusion temperature is increased.

### 1.2.4.2 Plasticizers

The important factors in selecting a plasticizer are viscosity, viscosity stability, clarity, compatibility, permanence, and fusion temperature. A plasticizer should have adequate compatibility for fusion of the paste at an elevated temperature. Alkyl phthalates are the most common primary plasticizer.

### 1.2.4.3 Stabilizers

It is preferable to use liquid stabilizers for good dispersion. Care should be taken that the stabilizer is compatible with other liquids of the paste or else precipitation may occur. Ba-Zn and Ca-Zn combinations are generally used. Tin-based systems are used where clarity is desired.

### 1.2.4.4 Fillers

Various fillers like clay, calcium carbonate, barytes, etc., are added to the pastes. They affect the flow properties and aging characteristics of the paste. Fillers increase the paste viscosity due to an increase of the particulate phase and adsorption of plasticizer by the filler particles. The adsorption can be reduced by using coated fillers, such as with organic titanates.

### 1.2.4.5 Viscosity Depressants

These additives, which are surface-active agents, lower the viscosity and improve viscosity stability and air release properties. Polyethylene glycol derivatives are generally effective.

### 1.2.4.6 Thickeners

For certain applications, paste should have a high viscosity at low shear rates and a low viscosity at high shear rates. An example is in spray coating or dip coating where no sag/drip property is desired. Various thickening agents like fumed silica, special bentonites, and aluminium stearates are used. These form a gel structure, and the paste varies in consistency from butter to putty. They are also known as plastigels.

### 1.2.4.7 Blowing Agents

The addition of azo dicarbonamide, which decomposes to form nitrogen gas, is the common method used to produce expanded vinyl. The decomposition of the blowing agent should occur at or above the fusion temperature for the formation of a closed-cell structure. If the blowing agent decomposes completely before gelation, an open-cell structure will be formed. The cell size is determined by the rate of decomposition of the blowing agent and the melt viscosity of the fused composition. Low molecular weight polymers are used in foam formulation, so that the melt viscosity of the fused paste is low. Foam pastes are not commonly deaerated prior to use as the air present acts as nucleating agent for cell formation as the azo decomposes. Blow ratios are controlled by the quantity of azo compound. A high blow ratio will blow the foam apart during fusion.

### 1.2.4.8 Manufacture

The pastes are made in a simple paddle-type mixer that provides an intermediate level of shear. The temperature should not rise during mixing. The mixing is generally carried out in vacuum, or entrapped air is removed after mixing by subsequent deaeration. The presence of air may result in bubbles and loss of clarity of the end product.

### 1.2.4.9 Fusion

On heating, the liquid paste is converted into a solid. As the temperature of the paste rises, more plasticizer penetrates the polymer particles, causing them to swell. This process continues until at about 100°C, the liquid phase disappears completely with the formation of a gel (gelation temperature). On further heating, a solution of polymer and plasticizer is formed, with the formation of an homogenous plasticized PVC melt (fusion temperature). On cooling, solid plasticized PVC is obtained. The processes of gelation and fusion are the conversion of suspended polymer particles in a plasticizer to a solid containing dispersion of plasticizer in a continuous polymer matrix. This is, therefore, a phase inversion (Figure 1.5).

### 1.2.4.10 Organosols

Diluents are added to reduce the viscosity of plastisols, to make it suitable for spray, roller, brush, and other forms of coatings. The thinned plastisols are known as organosols. The diluents are nonsolvents of PVC, like toluene, xylene,

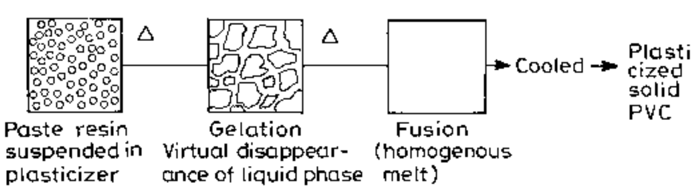


**Figure 1.5** Gelation and fusion processes.

naphtha, and mineral spirits. Addition of these diluents shifts the solubility parameter of the dispersing medium away from PVC, lowering the solvation and reducing the viscosity. As the diluent level increases, the viscosity passes through a minima and then increases with further dilution. This increase of viscosity is due to flocculation of the plastisol resin.

#### 1.2.4.11 Uses in Coating

Pastes are extensively used for flexible coatings applied by dipping, spraying, or the spreading process. The products are diverse, including upholstery, luggage fabric, wall coverings, floor coverings, tarpaulins, and shoe uppers.

### 1.2.5 COMPOUNDING OF PVC FOR SOLID COMPOSITIONS

The purpose of compounding is to blend the resin and additives into a homogeneous, well-dispersed form appropriate for further processing. PVC formulations are used in the industry in liquid phase, i.e., paste and solutions, or in solid form, as powder or pellets. Solid phase compounding can be broadly categorized into two types, melt compounding and dry blending.

#### 1.2.5.1 Melt Compounding

In this process, a premix is made in a ribbon or tumble blender. The premix is then fluxed and pelletized or may be directly sent to high shear mixers that break down the resin and simultaneously disperse and blend the additives with the fluxed resin. Two types of mixers are widely used: the batch-type mixers offer greater flexibility when frequent product and formulation changes are encountered and the continuous mixers are used when large volume and steady throughput is required. The batch-type mixers can be either a two roll mill or an internal mixer of the Banbury type, similar to those used for rubber compounding. Continuous mixers are single- or double-screw extruders.

#### 1.2.5.2 Dry Blending

Dry blending is a process of adding liquid and dry compounding ingredients into PVC to produce a granular, free-flowing powder. The resin is not fused during the compounding operation. The individual particles of the dry blend are much like the initial resin. Their size is, however, greater due to absorption of plasticizer and other additives. The resins used for commercially plasticized applications are suspension and mass polymerized homopolymer of PVC. The resins are porous and have high surface area for rapid absorption of plasticizer, etc. It is desirable to select a resin with a narrow particle size range. The penetration of plasticizer in a large particle size causes “fish eyes” in the processed product. Fine particles tend to float in the molten mass causing surface imperfections in the product.

The dry blends are produced in different mixing equipment. Mainly, two types of mixers are used: the steam jacketed ribbon blender or the high-intensity batch mixer. They are coupled to a cooling blender. In a ribbon blender, the resin and dry ingredients are added first and allowed to mix for a short time to break the agglomerates. The blender may be heated, if required, to increase the absorptivity of the resin for the plasticizer. The heated plasticizer mix containing other liquid additives is then sprayed onto the resin mix, and the blender is heated. The time and temperature of the mix is dependent on the formulation, but normally the temperature is between 100°C to 130°C, and the time is between 10–20 min. The powder is next discharged to a coupled cooling mixer. In a high-intensity mixer, the procedure of adding the ingredients is similar. In these mixers, heating is mainly due to the mechanical energy of the mixing process, i.e., shear and friction.

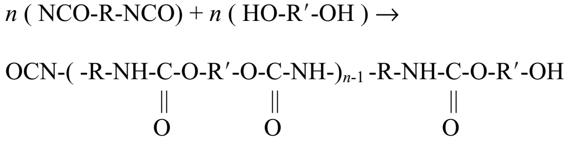
Sintered dry blends are partly fluxed pellets that are obtained by heating the dry blend to near its fusion point to sinter the particles into agglomerates. These can vary in size from coarse powder to regular pellets. These sintered blends are nondusting, easy to transport, more homogenous than dry blends, and have better processability. The production is usually done in a high-intensity mixer coupled with a cooler mixer. After the dry blend is formed, the temperature of the blender is increased until the particles agglomerate to the desired size. The blend is then discharged rapidly into the cooling blender, where it is rapidly cooled, and further agglomeration is prevented.

The investment in equipment for dry blending is substantially low, enabling processors to carry out their own blending.

## 1.3 POLYURETHANES

### 1.3.1 INTRODUCTION

Polyurethanes [12–15] are polyaddition products of di- or polyisocyanate with a di- or polyfunctional alcohol (polyol).



$$n\,(\mathrm{NCO\text{-}R\text{-}NCO}) + n\,(\mathrm{HO\text{-}R'\text{-}OH}) \rightarrow$$

$$\mathrm{OCN\text{-}(\text{-}R\text{-}NH\text{-}\underset{\underset{O}{\|}}{C}\text{-}O\text{-}R'\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}NH\text{-})_{\mathit{n}-1}\text{-}R\text{-}NH\text{-}\underset{\underset{O}{\|}}{C}\text{-}O\text{-}R'\text{-}OH}$$

Urethane (4)

If the functionalities of the reactants are three or more, branched or cross-linked polymers are formed. Variations in the R and R′ segments of the polyaddition reaction shown above permit preparation of polyurethane to meet specific needs. The extent of cross-linking, chain flexibility, and intermolecular forces can be varied almost independently. The range of polyurethane products is thus quite diverse and includes fibers, soft and hard elastomers, and flexible and rigid foams.

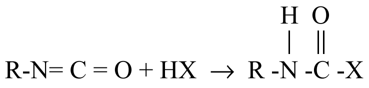
The two important building blocks are isocyanates and polyols. Chain extenders like short-chain diols or diamines and catalysts are frequently used in the synthesis of the polymer. A brief account of the chemistry of the raw materials and polyurethanes is being discussed to obtain a proper perspective.

## 1.3.2 BUILDING BLOCKS OF POLYURETHANE

### 1.3.2.1 The Isocyanates

#### *1.3.2.1.1 Basic Reactions of Isocyanates*

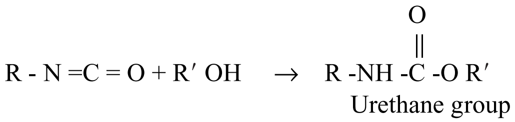
The isocyanate group is highly reactive. Its most important reaction is the nucleophilic addition reaction of compounds containing an active hydrogen atom. The general equation is given by



$$\text{R-N=C=O} + \text{HX} \rightarrow \text{R-}\overset{\overset{\text{H}}{|}}{\text{N}}\text{-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-X} \qquad (5)$$

Some important reactions are given below:

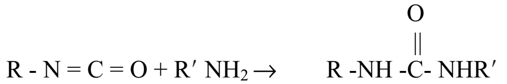
(1) Reactions with compound containing -OH groups



$$\text{R-N=C=O} + \text{R}'\text{OH} \rightarrow \underbrace{\text{R-NH-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-OR}'}_{\text{Urethane group}} \qquad (6)$$

The trivial name urethane, which is used for ethyl carbamate, is used as the generic name for all polyurethanes. Primary, secondary, and tertiary -OH show a decreasing order of reactivity.

(2) Reactions with compound containing -NH groups



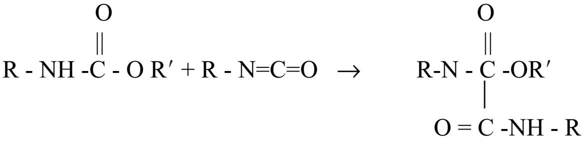
$$R-N=C=O+R'NH_2 \rightarrow R-NH-\overset{O}{\overset{\|}{C}}-NHR' \qquad (7)$$

Substituted urea

(7)

Primary and secondary amines react vigorously forming substituted urea. Primary amines react faster than the secondary amines. Ammonia and hydrazines react similarly.

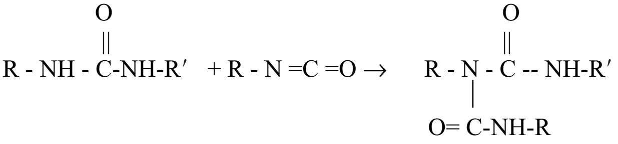
(3) The urethanes and ureas formed by the above reactions [Equations (6) and (7)] still possess acidic protons and react further with additional isocyanates to form allophanates [Equation (8)] and biurets [Equation (9)], respectively.



$$R-NH-\overset{O}{\overset{\|}{C}}-OR'+R-N=C=O \rightarrow R-N-\underset{\underset{O=C-NH-R}{|}}{\overset{O}{\overset{\|}{C}}}-OR'$$

Allophanate

(8)



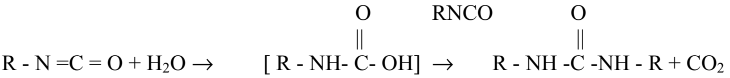
$$R-NH-\overset{O}{\overset{\|}{C}}-NH-R'+R-N=C=O \rightarrow R-\underset{\underset{O=C-NH-R}{|}}{N}-\overset{O}{\overset{\|}{C}}--NH-R'$$

Biuret

(9)

In the case of polyisocyanates, the above reactions [Equations (8) and (9)] lead to the formation of branching in the polymer.

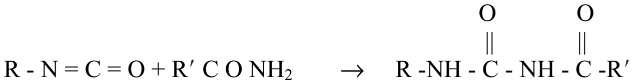
(4) Reaction with water: water reacts with isocyanate to form unstable carbamic acid that splits into carbon dioxide and the corresponding amine. The amine immediately reacts again with another molecule of isocyanate to form symmetrical urea. The carbon dioxide acts as a blowing agent in the production of foams.



$$R-N=C=O+H_2O \rightarrow [R-NH-\overset{O}{\overset{\|}{C}}-OH] \xrightarrow{RNCO} R-NH-\overset{O}{\overset{\|}{C}}-NH-R+CO_2$$

(10)

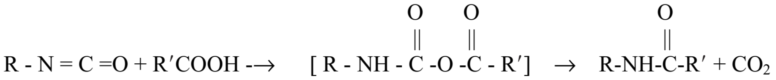
(5) Amides react to form acyl urea



$$R\text{-}N{=}C{=}O + R'CONH_2 \rightarrow R\text{-}NH\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NH\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}R'$$

Acyl urea (11)

(6) Carboxylic acids: substituted amides are formed with liberation of carbon dioxide

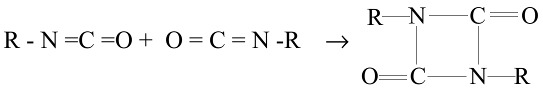


$$R\text{-}N{=}C{=}O + R'COOH \longrightarrow [R\text{-}NH\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}R'] \rightarrow R\text{-}NH\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}R' + CO_2$$

Substituted amide

(12)

(7) Self-addition reactions of isocyanate: highly reactive aryl isocyanates dimerize in the presence of catalysts to form uretidinediones. The formation of uretidinedione results in loss of reactivity of the isocyanate in storage. The uretidinedione formation is a means to block isocyanates and to make the isocyanate group available at elevated temperatures. Catalyzed by strong bases, isocyanates also undergo trimerization to form isocyanurate ring structure, which is very stable toward heat and most chemicals. In the case of polyisocyanate, highly branched polyisocyanurates are formed.



Uretidinedione (13)

### *1.3.2.1.2 Important Polyisocyanates and Their Synthesis*

The most important route for the synthesis of isocyanates is the phosgenation of primary amines.

$$R\text{-}NH_2 + COCl_2 \rightarrow R\text{-}N{=}C{=}O + 2\,HCl \qquad (14)$$

Toluene diisocyanate (TDI) is one of the most important diisocyanates. The synthetic steps are dinitration of toluene, reduction to the corresponding diamines, followed by phosgenation to yield TDI. It is used as a mixture of 2,4 and 2,6 isomers in the ratio of 80:20. The two isomers differ considerably in reactivity, so the actual ratio of the two components is quite important.

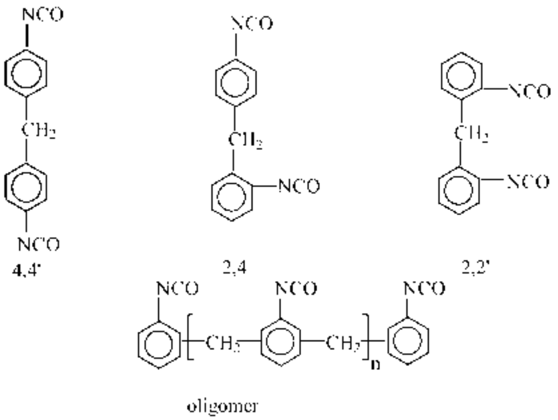


**Figure 1.6** Isomers of MDI.

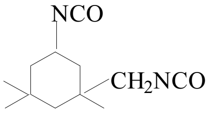
Another important aromatic diisocyanate is diphenyl methane diisocyanate (MDI). Condensation of aniline with formaldehyde leads to a mixture of 4,4′-, 2,2′- and 2,4′-diamino diphenyl methanes as well as polyamines. These on phosgenation form the corresponding isocyanates (Figure 1.6).

Other common aromatic isocyanates used are naphthalene 1,5-diisocyanate, xylelene diisocyanate XDI, *p*-phenylene diisocyanate PPDI, and 3,3′-tolidine diisocyanate TODI.

Aromatic isocyanates yield polyurethanes that turn yellow with exposure to light. Various aliphatic and cycloaliphatic diisocyanates are used in the industry to produce polyurethanes, which do not turn yellow upon light exposure. These are extensively used for coatings. The most important among the aliphatics is hexamethylene diisocyanate (HMDI) obtained by the reduction of adiponitrile and phosgenation of hexamethylene diamine. Among the cycloaliphatics, isophorone diisocyanate (IPDI) is the most common. Others are cyclohexyl diisocyanate (CHDI), 4,4′-dicyclohexyl methane diisocyanate ($H_{12}$MDI), and 2,2,4-trimethyl-1,6-hexamethylene diisocyanate (TMDI).

$OCN\text{-}(CH_2)_6\text{-}NCO$

HMDI



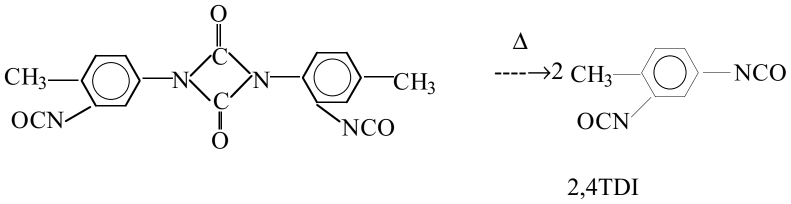
IPDI

### 1.3.2.1.3 Blocked Isocyanates

In blocked isocyanates, the isocyanate groups are reacted with compounds to form a thermally weak bond. On heating, the bond dissociates to regenerate the isocyanate group. The most common example is the reaction product of phenols to yield aryl urethanes that dissociate at ~150°C.

$$\text{R-N=C=O} + \text{ArOH} \rightarrow \text{R-NH-COOAr} \tag{15}$$

Similar adducts are formed by the reaction of isocyanates with diphenylamine, succinimide, acetoacetic ester, oximes, triazoles, caprolactams, etc. Dimers of isocyanates can also be considered as blocked isocyanate. The ring opening can be thermal or catalytic, without the liberation of any volatile blocking agent.



(16)

The blocked isocyanates are specifically used in one component systems for coatings adhesives. They are also used for preparing aqueous polyurethane dispersions. The blocked isocyanate group does not react with water. The isocyanate group is regenerated for reaction after drying and heating of the dispersion.

### 1.3.2.2 Polyols

Besides the polyisocyanates, the other important building blocks of polyurethanes are polyfunctional alcohols. Polyurethanes made from short-chain diols yield linear crystalline fiber-forming polymers, lower melting than the corresponding polyamides, that are of little commercial interest. However, reaction of isocyanates with polymeric glycols lead to the formation of polyurethanes of diverse physical and mechanical properties, suitable for a variety of applications. The molecular weight of the polyols ranges from 200 to 10,000. Two types of polyols are used in the synthesis of polyurethane: polyester polyols and polyether polyols containing at least two hydroxyl groups in a polyester or polyether chain.

#### *1.3.2.2.1 Polyester Polyols*

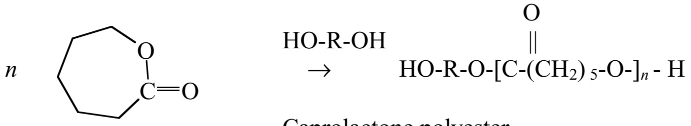
These are saturated dicarboxylic esters, the reaction product of dibasic acid and a diol. The commonly used acids are adipic, phthalic, sebacic, and dimer acids (dimerized lineoleic acid). The diols are ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, etc. For higher functionality, glycerol, trimethylol propane, penta erythritol, sorbitol, etc, are used where chain branching and higher cross-linking are required.

For preparation of the polyester, conventional methods of polyesterification are used. The molecular weight can be controlled by the molar ratio of the reactants and the reaction conditions, however, it is essential that the terminal groups be hydroxyl for reaction with the isocyanate. For this purpose, esterification is carried out with stoichiometric excess of the diol.

$$\text{H-[OR-OOCR}'\text{-CO---]}_n\text{-OROH}$$

Polyester polyol

Caprolactone polyester formed by polyaddition with a diol and $\varepsilon$-caprolactone in the presence of an initiator is also of commercial interest. The advantage of this reaction is that no water is formed.



$$\text{HO-R-O-[}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-(CH}_2)_5\text{-O-]}_n\text{- H}$$

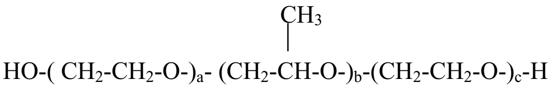
Caprolactone polyester (17)

### 1.3.2.2.2 Polyether Polyols

Polyether polyols are also known as polyalkylene glycols or polyalkylene oxides. The common polyether polyols are polypropylene glycols and polytetramethylene glycol (Figure 1.7).

Polypropylene glycol, the most commercially important polyol, is prepared by a base-catalyzed ring opening polyaddition reaction. However, polytetramethylene glycol is obtained by acid-catalyzed ring opening polyaddition.

Block copolymers of polyethylene and polypropylene glycols are commonly used in the industry. These are obtained by reacting ethylene oxide with polypropylene glycol or propylene oxide with polyethylene oxide in the presence of a base catalyst. This offers a means of adjusting the ratio of primary and secondary hydroxyl groups. The general formula of the block copolymer is given by the following:



$$\text{HO-( CH}_2\text{-CH}_2\text{-O-)}_a\text{- (CH}_2\text{-}\overset{\text{CH}_3}{\overset{|}{\text{CH}}}\text{-O-)}_b\text{-(CH}_2\text{-CH}_2\text{-O-)}_c\text{-H}$$

Copolymer of ethylene and propylene oxide

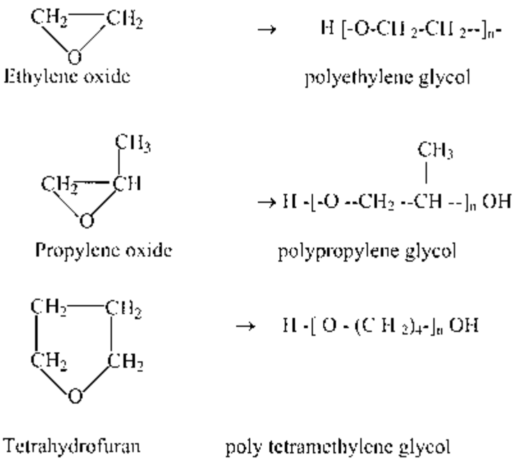


**Figure 1.7** Common polyether polyols.

### 1.3.2.3 Cross-linkers and Chain Extenders

These are low molecular weight polyfunctional alcohols and amines that act as chain extenders or cross-linkers by reaction with the -NCO group. The alcohols form urethane, and the amines form urea linkages. The difunctional compounds are essentially chain extenders, while the compounds with functionality greater than two are cross-linkers. The end properties of the polyurethanes are considerably influenced by these compounds, as they alter the hard to soft segments proportion of the polymer. Some important diol chain extenders are ethylene glycol, 1,4-butanediol, etc. Trifunctional alcohols like glycerol and trimethylol propane act as cross-linkers. Among the amines, derivatives of diamino phenyl methane and *m*-phenylene diamines are of commercial interest as chain extenders. The most common in this category is 3,3′dichloro 4,4′diamino diphenyl methane (MOCA).

### 1.3.2.4 Catalysts

The rate of the reactions of isocyanates can be greatly enhanced by using appropriate catalysts. The most important catalysts are the tertiary amines and organo tin compounds. The rate increase of urethane link formation by -NCO/OH reaction depends on the basicity and the structure of the amines. Some important amines are triethyl amine, triethylene diamine and peralkylated aliphatic polyamines. Prominent among the organo tin compounds are dibutyl tin dilaurate and tin dioctoate. They are readily soluble in the reaction mixture and have low volatility and little odor. Basicity favors formation of branching and cross-linking. Commercially, a mixture of amine and tin catalysts are used for synergistic effect.

### 1.3.3 METHOD OF PREPARATION OF POLYURETHANES

There are two methods of preparation of polyurethanes.

(1) *One-shot process:* in this process, the entire polymer formation takes place in one step by simultaneously mixing polyol, diisocyanate, chain extender, and catalyst. The reaction is very exothermic and requires similar reactivities of different hydroxy compounds with the isocyanate.

(2) *Prepolymer process:* this is a two-stage process. In the first stage, diisocyanate and polyol are reacted together to form an intermediate polymer of a molecular weight of about 20,000, which is called a prepolymer. Depending on the stoichiometry of the diisocyanate and polyol, the prepolymer can be NCO terminated or OH terminated. The NCO-terminated prepolymers are of great technical importance, as the NCO groups are available for reaction with compounds containing active hydrogen atoms. The prepolymer is then reacted with a chain extender to form the final high molecular weight polymer, either by a polyfunctional alcohol or amine (Figure 1.8).

### 1.3.4 STRUCTURE OF POLYURETHANES

Polyurethanes prepared from short-chain diols and diisocyanate have a large concentration of urethane linkage which results in a high degree of hydrogen bonding between the -NH and C=O groups of the chains. Consequently, these polymers are hard and have a low degree of solubility. On the other hand, the reaction product of long-chain polyols and diisocyanates results in polymers with a low concentration of urethane groups. The intermolecular forces are, therefore, mainly weak van der Waals forces, and the polyurethane is low in hardness and strength. Most polyurethanes are prepared from at least three basic starting materials, viz., (1) long-chain polyol, (2) diisocyanate, and (3) a chain extender. These linear chains of polyurethane elastomer show segmented structure (block copolymer), comprised of an alternate soft segment of the polyol with weak interchain interaction, present in coiled form, and a hard segment formed by reaction of diol/diamine and the diisocyanate (Figure 1.9). The hard segments have strong interchain H-bonding and dipolar interactions due to the presence of a large number of polar groups—urethanes and ureas.

The hard and soft segments are partly incompatible because of their difference in polarity; as such, they show two-phase morphology. The hard segments

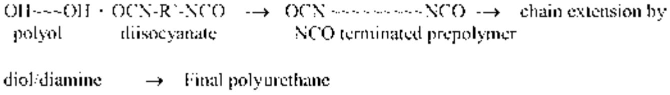


**Figure 1.8** Prepolymer process.

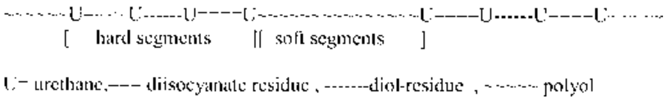


**Figure 1.9** Segmented polyurethane.

form discrete domains in a matrix of soft segments. The aggregated hard segments tie the polymeric chains at localized points, acting as cross-links and as reinforcing filler matrix in a soft segment matrix (Figure 1.10). The two-phase morphology is applicable to linear elastomers as well as to most of the cross-linked polyurethanes.

### 1.3.5 THERMOPLASTIC URETHANE ELASTOMERS [13,16]

TPUs are high molecular weight polymers obtained by the reaction of polyol, diisocyanate, and chain extender. These are fully reacted linear chains, segmented in structure with hetero-phase morphology as described in the previous section. If however, stoichiometric excess of isocyanate is taken, i.e., NCO/OH $>$ 1.0, the free NCO groups react with urethane groups forming allophanate branched or cross-linked structures.

The cross-links formed due to hard segment domains impart elasticity to the polymer, however, these are reversible to heat and solvation, permitting thermoforming and solution application of TPU. They can, therefore, be termed virtual cross-links. The soft matrix has $T_g$ lower than room temperature, and is amorphous in nature, but the hard segments are paracrystalline or crystalline.

The property of the elastomer is dependent on the type of polyol, molecular weight, and the ratio of hard to soft segments. The molecular weight of the polymer for optimum physical properties is between $\bar{M}_w$ 100,000–200,000. Polyethers generally give elastomers having a lower level of physical properties than the polyester polyols. The elastomer can be compounded in a plastic or rubber mill. Stabilizers, processing aids, and extenders are the additives used. They do not require any curing.

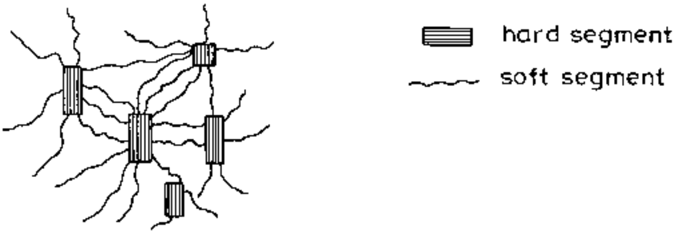


**Figure 1.10** Two-phase morphology of polyurethane.

### 1.3.6 POLYURETHANE COATINGS [12,14,17]

The conventional solution-based coatings are of two types, viz., one-component systems and two-component systems.

#### 1.3.6.1 One-Component System

These are two types of one-component systems: reactive and completely reacted systems.

a. *Reactive one-component systems:* these systems are low molecular weight prepolymers with terminal isocyanate groups. They are dissolved in solvents of low polarity. After coating, they are moisture cured. The water acts as a chain extender and cross-linking agent with the formation of urea and biuret linkages. The generation of carbon dioxide is sufficiently slow, so that slow diffusion of the gas from the film occurs without bubble formation. The rate of cure is dependent on the temperature of the cure and the humidity of the ambient. Use of blocked isocyanate prepolymers allows formulations of one-component systems that are stable at room temperature.
b. *Completely reacted one-component system:* this consists of totally reacted high molecular weight thermoplastic polyurethane elastomers. The PU is dissolved in a highly polar solvent like dimethyl formamide. These coatings dry physically.

#### 1.3.6.2 Two-Component System

In this type of coating system, isocyanate-terminated prepolymers or polyfunctional isocyanates are reacted with polyhydroxy compounds that may already be urethane modified. The polyisocyanate component, usually in the form of a solution, is mixed with the polyhydroxy component prior to coating. Curing of these coatings occurs due to the formation of urethane linkages. In addition, reaction with moisture also takes place. The properties of the resulting coatings depend on various factors, viz.,

(1) The polyol type and molecular weight
(2) The temperature of the reaction
(3) The concentration of polar groups, i.e., urethane and urea
(4) The cross-linking density

In the U.S., for PU-coated fabrics, TPU systems are preferred. By varying the polyol and NCO/OH ratio in the TPU manufacturing process, the same wide range of flexibility can be obtained as mentioned for the two-component systems. Proper choice of TPU adhesive is critical. It is common practice to add a polymeric isocyanate to the TPU adhesive layer to aid in adhesion to the base fabric. There is almost no transfer coating done in the U.S. today for wearing apparel. It is all done overseas. In the U.S., fabrics for tenting, recreational clothing, etc., are direct coated with TPU solvent system.

Solvent-free coating by TPU elastomers: these can be coated on the fabric by hot melt process of the solid polymer. The common method employed is the Zimmer coating method. The PU can also be extrusion fed to a Bema or a calender.

### 1.3.6.3 Additives

The additives used for urethane coatings are generally silica fillers to reduce gloss, UV absorbers, antioxidants, and flow improvers. The solvents used for coating should be free of moisture and reactive hydrogen to prevent reaction with free isocyanate in two-component systems. They are generally polar in nature, and care should be taken for their selection to ensure storage stability and blister-free film. Similarly, the pigment used should also be moisture free.

## 1.3.7 AQUEOUS DISPERSION OF POLYURETHANES [12,13,18–21]

In recent years, there has been a trend to use PU latices for coating for the following reasons.

- low emission of organic volatiles to meet emission control regulations
- lower toxicity and fire hazard
- economy of the solvent
- viscosity of latex independent of molecular weight

Chemically PU latices are polyurethane-urea elastomers dispersed in water. The starting materials are polyether/polyester polyol, diisocyanates, and polyfunctional amines-chain extenders. Isocyanates should have low reactivity to water, as the carbon dioxide produced leads to foaming. For chain extension purposes aliphatic or cycloaliphatic amines are preferred, because they react faster with the isocyanate group.

### 1.3.7.1 Emulsifiers

Hydrophobic polyurethane can be dispersed in water with a protective colloid. Alternately, hydrophilic groups can be incorporated in the polymer chain by internal emulsifiers that have the following advantages:

*a.* Dispersion does not require strong shear force

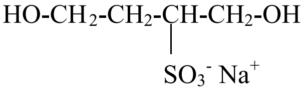
*b.* Leads to better dispersion stability

*c.* Finer particle size

These emulsifiers are of two types: ionic and nonionic. Ionic internal emulsifiers are anionic or cationic groups built in the polymer chain. Common ionic emulsifiers are as follows:

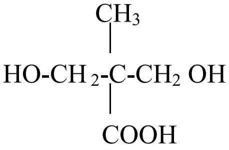
(1) Sulfonated diamine: $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}SO_3^-\ Na^+$

(2) Sulfonated diols:



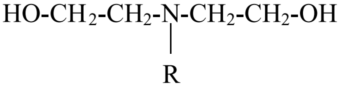
$$HO\text{-}CH_2\text{-}CH_2\text{-}\underset{\underset{SO_3^-\ Na^+}{|}}{C}H\text{-}CH_2\text{-}OH$$

(3) Dihydroxy carboxylic acids:



$$HO\text{-}CH_2\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{COOH}{|}}{C}}\text{-}CH_2\ OH$$

(4) A tertiary amine:



$$HO\text{-}CH_2\text{-}CH_2\text{-}\underset{\underset{R}{|}}{N}\text{-}CH_2\text{-}CH_2\text{-}OH$$

Polyurethane ionomers with built in ionic/hydrophilic groups are obtained by reacting NCO terminated prepolymer with ionic internal emulsifiers. Nonionic internal emulsifiers are polyether chains of polyethylene oxide, which are incorporated in the PU chain. These segments, being hydrophilic in nature, act as emulsifiers of the elastomer. The disadvantage of such emulsification is the water sensitivity of the dried film. Anionic dispersions are more widely used.

Typically, polymer particle size ranges from 0.01 to 0.1 micron. In the ionically stabilized dispersions, the ionic centers are located at the surface, and the hydrophobic chain segments are at the interior. They are sensitive to electrolytes. Nonionically stabilized dispersons are sensitive to heat, as polyethylene glycol polyol lose their hydrophilicity at higher temperatures.

### 1.3.7.2 Preparation of Dispersions

There are different methods for preparing dispersions [12,18], e.g., acetone process melt dispersion process, etc.

#### *1.3.7.2.1 Acetone Process*

A solution of high molecular weight polyurethane-urea ionomer is built up (after reaction and chain extension) in a hydrophilic solvent like acetone, dioxane, or tetrahydrofuran. The solution is then mixed into water. On removal of the solvent by distillation, an aqueous dispersion of the polymer is obtained

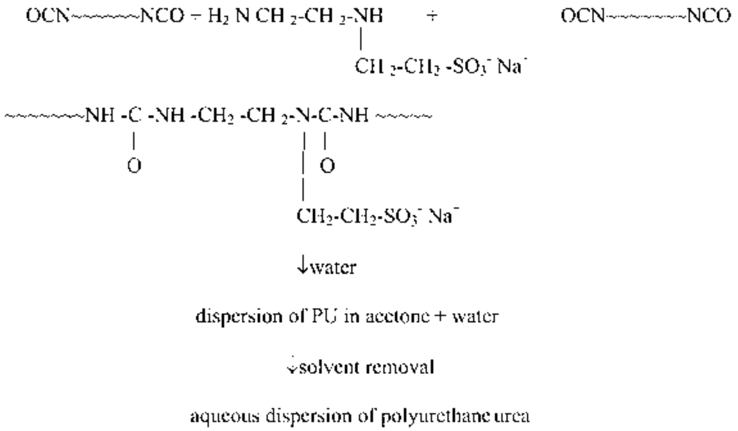


**Figure 1.11** Acetone process of PU dispersion.

by phase inversion of the emulsion originally formed with the water-organic solvent. A typical reaction sequence is shown above (Figure 1.11).

#### *1.3.7.2.2 Melt Dispersion Process*

A -NCO terminated prepolymer is reacted with ammonia or urea to form urea or biuret end groups. The reaction with urea is carried out at a high temperature ~130°C. The hot melt is poured into water at an elevated temperature to form a spontaneous dispersion. The end capping of -NCO groups renders them nonreactive to water. Chain extension is carried out by reaction of the oligomer with formaldehyde through the formation of methylol groups at the biuret functionality at a lower pH. The reaction sequence is shown in Figure 1.12.

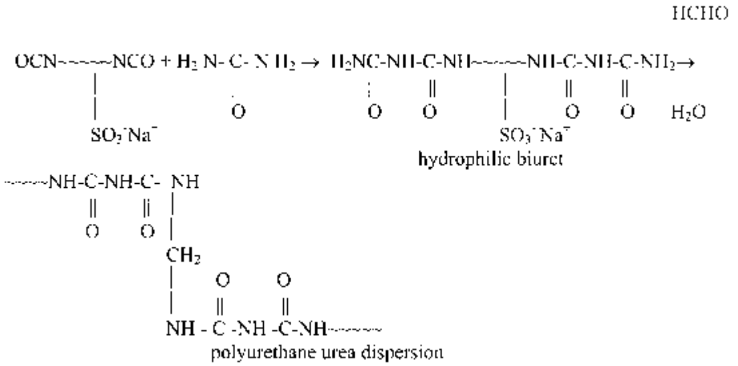


**Figure 1.12** Melt dispersion process.

### 1.3.7.3 Film Properties [18,21]

On drying of the dispersion on a substrate, the discrete polymer particles should fuse to form a continuous organic phase with entanglement of polymer chains. Poor fusion leads to poor gloss and poor physical properties of the film. If cross-links are present, the film-forming property decreases. An improvement can be made by adding high boiling, water miscible solvent in the latex. On evaporation of water, a solution of PU in the solvent is left behind. The solvent on evaporation gives a continuous film. A commonly used solvent is *N*-methyl pyrrolidone.

The main drawbacks of PU dispersion compared to two-component solution are the poor solvency and water resistance. Improvement in these properties can be obtained two ways:

(1) Grafting hydrophobic chains, usually acrylics, on the PU backbone
(2) Cross-linking of the polyurethane chains particularly those containing carboxylate ion, using polyfunctional aziridines

For coating purposes, certain additives are added in dispersion. These include thickening agents (e.g., polyacrylate resins), extenders, pigments, flame retardants, and external cross-linking, e.g., aziridines and melamine resins.

Great improvements have been made in water-based polyurethane chemistry; however, the wide flexibility of properties that can be obtained by solvent-based systems has not been demonstrated with the water-based coatings. To date, where strength, flexibility, toughness, etc., are the required physical properties of the end product, solvent-based systems are the coatings of choice.

## 1.3.8 FEATURES OF POLYURETHANE COATING

Polyurethane coating on textiles gives a wide range of properties to the fabric to meet diverse end uses like apparel, artificial leather, fuel and water storage tanks, inflatable rafts, containment liners, etc. This is because of a wide selection of different raw materials for their synthesis. For a breathable microporous coating, PU is the polymer of choice. PU-coated fabric offers advantages, which are given below, over other polymeric coatings [20,22,23].

- dry cleanability, as no plasticizers are used
- low temperature flexibility
- overall toughness—very high tensile, tear strength, and abrasion resistance requiring much less coating weight
- softer handle
- can be coated to give leather-like property and appearance

### 1.3.8.1 Structure-Property Relationship [13,24–26]

As has already been discussed, polyurethanes show two-phase morphology of soft and hard segments. The types and content of these segments profoundly influence the properties of the polyurethane. The soft segments obtained from the polyol determine the elastic and low temperature properties. Increasing the molecular weight of the polymer by increasing the soft segments results in lowering of the mechanical property, making the polymer softer and more extensible. Similarly, the presence of pendant side groups in the polyol also results in lowering of the physical properties. Increase in hard segment in the polymer increases its hardness, tensile modulus, and tear resistance. Diamine chain extenders form urea linkages, that enter into stronger hydrogen bonds and yield stiffer hard segments, thus, the PU formed has higher hardness and modulus than that obtained by diol extenders.

Polyester polyurethanes generally show higher modulus, tensile strength, hardness, and thermal oxidative stability than the polyether urethanes. This is because of the higher cohesive energy of the polyester chains. They also show better resistance to hydrocarbons, oils, and greases, but they show poorer hydrolytic stability due to the ester linkages. The hydrolytic stability of the polyester polyurethane can be increased by using sterically hindered glycols like neopentyl glycol and long-chain or aromatic diacid-like terephthalic acid.

Hydrolytic stability increases with hydrophobicity of the chain, thus, polyether polyurethanes have better hydrolytic stability. The thermal oxidative stability of polyether polyurethanes can be improved by adding antioxidants. Polyether urethanes also show better resistance to mildew attack.

The structure of isocyanates also influences the properties of the polyurethane. Symmetrical aromatic diisocyanates like naphthalene diisocyanate, diphenyl methane diisocyanate, and *p*-phenylene diisocyanate give a harder polymer with a higher modulus and tear strength compared to those obtained using less symmetrical ones such as 2,4- and 2,6-TDI. Polyurethanes of aliphatic and cycloaliphatic diisocyanates are less reactive and yield PU that have greater resistance to UV degradation, and thermal decomposition. They do not yellow on weathering but have a lower resistance to oxidation. The yellowing of polyurethanes containing aromatic diisocyanates is due to UV-induced oxidation that results in the formation of quinone imide [27] (Figure 1.13).

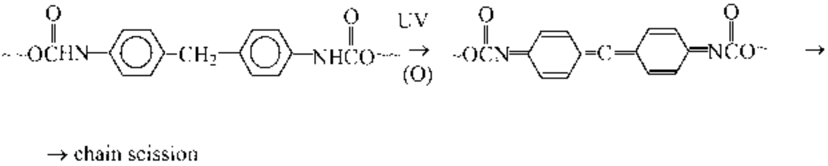
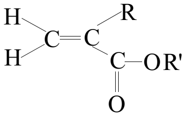


**Figure 1.13** UV-induced oxidation of MDI.

## 1.4 ACRYLIC POLYMERS

They are commonly known as acrylics. The monomers are esters of acrylic and methacrylic acid.



Acrylic ester

This is the general formula of acrylates (R = H for acrylates, R = $CH_3$ for methacrylates). Some common esters are methyl, ethyl, *n*-butyl, isobutyl, 2-ethyl hexyl, and octyl. The esters can contain functional groups such as hydroxyl, amino, and amido. The monomers can be multifunctional as well, such as trimethylol propane triacrylate or butylene glycol diacrylate. The nature of the R and R′ groups determines the properties of monomers and their polymers. Polymers of this class are noted for their outstanding clarity and stability of their properties upon aging under severe service conditions.

Polymerization of the monomers occurs by free radical polymerization using free radical initiators, such as azo compounds or peroxides. Acrylic polymers tend to be soft and tacky, while the methacrylate polymers are hard and brittle. A proper adjustment of the amount of each type of monomer yields polymers of desirable hardness or flexibility. A vast majority of commercially available acrylic polymers are copolymers of acrylic and methacrylic esters. The polymerization can occur by bulk, solution, emulsion, and suspension methods. The suspension-grade polymer is used for molding powders. The emulsion and solution grades are used for coatings and adhesives.

Acrylate emulsions are extensively used as thickeners and for coatings. Acrylics have exceptional resistance to UV light, heat, ozone, chemicals, water, stiffening on aging, and dry-cleaning solvents. As such, acrylics are used as backcoating materials in automotive upholstery fabric and carpets, window drapes, and pile fabrics used for outerwear.

## 1.5 ADHESIVE TREATMENT

### 1.5.1 MECHANISM OF ADHESION

The adhesion of the polymer to the textile substrate is an important aspect of coating technology, especially when the articles are put to dynamic use. The main mechanisms of adhesion are as follows [28]:

(1) Mechanical interlocking: this mechanism operates when the adhesive interlocks around the irregularities or pores of the substrate, forming a mechanical anchor. A rough surface has a higher bonding area.
(2) Adsorption: the attractive forces may be physical, i.e., physical adsorption by van der Waals forces, H-bonding, or chemical bonding (chemisorption).
(3) Diffusion: the adhesive macromolecules diffuse into the substrate, i.e., interpenetration occurs at the molecular level. It requires that the macromolecules of the adhesive and the adherend have sufficient chain mobility and are mutually compatible.

The irregularities on the textile substrate for mechanical interlocking of the elastomer are fiber ends, twists, crimps of the yarn, and interstices of the weave pattern. Cotton fabric and yarns made from staple fiber have a much higher surface area, and the fiber ends become embedded in the elastomeric matrix. In contrast, the synthetic fibers normally produced in continuous filament are smooth and, hence, have relatively poor adhesion.

All textiles of practical interest have surfaces that contain oriented dipoles that induce dipoles in the elastomer. As such, the contribution of dipole-induced interactions is quite prominent. Hydrogen bonding also provides significant contribution to many coatings. Chemical bonding due to formation of cross-links is also important, particularly when keying agents or special adhesive treaments are given to the fabric.

Textile substrates made from cotton or a high proportion of cotton do not generally require an adhesive treatment because the mechanical interlocking of the staple fiber ends into the elastomeric matrix imparts adequate adhesion. Rayon, nylon, and polyester used mainly in continuous filament forms require an adhesive pretreatment. The type of bonding systems in use are the resorcinol-formaldehyde-latex (RFL) dip systems, dry bonding systems and isocyanate bonding.

### 1.5.2 RESORCINOL-FORMALDEHYDE-LATEX SYSTEM [3,29,30]

This system is used for adhesive treatment of rayon and nylon. The latices used are generally of natural rubber, SBR, or vinyl pyridine copolymer (VP). A typical method of preparation consists of mixing resorcinol and formaldehyde in the molar ratio of 1:1.5 to 1:2.5 (in an alkaline medium resole process) in a rubber processer. The mixture is stored for about 6 hrs at room temperature. To this is then added appropriate latex or latex mixture. This mix is matured for 12–24 hrs prior to use. Many factors affect the performance of the RFL dip such as (1) the resorcinol-to-formaldehyde ratio (2) the pH and conditions of reactions, (3) the type of latex used, (4) the ratio of latex to resin, and (5) total solids, etc. A SBR-VP latex mixture is commonly used for rayon, and nylon. For standard tenacity rayon, the ratio of SBR to VP latex is about 80:20, but for higher tenacity yarns, a higher ratio (50%–80%) of VP latex is used. The solid content of the dip is adjusted to the type of fiber used, e.g., about 10–15 wt.% for rayon and about 20 wt.% for nylon. For nylon 6 and 66, better adhesion is achieved at 75% VP latex or higher.

The process of application consists of impregnating the fabric by passing through a bath of the dip. Excess dip is removed by squeezing through rollers. The water is then removed by drying at around 100–120°C. The treated fabric is then baked by heating at temperatures ranging from 140–160°C for a short period of time (1–2 mins). Total solid pickup is controlled mainly by solid content of the dip. The add-on required depends on the fiber. For rayon, the add-on ranges from 5–8 wt.%, for heavier nylon fabrics, an add-on of up to 15% may be required. In the case of nylon, curing is combined with heat setting at 170–200°C. The baking enhances adhesion due to increased condensation of the resin and creation of more reactive sites [31].

The RFL dip discussed above is adequate for olefin rubbers. For polymers like CR, NBR, PVC, IIR (butyl), and EPDM, the RFL dip has to be modified for better adhesion. With CR and NBR, replacement of latex of the RFL dip by 50–100% of the latex of the corresponding polymer gives satisfactory results. Latices of IIR and EPDM do not exist, although their emulsions are available that can be used to substitute the latex of RFL dip. However, the performance with emulsions is not satisfactory. For PVC, the latex has to be carefully selected, as all PVC latices do not form coherent film, and it may be desirable to incorporate an emulsion of the plasticizer in the dip for proper film formation.

Polyester fabric requires a two-stage dip. In stage one, the fabric is dipped into an adhesive consisting of water-miscible epoxy (derived from epichlorohydrin and glycerol) and a blocked isocyanate dispersion, to give a pickup of about 0.5%. The blocked isocyanate is activated at about 230°C. In stage two, the fabric is dipped in a standard RFL system. A two-stage dip is also used for aramid fabrics.

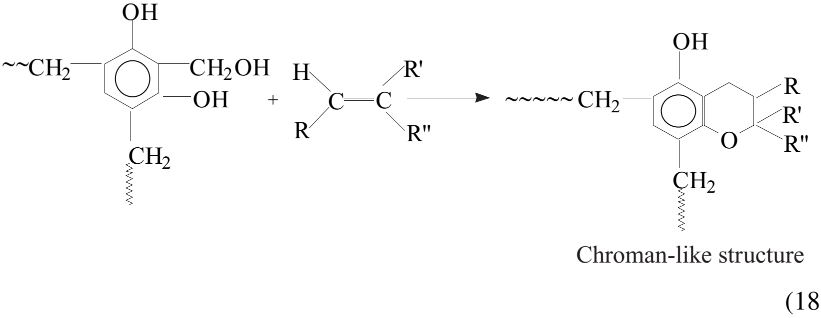
Estimation of add-on of RFL dip is critical for determining the adhesion level. The conventional ASTM method based on acid extraction of the coated material is time consuming. Faster results have been reported using near infrared (NIR) reflectance measurement [32].

### 1.5.3 DRY BONDING SYSTEM [3,30,33]

In this system, the adhesion promoting additives are added to the elastomer compound itself. Adequate bonding is achieved by coating the compound on untreated textile substrate. The important ingredients of the system are resorcinol, a formaldehyde donor-hexamethylene tetramine (HMT), and hydrated silica of fine particle size. The resorcinol formaldehyde resin formation takes place during the vulcanization process, which then migrates to the rubber-textile inerface, resulting in an efficient bond between the two surfaces. The role of silica is not fully clear. It probably retards the vulcanization process, allowing time for the formaldehyde donor to react with resorcinol and the resin to migrate to the interface for bond formation. The process is universally applicable to all types of rubber in combination with all types of textile materials. With polyester, however, hexamethoxymethyl melamine (HMMM) is used as a methylene donor instead of HMT, as the amine residue of HMT degrades the polyester by ammonolysis of the ester linkage. Because this system acts by migration of the resin components, a minimum thickness of the adhesive compound is required at the interface to prevent back migration of the adhesive components to the bulk. The normal amounts of resorcinol and HMT added are around 2.5 phr and 1.5 phr, respectively, however, the concentration is dependent on the formulation of the compound and the type of fabric. For dry bonding, the composition of the rubber compound should be carefully balanced. Nonsulfur curing systems lead to poorer adhesion. Use of ultraaccelerators is unfavorable because they often do not give sufficient time for the release of the required amount of formaldehyde for resin formation. On the other hand, too much delay in curing also leads to poor adhesion. Accelerators like *N*-cyclohexyl-2-benzothiazyl sulfonamide (CBS), used alone or in combination with basic secondary accelerators like *N,N*-diphenyl guanidine (DPG), give good adhesion.

### 1.5.4 MODE OF ACTION OF RFL DIP

The mechanism of action of the RFL system has been investigated. The RFL film forms a bond with the coated elastomer as well as the textile substrate. The dip film to elastomer bond occurs due to cross-linking of the rubber (latex) part of the film by migration of sulfur and curatives from the main elastomer. A minor contribution is due to the reaction of the resin part of the dip film with the active hydrogen atom of the main elastomer, forming a chroman-like structure, as given below [30] [Equation (18)]. Such a mechanism and formation of an interpenetrating network explains the adhesion of the dry bonding system.



Chroman-like structure

(18)

The adhesion of the textile substrate with the dip is believed to be due to its resin component. Various mechanisms are operative; they are mechanical interlocking, diffusion, and chemical bond formation. The methylol group of resins reacts with the hydroxyl groups of the cellulosics and amido group of nylon forming covalent bonds. This mechanism is applicable to the dry bonding system as well. In the case of polyester, the blocked isocyanate of the two-stage system forms a polyurethane with a solubility parameter similar to that of polyester, thus favoring adhesive bond by diffusion. The new surface is reactive toward the second-stage RFL dip [30].

### 1.5.5 ISOCYANATE BONDING SYSTEM

Polyisocyanates are used for binding elastomer and fabric. The isocyanate groups are highly reactive, and they bond elastomer and textile by reacting with their reactive groups. The common isocyanates used are 4,4,4-triphenyl methane triisocyanate (TTI), diphenyl methane diisocyanate (MDI), dianisidine diisocyanate (DADI), and polymethylene polyphenyl isocyanate (PAPI). There are two general procedures, viz., the solution process and the dough process [13]. In the solution process, a dilute solution of the polyisocyanate ($\sim$2% concentration) in toluene or methylene dichloride is applied on the fabric by spraying or dipping. After evaporation of the solvent, an elastomeric coating is applied in the usual manner. In the dough process, compounded rubber stock is dissolved in a suitable solvent like toluene, chlorobenzene, or gasoline, and is then mixed in a sigma mixer. To this solution (cement) is added isocyanate solution with agitation. This solution is then applied on the fabric using a conventional method to an add-on of about 10–15% and then dried. This coating acts as a primer for adhesion of the elastomeric coat to the fabric. The treated fabric in this case is better protected from moisture than in the solvent process. The composite-coated fabric can be cured in the usual manner. Isocyanate bonding agents give coated fabrics better softness and adhesion than that provided by the RFL system. The use of blocked isocyanate along with the rubber dough increases the pot life of the adhesive dip.

The adhesive treatments discussed in this section are primarily for elastomeric coatings on fabric. The formulation systems for other polymers and the factors responsible for proper adhesion have been discussed in Chapter 4.

## 1.6 RADIATION-CURED COATINGS

### 1.6.1 GENERAL FEATURES

Conventionally, curing of a polymer composition is done by thermal energy from sources such as electrical heaters, high pressure steam, hot air from electric heaters and infrared heaters. Curing by heat generated by a microwave is also being used for continuous vulcanization of rubber compounds. Radiation curing, i.e., curing by ultraviolet and electron beam radiation, does not involve heating, instead ions or free radicals are generated and the macroradicals so generated couple together to produce a three-dimensional network. In both UV/E beam, the formulation used for coating consists of an oligomer, a reactive monomer, and in the case of UV curing, a photoinitiator. Radiation-cured coatings have several advantages [34–36].

- fast curing speeds
- high solid content—usually 100% solids
- compact curing lines and decreased floor space
- low capital investment
- ability to cure heat-sensitive substrates
- wide variety of formulations
- reduced pollution
- lower energy consumption

### 1.6.2 CHEMISTRY

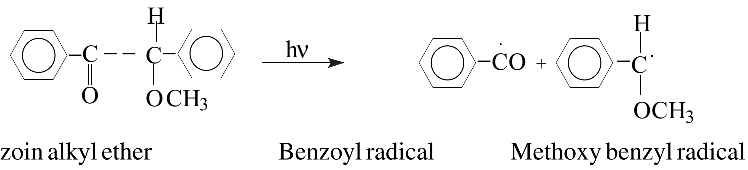
The chemistry discussed here is for ultraviolet radiation technology. In a general sense, the same formulations are used for both UV and E beam, except that in the case of UV curing, a photoinitiator is required to initiate free radical formation. The formulation of UV curing consists of the following [35–37]:

(1) A monomer and/or an oligomer bearing multifunctional unsaturated groups
(2) A photoinitiator that must effectively absorb incident UV light and produce initiating species with high efficiency

#### 1.6.2.1 Photoinitiators

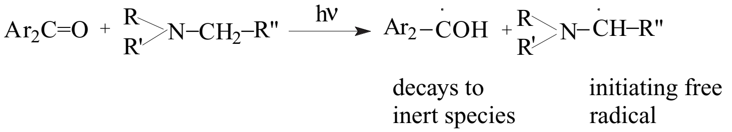
The different photoinitiators can be classified into three major categories:

(1) Free radical formation by homolytic cleavage: Benzoin alkyl ethers, benzil ketals, and acetophenone derivatives belong to this class. Here, the photoinitiator undergoes fragmentation when exposed to UV light. The benzoyl radical is the major initiating species in the cleavage of benzoin alkyl ether. Cleavage of benzoin methyl ether is shown in Equation (19).



(19)

(2) Radical generation by electron transfer: This mechanism involves photolytic excitation of the photoinitiator followed by electron transfer to a hydrogen atom donor, a tertiary amine [Equation (20)].



$$Ar_2C{=}O + \overset{R}{\underset{R'}{>}}N{-}CH_2{-}R'' \xrightarrow{h\nu} Ar_2{-}\dot{C}OH + \overset{R}{\underset{R'}{>}}N{-}\dot{C}H{-}R''$$

(20)

Typical photoinitiators in this category are 2,2-diethoxyacetophenone, 2,2-dimethoxy-2-phenyl acetophenone, etc.

(3) Cationic type: Aryl diazonium salts $PhN_2^+X^-$ undergo fast fragmentation under UV radiation with the formation of free Lewis acids, which are known for cationic cure of epoxides [Equation (21)]

$$PhN_2{}^+BF_4{}^- \overset{h\nu}{\rightarrow} PhF + N_2 + BF_3 \qquad (21)$$

### 1.6.2.2 Polymer Systems

One of the early UV curable systems was based on unsaturated polyester and styrene. The unsaturation located in the polymer chain undergoes direct addition copolymerization with the vinyl group of the monomer leading to a cross-linked network (Figure 1.14).

Multifunctional acrylates are the most widely used systems. The oligomer is usually a urethane or epoxy chain end capped on both sides by acrylate groups. The molecular weight ranges from 500–3000. Reactive diluents are added to lower the viscosity of the oligomers and to increase the cure rate. The reactive diluents are generally mono- or multifunctional acrylate compounds with a molecular weight less than 500. A reaction sequence is given below (Figure 1.15).

Cationic polymerization of epoxides is another method used. As discussed earlier, Lewis acids promote ring opening polymerization of epoxides, lactones, or acetals.

The free-radical-induced polymerization is inhibited by oxygen. Several methods have been developed to reduce the undesirable effects of oxygen.

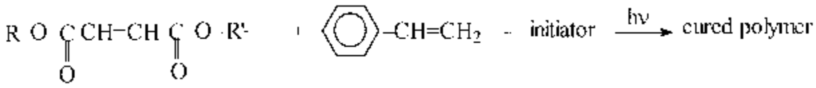


**Figure 1.14** Unsaturated polyester system.

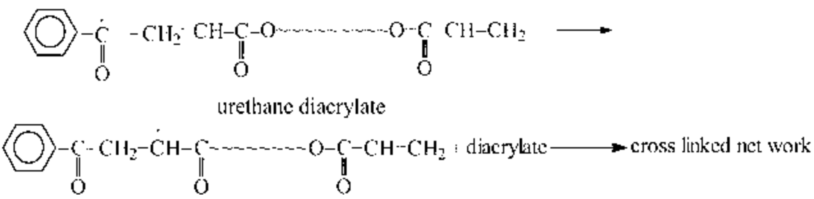


**Figure 1.15** Cross linked acrylate system.

Some of these are as follows:

- increase of UV lamp intensity
- optimization of the photoinitiator system
- curing in an inert atmosphere
- addition of oxygen scavengers

### 1.6.3 EQUIPMENT

(1) Ultraviolet light: different types of UV curing technologies are known. They are medium pressure mercury vapor lamp, electroless vapor lamps, and pulsed xenon lamps.

(2) Electron beam: the source of electrons is a tungsten filament that is inside a vacuum tube. The electrons are accelerated by the application of high voltage, 150,000 to 300,000 V. The accelerated electrons pass through a metallic foil window and are directed on the polymer meant for curing. X-rays are generated along with the electrons; therefore, it is necessary to shield the entire housing of the EB equipment. The energy received by this formulation is known as a dose and is termed megarad (1 Mrad = 10 joules).

### 1.6.4 APPLICATIONS IN TEXTILE COATING

Radiation cure has been in use in graphic arts, inks, printing, laminating, packaging, and in the electronic industry [36–38]. Motivated by the significant advantages of radiation-cured coatings over the conventional solvent-based thermal cure systems, Walsh and coworkers carried out an extensive study of radiation-cured coatings for textiles for different end uses. The work has been reported in a series of publications [39–43]. One application investigated was the backcoating of upholstery fabric [39], usually done by a thin latex coating, to stabilize the fabric against distortion and yarn raveling. A comparative study was done on nylon-viscose upholstery fabric. The latex coating was carried out by spraying and thermal curing, while the UV coating formulation was transfer coated on the fabric and cured by UV radiation. The flexural rigidity and yarn raveling tests showed that UV-cured samples were comparable to the latex-coated samples. A cost analysis showed that UV curing was only economical at low weight add-on ($\sim$2%). Studies were also conducted to achieve thicker coatings for synthetic leather applications, by radiation cure process, in lieu of the conventional solution-based polyurethane coating [40]. A suitable EB cure formulation consisting of acrylated urethane oligomer and acrylate monomer was coated on woven and knitted textile substrates by transfer coating and cured by electron beam (5 Mrads). The transfer coating was done by different ways.

None of the coated specimens, however, passed the flex fatigue test required for apparel fabric. This is largely due to the high degree of cross-linking in the cured film. A novel application studied by the authors was the simultaneous coating on both sides of nonwoven fabric by EB cure, in order to improve the durability and aesthetics of the coated fabric [41]. Simultaneous coating on both sides of the fabric is not possible in conventional solution-based processes. Essentially, the coating formulation was cast on two release papers and transfer coated on nonwoven substrate on both sides. This sandwich construction was then cured by electron beam.

Walsh et al., [42,43] continued their studies on the mechanical properties of EB-cured films using polyester acrylate urethane oligomers of different molecular weights and different reactive monomers with a view to developing suitable coatings for textiles. It was found, that higher molecular weight of the oligomer lowers the modulus of the film, the $T_g$, and the breaking strength. Addition of a chain transfer agent improved toughness as well as extensibility. Studies have also been carried out at TNO laboratory Holland [37,44]. They have carried out studies on UV curable coatings and the development of UV curable binders for pigment printing. Pigments have to be carefully selected so that photoinitiators and the pigment have different absorption characteristics, otherwise, insufficient curing occurs and bonding is poor.

The use of radiation cure for textiles has not yet become popular, because few systems can meet the requirements of textile coating, i.e., flexibility, strength of the film, bonding, and chemical resistance [37].

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## CHAPTER 2

# Textile Substrate for Coated Fabric[1]

## 2.1 MATERIALS AND TRENDS

A wide range of textile materials is used as substrates for coated fabrics. These may be woven, knitted, or nonwoven materials. The importance of textile materials can be gauged from the use of several billion square meters of fabric every year.

The types of fiber commonly used in coating are cotton, rayon, nylon, polyester, and blends of polyester with cotton or rayon, depending on the end use requirements. Polyester is the most popular in staple form for nonwoven material and in spun form for woven material. Polypropylene is emerging as the fiber of choice because of its low specific gravity, strength properties, chemically inert nature, and low cost. However, its poor dyeability, adhesion, and thermal stability are disadvantages that need to be overcome. High performance fibers like Kevlar®, Nomex®, PBI, etc., are used in specialized applications.

In woven form, plain, basket, twill, and sateen constructions are generally used. Among the knitted constructions, circular knits are used as a substrate for upholstery fabric. Warp knit fabrics, particularly weft inserted warp knits (WIWK), are preferred for making coated fabrics for special applications. Nonwoven fabrics, produced by different techniques, find use in sanitary and medical products, apparel, artificial leather, dot-coated fabrics for fusible interlinings, etc.

The emerging trends in the use of textiles can be summarized as follows [1]:

(1) Development of polyester fiber with lower elongation or higher modulus, higher adhesion, and microdenier filament for greater cloth cover/surface area
(2) Greater use of polypropylene

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[1] This chapter was contributed by N. Kasturia, R. Indushekhar, and M. S. Subhalakshmi, DMSRDE, Kanpur, India.

(3) Use of longer roll length and wider fabric to lower the cost

(4) More use of textured, Dref, and core spun yarns for improved adhesion

(5) Greater use of nonwoven and WIWK

The choice of proper fabric for coating is as important as the selection of the polymer, because it offers the primary physical property to the end product. For proper selection of fabric, the following aspects need to be considered:

- strength and modulus
- creep behavior
- resistance to acids and chemicals
- adhesion requirement
- resistance to microbiological attack
- environment of use
- durability
- dimensional stability
- cost

The following characteristics should be considered when designing a textile substrate to meet specific end use requirements:

(1) Fiber type and form such as staple, filament, etc.

(2) Yarn type and construction

(3) Fabric form, i.e., woven, nonwoven, and knitted and their construction

## 2.2 TEXTILE FIBERS

The textile fabric/substrate used for coating is made of textile fibers. There are two main types of fibers: natural fibers and man-made or synthetic fibers. The natural fibers may be of vegetable origin, such as cotton, kapok, flax, coir, sisal, etc.; of animal origin such as wool, silk, etc.; and of mineral origin, such as asbestos. The vegetable fibers are cellulosic in nature, the animal fibers are proteins, and asbestos is a silicate. The organic man-made fibers are essentially of two types: derived from cellulose, such as rayon and acetate, and synthetic polymers, such as nylon, polyester, acrylics, polypropylene, etc. Metallic fibers and glass fibers are inorganic man-made fibers. The properties of some important fibers used in the coating industry are discussed in this section. The physical and chemical properties of the fibers have been summarized in Tables 2.1 and 2.2, respectively.

### 2.2.1 COTTON

It is known as the king of fibers. Cotton is a cellulosic (~94% cellulose) staple fiber. The fiber length varies from 10–65 mm, and fiber diameter ranges

TABLE 2.1. Important Physical Properties of Fibers.

| Fibers | Cotton | Rayon | | Nylon | | Polyester | | Polypropylene | | | Aramid (Nomex®) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Properties | | Viscose | Acetate | Normal apparel grade | Industrial grade | Normal Staple Fiber | High tenacity fiber | Multifilament fiber | Staple fiber | High tenacity fiber | |
| Specific gravity | 1.52–1.55 | 1.52 | 1.32 | 1.14 | 1.14 | 1.36 | 1.36 | 0.90 | 0.90 | 0.90 | 1.38 |
| Tensile strength g/d | 3–5 | 2.6 | 1.4 | 4.1–5.5 | 6.3–8.18 | 3.5 | 9.5 | 5–7 | 4–6 | 5.5–8.5 | 5.3 |
| Elongation at break % | 4–13 | 10–30 | 25–50 | 26–32 | 14–22 | 10–40 | — | 15–35 | 20–35 | 15–25 | 22 |
| Moisture regain % at 21°C, 65% RH | 8.5 | ≅13 | 6.3–6.5 | 4 | 4 | 0.4 | 0.4 | negligible | negligible | negligible | 5–5.2 |
| Effect of heat | | | | | | | | | | | |
| (a) Resistant temperature | 150°C | 150°C | | 180°C | | 180°C | | — | | | 370°C |
| (b) Decomposition temperature | 230°C | 210°C | | — | | — | | — | | | ~500°C |
| (c) Melting temperature | Decomposes | Decomposes | | 250°C (Nylon 66)<br>215°C (Nylon 6) | | 250°C | | 160–175°C | | | Decomposes |

TABLE 2.2. Important Chemical Properties of Fibers.

| Fibers | Cotton | Rayon | Nylon | Polyester | Polypropylene | Aramid (Nomex®) |
|---|---|---|---|---|---|---|
| Properties | | | | | | |
| Effect of sunlight and atmosphere | Loss of tensile strength and discoloration of fibers occur | Loss of tensile strength | Appreciable degradation by sunlight | Low degradation in shade. Direct sunlight weakens fibers | Rapid degradation to sunlight and weathering. | Resistance to aging is excellent |
| Effect of microorganism | Mildew, microorganisms degrade the fiber | More resistant than cotton | Resistant | Resistant | Resistant | Resistant |
| Effect of acids | Deteriorates the fiber. Mineral acids degrade more readily than organic acids | Same as cotton | Affected by concentrated mineral and organic acids | Resistant to most mineral acids. Concentrated sulfuric acid decomposes fiber | Excellent resistance to acids | Not significantly affected, but is attacked by boiling sulfuric acid |
| Effect of alkalis | Resistant at room temperature but swelling occurs | Same as cotton | Virtually no effect | Resistant to alkali at room temperature but hydrolytic degradation occurs at boiling temperature | Resistant to alkalis | Resistant to alkalis |
| Effect of solvents/ oxidizing agents | Resistant to common hydrocarbon solvents. Oxidizing agents convert it to oxycellulose | Same as cotton | Benzene, chloroform, acetone, and ether do not affect, but it dissolves in phenols and strong acids | Resistant to hydrocarbon solvents. Soluble in m-cresol, o-chlorophenol at high temperature | Insoluble in organic solvents at room temperature. Dissolves in hot decalin, tetralin. Attacked by oxidizing agents | Resistant to most organic solvents |

from 11–22 $\mu$m, respectively. The fiber has good strength due to the large number of interchain hydrogen bonds present in the polymer chain. Cotton is a natural fiber with wide variation in properties. This variation is caused by differences in climatic conditions in the regions where the cotton is grown. A good quality cotton fiber is characterized by its finer fiber diameter and longer staple length. The important commercial varieties are (1) Sea Island, (2) Egyptian, (3) American upland, and (4) Indian cotton. Sea Island and Egyptian cotton have higher staple length and produce finer quality yarns. Indian cotton has shorter fiber length and produces coarser yarns. American upland cotton lies between these two categories for quality and fiber length.

Cotton has moderate mechanical strength when dry but good wet strength. The resiliency of the fiber is low, therefore, cotton fabrics wrinkle easily. Due to high moisture absorption of the fiber, cotton fabrics are comfortable as summer wear. Cotton is extensively used for apparel fabrics as well as industrial textiles like canvas, ducks, etc. The fabric has excellent adhesion to coated/laminated polymeric film.

### 2.2.2 RAYON

Rayons are man-made fibers derived from cellulose. Viscose rayon is regenerated cellulose, while acetate rayon is obtained by acetylation of cellulose. Both the fibers are characterized by high luster and are considered as artificial silk. Viscose is obtained by treating wood pulp with caustic soda solution to form soda cellulose. It is then treated with carbon disulfide to form cellulose xanthate solution. The alkaline cellulose-xanthate, is ripened, and on achieving the required viscosity, the solution is spun into a coagulating bath of dilute (10%) sulfuric acid. The viscose filament gets precipitated there. For making acetate rayon, wood pulp or cotton linters are treated with a solution of acetic anhydride in glacial acetic acid to form secondary cellulose acetate, which has fiber-forming properties. The secondary cellulose acetate is made into a dope with acetone. The dope is forced through holes of a spinnerette, and the filament is solidified by evaporation of acetone in hot air.

Like cotton, rayons are cellulosic in nature, as such, their chemical and physical properties are similar to those of cotton. It is used in blends with polyester for apparel fabrics, household textiles like furnishings and carpets, and in medical fabrics.

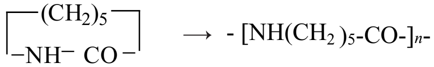
### 2.2.3 NYLONS

Nylon is the common name of linear aliphatic polyamides. The most important fibers in this class are nylon 66 and nylon 6. Nylon 66 is polyhexamethylene adipamide, a condensation polymer of hexamethylene diamine and adipic acid. The suffix 66 stands for the number of carbon atoms in the monomers.

Nylon 6 is polycaprolactamide, the monomer being ε-caprolactam. The reaction sequences are given below.

$$n\mathrm{H_2N(CH_2)_6NH_2} + n\mathrm{HOOC(CH_2)_4COOH} \longrightarrow \mathrm{-[NH(CH_2)_6\text{-}NH\text{-}CO\text{-}(CH_2)_4\text{-}CO]}_n\text{-}$$

Hexamethylene diamine Adipic acid Nylon 66



$\mathrm{(CH_2)_5}$, $\mathrm{-NH-\ CO-} \longrightarrow \mathrm{-\ [NH(CH_2)_5\text{-}CO\text{-}]}_n\text{-}$

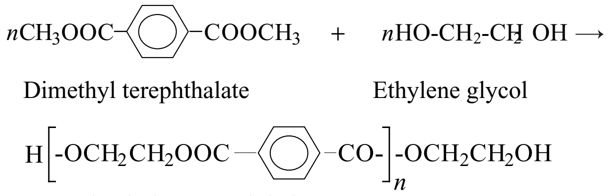
ε-Caprolactam Nylon 6

Nylon is a group of synthetic super polymers, with much higher strength and elongation than cellulosic fibers. It is available as regular translucent fine filament and can be converted into staple fibers.

Being a thermoplastic material, nylon fabric undergoes thermal shrinkage, and besides, it generates static electricity on friction. Special precautions therefore have to be taken while processing nylon fibers. Nylon fabrics are widely used for carpets, upholstery, and apparel. The high strength, elasticity, and abrasion resistance enables nylon to be used for a variety of industrial end uses such as filter fabrics, nets, webbings, cordages, parachutes, ropes, ballistic fabrics, etc.

### 2.2.4 POLYESTER

Polyester refers to a class of polymers containing a number of repeat ester groups in the polymeric chain. Commercially available polyester fiber is polyethylene terephthalate. It is known in different countries by different brand names. In the U.K., it is known as Terylene, and in the U.S., it is known as Dacron. The fiber is available in filament as well as in staple fiber form. A number of other polyesters have been converted into fibers, but they have not been exploited commercially.



Dimethyl terephthalate Ethylene glycol

Polyethylene terephthalate

Like nylon, polyester fabrics also generate static electricity and undergo thermal shrinkage. Fabrics show poor adhesion to the coated polymeric film.

The major use of polyester and its blends with cotton, rayon, and wool are in apparel fabrics, household fabrics, and industrial textiles.

### 2.2.5 POLYPROPYLENE FIBER

Polypropylene is a hydrocarbon fiber, the properties are dependent on the microstructure of the fiber. From the textile point of view, only isotactic polypropylene can be fibrillated, and the isotacticity index should be higher than 90%. The average molecular weight of polypropylene fiber ranges from 100,000–300,000. Polypropylene fibers are produced in different forms like staple, monofilament, and multifilament.

Due to its light weight, negligible water absorption, and high abrasion resistance, polypropylene is widely used for making ropes, fishing nets, tufted carpets, etc.

### 2.2.6 ARAMIDS

These are aromatic polyamides that are closely related to nylons. In aramids, the aliphatic carbon chain is replaced by aromatic groups, bringing about considerable change in the properties of the resultant fiber. The first fiber introduced in this class by Dupont U.S.A. was Nomex®, which is chemically poly-*m*-phenylene isophthalamide, a condensation product of m-phenylene diamine and isophthalic acid. Nomex® is flame resistant and is widely used for fireproof clothing. The *p* isomer, viz., polyparaphenylene terephthalamide (PPT) is known as Kevlar® fiber which possesses ultrahigh strength and modulus. The properties of Nomex® are given in Tables 2.1 and 2.2.

Aramids are high strength and high modulus fibers. They are mainly used in composite reinforcement for ballistic protection, ropes, cables, and for fire-resistant clothing.

## 2.3 SPINNING

Spinning refers to the process of conversion of small fibers into yarns, or in case of synthetic fibers, spinning refers to the processes that convert polymers into filaments. Most of the natural fibers like cotton, wool, etc., are available only as staple fibers having different fiber lengths. Spinning of natural fibers is divided into the following systems depending upon the fiber lengths:

*a.* Short staple spinning system or cotton spinning system
*b.* Long staple spinning system or wool spinning system

Synthetic filaments, when converted to staple fibers, are spun by a process similar to that of cotton or wool.

### 2.3.1 COTTON SPINNING SYSTEM

Cotton, which is a vegetable fiber, undergoes a sequence of processes before being spun into yarn. This sequence includes ginning, opening and cleaning (blow room), carding, lap formation (sliver and ribbon lap), combing (optional), drawing, roving, and, finally, spinning. The flowchart (Figure 2.1) gives an overview of the sequential operations involved in cotton spinning.

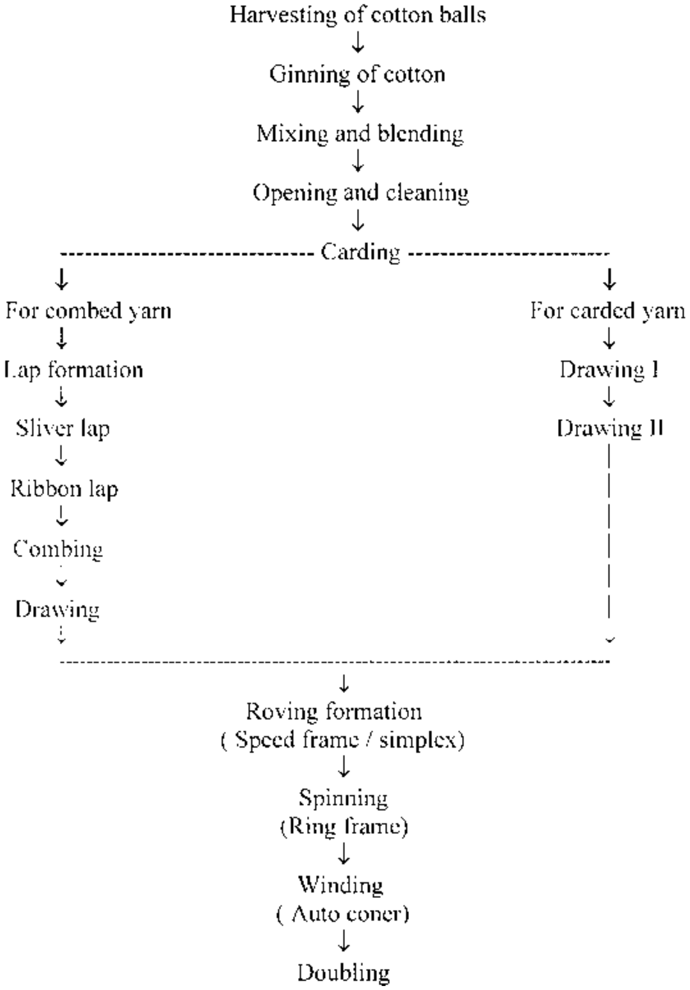


**Figure 2.1** Spinning of cotton.

#### 2.3.1.1 Ginning

Ginning is the starting process to which cotton is subjected on its way from the field to the textile mill before it is spun into yarn. Ginning is the process of separating cottonseed from the fiber. During this process, foreign matter like leaf bits, stalks, hulls, etc., are removed. Care is taken to preserve the quality of fiber, particularly the fiber length. The cotton fibers removed from the seed are compressed into large bales and sent to mills for processing.

#### 2.3.1.2 Blow Room

In a textile mill, this is the first preparatory process. In the blow room, cotton bales are subjected to mixing, opening, and cleaning processes. The cotton bales from different farm fields are fed into a mixing bale opener (MBO). Mixing of different varieties of cotton is done to improve the uniformity, thereby improving the quality and minimizing the raw material cost. In some cases, cotton fibers are blended with other fibers to manufacture special yarns with desired properties. The MBO opens the compressed cotton and mixes the different varieties of cotton by rotating cylindrical beaters. Thus, the closely packed fibers are loosened, and during this process, dirt and other heavy impurities are separated from the fiber, either by gravity or by centrifugal force. The loosened fibers are converted into a lap of smaller tufts called flocks.

#### 2.3.1.3 Carding

The fibers are received at the carding machines either in lap form or as flocks. Lap and flock feeding have their own advantages and disadvantages. However, most modern mills have flock feeding systems. The main objectives of the carding process are to continue the cleaning process, removing some amount of short fibers, fiber individualization, partially aligning the fibers in the direction of the fiber axis, and disentangling neps (small entangled collection of immature fibers). In the carding zone, the fibers pass over the main cylinder. The main cylinder is made of cast iron and is 120–130 cm diameter. This cylinder is covered with fine sawtooth wires. On the top of the cylinder, there are a number of moving flats that are joined to form an endless, circulating band. The flats are cast iron bars with one side clamped with a clothing strip, which is rubberized fabric fixed with angled steel wires. These flats and main cylinder together form the main carding zone. The carding action involves the transfer of fibers from the cylinder surface to the flat surface and vice versa. During the multiple transfer, the wire points in the cylinder try to retain the fiber, and at the same time, the wire points in flats try to pluck the fiber. But, most of the fibers are retained in the cylinder wire points, as the flats rotate at a much slower speed than the main cylinder. This process leads to fiber individualization.

### 2.3.1.4 Lap Formation

The carding process opens up the collected mass of fibers so that the fibers become individual. However, the fibers in the card sliver are not completely aligned or oriented in the fiber axis. Some fibers lie haphazardly in the sliver. Thus, the card sliver is given a minimum of two drafting processes before it goes to the next machine. In this process, the sliver is passed between sets of rollers that are running at different speeds, each succeeding pair rotating faster than the previous so that the fibers are pulled in a lengthwise direction. These two drafting operations are achieved by the sliver lap and ribbon lap machines. To improve the uniformity of the sliver, it is subjected to the process called doubling: Doubling is the process of combining a number of slivers. By this process, the thin and thick places present in the sliver are evened out. In the sliver lap machine, 16–20 card slivers are creeled and passed through the feed table to three pairs of drafting rollers for the drafting operation. The drafted slivers are then taken to two pairs of calender rollers that compress the sliver material. This drafted and compressed sliver material called lap is wound finally on a spool.

### 2.3.1.5 Combing

Combing is an optional process, which is introduced into the spinning of finer and high quality yarns from finer cotton. For coarser cotton fibers, the combing operation is usually omitted. This is the process of removal of a predetermined length of short fibers present in the fiber assembly, because the presence of short fibers reduces the yarn quality by increasing the number of thin and thick places, neps, and hairiness, and also lowers the tenacity. The presence of short fibers and the inappropriate configuration of the fibers in the drawn sliver would not allow drafting and the ring frame operations to be effective. Thus, combing is an important process next to carding for spinning fine yarns.

In the combing operation, lap from the lap roller is unwound and fed to the nippers by the feed rollers periodically. The fiber material is gripped between the top and bottom nippers that keep the material ready for rotary combing. The rotary comber is a cylindrical device having needles fitted in a part of its surface. The comber needles enter the fringe and comb and straighten the fibers. During this operation, short fibers, which are not under the grip of the nippers, are combed away with the needles. Drafted slivers are finally delivered into the can. In a comber, there are eight feeding heads. In each head, one lap is fed, and the comber output is in the form of a sliver.

### 2.3.1.6 Drawing

Sliver is taken from combing machine to the drawing machine. The main objectives of the drawing process are to further straighten the fibers, make them parallel to the fiber or sliver axis, and improve the uniformity by doubling. Blending of two different fibers like polyester and cotton, polyester and viscose, etc., is also carried out in draw frame in the case of manufacturing blended yarn. Fiber straightening is achieved by drafting the slivers. During the drafting process, the linear density (weight per unit length) of sliver is also reduced. The operating principle of draw frame is that four to eight card/comber slivers are fed to the drafting arrangement through feed rollers, which are carried in a creel frame or table. The drafted slivers come out as an even web that is immediately condensed into a sliver to avoid disintegration of the web by a converging tube.

#### 2.3.1.7 Speed Frame/Fly Frame

The uniform sliver obtained from the draw frame, subsequently goes to the speed frame, which is the final machine in the spinning preparatory operations. The main tasks here are attenuation of fibers and formation of a suitable intermediate package. Attenuation is the reduction in the linear density of the sliver. The extent of reduction is such that it is suitable for spinning into a yarn. The attenuation of the sliver is achieved by drafting. By this drafting operation, the sliver becomes finer and finer, and the resultant product is called the "roving." After the drafting operation, the roving is wound on the bobbin. During winding, a little amount of twist is imparted to the roving.

#### 2.3.1.8 Ring Spinning

The final process of yarn formation, i.e., spinning, is carried out in the machine called a ring frame. In this process, the roving is attenuated into yarn by drafting. Substantial amount of twist is inserted to the yarn, then it is wound on a bobbin. In other words, drafting, twisting, and winding are the steps taking place during the spinning operation. In the spinning process, the roving, which is several times thicker than the yarn, is subjected to a higher amount of draft when it passes through three pairs of closely associated rollers moving at different surface speeds. For attenuation, the yarn delivery rollers revolve at a higher speed than the feed rollers.

The yarn produced from the spinning machine is a single yarn. However, as per the end use requirement, it may be twisted together with two or more single yarns in the doubling machine to achieve stronger and more uniform yarn.

#### 2.3.1.9 Newer Methods of Spinning

Over the centuries, many ways have been devised for conversion of fibers into yarns, but in the past thirty years, the search for a new and more economical spinning system has been actively pursued in many parts of the world. A new spinning system popularly known as rotor spinning or open-end spinning was introduced in the late 1960s. It has made great impact on the textile industry, especially in terms of rate of production. Other spinning processes, like electrostatic spinning, air-vortex spinning, friction spinning, and disc spinning, are also different types of open-end spinning processes. The twist spinning, self-twist spinning, wrap spinning, false twist spinning, and adhesive processes are only of academic interest and have not become popular. All of these new spinning systems produce yarns having quality that differs to a certain extent from that produced by the more traditional ring-spinning process.

### 2.3.2 SYNTHETIC FIBER SPINNING

Synthetic fiber spinning is entirely different from staple fiber spinning which was discussed earlier. In synthetic fiber spinning, the fiber/filament is made by extruding the polymer liquid through fine holes. In synthetic fiber spinning, the diameter of the filament is determined by three factors, i.e., the rate at which the dope is pumped through the spinnerette, the diameter of the spinnerette holes, and the rate at which they are taken up by the take-up rollers.

Synthetic fiber spinning is divided into three systems based on the meltability and solubility of the polymer. They are melt spinning and solution spinning. Solution spinning may be further divided into two systems on the basis of nature of the solvent: dry spinning and wet spinning.

#### 2.3.2.1 Melt Spinning

Polymers that melt on heating without undergoing any decomposition are spun by a melt spinning system. In this system of spinning, the polymer chips are fed into a hopper. From the hopper, the chips are passed to a spinning vessel through a pipe. In the spinning vessel, the polymer chips fall onto an electrically heated grid that melts the chips and has a mesh too small to pass the chips until they are melted. The molten polymer then passes into the pool and filtering unit. The filtering unit consists of several layers of metal gauge and sand kept alternately with coarse, fine, and very fine mesh and particle size, respectively. This filtering unit filters any impurities out of the molten polymer mass, as they may block the fine holes present in the spinnerette plate. After passing out of the filtering unit, the polymer is forced through the holes in the spinnerette plate and emerges from the plate. As the filaments emerge, they are drawn away from the outlet, stretching the polymer before it cools. Immediately after emerging, cool air is passed to solidify the melt. The solidified melt, now called filament, is then passed through a spin finish bath, an antistatic agent is added, and the filament is wound onto a bobbin by a winder. The filament is then used as such or is imparted crimped or cut into staple fibers. Polyester, nylon, and polypropylene polymers are converted into filaments by this technique.

#### 2.3.2.2 Solution Spinning

Some polymers, e.g., acrylics, undergo decomposition on heating. Therefore, they cannot be spun by the melt spinning system. These polymers are spun by a solution spinning system. In this system, the polymer is dissolved in a suitable solvent, and the polymer solution, generally called dope, is extruded through the holes of the spinnerette for making filaments. If the solvent selected is a volatile solvent, then the polymer is spun by a dry spinning system; if it is a nonvolatile solvent, the polymer is spun by a wet spinning system. Polyacrylo nitrile (PAN) polymer (acrylic fiber) can be spun by either a dry or wet spinning system.

In a dry spinning system, the polymer is dissolved in a suitable volatile solvent and forms a solution called dope. This dope is fed to the spinning head from a feed tank through pipes. A metering pump controls the constant and uniform flow through the spinnerette. The extruded stream of solution flows out into a hot air chamber. On evaporation of the solvent by hot air, the solidified polymer filament is drawn, taken up through a spin finish bath, and wound. The solvent may be recovered from air by adsorption on active carbon.

In wet spinning, the polymer is dissolved in a nonvolatile solvent, and the polymer solution is regularly fed to the filter and spinning head. The spinnerette is submerged in a coagulation bath, and as the polymer emerges out of the spinnerette, the polymer in the solution is precipitated by the bath liquid and soldifies in filaments. The filament is then wound onto the bobbin after spin finish application.

## 2.4 WOVEN FABRICS

The process of converting a set of yarns into a fabric, on a loom, is called weaving. The mechanism of interlacing two sets of yarns at right angles to each other, according to a desired design, is done on the loom. Woven fabrics are more widely used in apparel and industrial applications. The two sets of yarns, warp (longitudinal thread), and weft (lateral thread) require a separate set of processing before they are ready to be woven on the loom. This becomes pertinent, especially if one is looking for special properties like rib effect, absorbancy, and adhesion properties of the fabric. The properties of a gray fabric (fabric coming out from a loom) depend on fiber properties, yarn properties, density of yarns in the fabric, weave, and yarn crimp.

### 2.4.1 WEAVING

To produce a fabric on any loom, the five operations given below are necessary. The first three operations are generally termed fundamental operations.

(1) Shedding: the separation of warp threads (longitudinal) into two layers, one set of which is lifted and the other which is lowered to form a space sufficient enough to send a shuttle of weft yarn (lateral yarn) for interlacement. Each specific set of warp yarns is raised by means of a harness or heald frame. The design of the weave depends on the sequence of raising of the set of yarns forming the shed during insertion of the filling yarn. Tappets, cams, dobby, and Jacquard mechanisms are used as shedding devices.

 Tappet and cams can handle up to fourteen different harnesses and are widely used for simple fabrics. Dobby is a shedding device placed on top of the loom that can handle up to forty harnesses and is used for producing small, figured patterns. Jacquard device is also placed on the top of the loom and can handle individual warp yarns. This enables the weaving of complicated and elaborate designs.

(2) Picking: the insertion of weft yarn by passing from one end of the fabric to the other end through the shed created due to parting of warp yarns into upper and lower layers. Generally, shuttles, projectiles, rapiers, etc., are used as vehicles for the transfer of weft.

(3) Beating up: pushing the newly inserted weft (pick) into the already woven fabric to the end point (fell) is known as the beating process. The beating force employed has a significant influence on the closeness of the fabric.

(4) Warp let off: delivering the series of warp threads simultaneously at a required rate at a suitable constant tension is termed as warp let off. The rate of releasing the warp threads in conjunction with the take up of cloth decides the pick density in the fabric.

(5) Cloth take up: moving the fabric from the formation zone at a constant rate and winding the fabric onto a roller is called cloth take up. By controlling the warp tension, the let off motion decides the crimp in the threads.

### 2.4.2 FUNDAMENTAL WEAVES

The fundamental weaves are plain, twill, and satin weaves. These are the basic weaves from which many new kinds of weaves are derived. The smallest unit of design that appears repeatedly in a weave pattern is called the repeat. The weaves that are generally used in the coating industry are discussed below.

#### 2.4.2.1 Plain Weave

Plain weave is the simplest form of interlacing two sets of yarns. The yarns interlace each other at right angles in alternate order. It has the smallest number of yarns in the repeat, which is two. The maximum possible number of intersections of warp and weft yarns makes a plain weave fabric the strongest and stiffest among the various woven structures. About 40% of all fabrics produced are in plain weave. Some examples of plain weave fabrics are voile, muslin sheeting, mulmul, poplin, cambric, lawn, organdy, shantung, taffeta, canvas, etc. Apart from the plain weave, derivatives of plain weave (weave construction based on plain weaves) are widely used in various industrial fabrics, e.g., tents/shelters, protective clothing, parachutes, and other specialized clothing.

The derivatives of plain weave are as follows:

(1) Basket weave: this is a variation of the plain weave that uses two or more warp yarns simultaneously interlaced with two or more fillings, giving a balanced structure to produce a design that resembles the familiar pattern of a basket. They are woven in a pattern of 2 × 2, 3 × 3, or 4 × 4 with two or more filling yarns interlaced with a corresponding number of warp yarns.

(2) Oxford weave: it varies slightly from the regular basket weave in that it has 2 × 1 construction, i.e., one filling yarn passes alternately over and under two warp yarns that act as one thread. Generally, the fineness of the weft yarn is approximately equivalent to the fineness of the warp yarns.

The basket/mat weave consists of a fewer number of interlacings per cm compared to plain weave, and hence, it allows more threads to be inserted per cm. For this reason, the cloth cover of basket weave is high compared to basic plain weave, but due to fewer intersections/cm, this fabric is more flexible and drapes (hangs) well. In applications where tear strength is important, basket weaves are preferred to plain weave.

#### 2.4.2.2 Twill Weaves

In twill weave, the first warp yarn interlaces with the first weft yarn, the second warp yarn with the second weft yarn, the third warp yarn with the third weft yarn, and so on up to the end of the repeat. Owing to this order of warp and weft yarns interlacing, fabrics with a twill weave pattern exhibit a diagonal stripe directed at an angle of 45° (diagonal lines) from the left upward to the right. These weaves are employed for the purpose of ornamentation and to make the cloth heavier and have better draping quality than that which can be produced with the same yarns in a plain weave. Twill lines are formed on both sides of the cloth. The direction of diagonal lines on the face side of cloth is opposite to that on the back side, coinciding, respectively, with the weft and warp floats on the other side. Thus, if the warp floats predominate on one side of the cloth, weft floats will predominate on the other side of the cloth. The twill weave fabrics include canton flannel, covert cloth, denim, drill, gabardine, jean, khaki, whipcord, etc.

#### 2.4.2.3 Satin and Sateen Weaves

In a satin weave, the warp skips a number of weft yarns before interlacement, thus, warp yarn dominates the face of the fabric. On the other hand, in a sateen weave, the weft yarn skips a number of warps prior to interlacement, and weft dominates the fabric face. For example, when a warp skips seven fillings before it interlaces, the weave is termed an eight float satin. Because of the long yarn floats, satin and sateen fabrics reflect more light and impart high gloss to the surface. These fabrics are also characterized by a maximum degree of smoothness. Satin weave fabrics drape well because the weave is heavier than the twill weave, which in turn, is heavier than the plain weave. Some satin weave fabrics include antique satin, bridal satin, cotton satin, etc.

Each weave can be presented in a square paper design (point paper design) to illustrate weave pattern. Vertical columns of squares on a point paper represent warp ends, and horizontal rows of squares represent picks. A marked square on the point paper indicates that the warp end is raised above the pick, while a blank square means that the warp end is lowered under the pick during weaving. Figure 2.2 shows the graphic symbol of some basic weaves.

### 2.4.3 LOOMS

All woven cloth is made on some sort of loom. The conventional looms are shuttle looms. The shuttle that carries the yarn through the shed of warps is a wooden boat-like container about 30 cm long that carries a bobbin called pirn onto which filling yarn is wound. The shuttle is propelled through the shed formed by warps carrying the filling yarn across the width of the material as it unwinds from the bobbin. The conventional shuttle looms consume a great deal of power and are relatively slow in operation, noisy, and not satisfactory for wide fabrics. Because of these drawbacks, shuttleless looms have been developed. In these looms, the yarn is carried directly from a large cone of yarn located outside of the loom. The operations of some important shuttleless looms are discussed below.

(1) Projectile looms: the picking action is accomplished by a series of small bullet-like projectiles that grip the filling yarn and carry it through the shed and then return empty. These looms have speeds between 300–600 picks per minute (ppm) depending on the width of the fabric.

(2) Rapier looms: instead of the projectile, a rapier-like rod or steel tape is used in these looms to carry the filling yarn. More commonly, two rods are

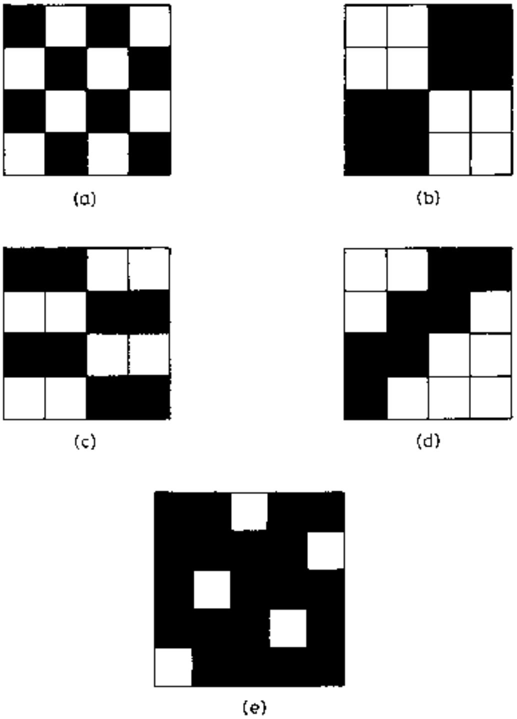


**Figure 2.2** Graphic symbol of some basic weaves: (a) plain weave, (b) 2 × 2 basket weave, (c) 2 × 1 basket/oxford weave, (d) 2 × 2 twill weave, and (e) 4 × 1 satin weave.

used: one carries the yarn halfway, where the end of the yarn it carries is transferred to a rod propelled from the other side that pulls the yarn the rest of the way, while the first rod retraces. This speeds the operation.

(3) Water-jet looms: in water-jet looms, a predetermined length of pick is carried across the loom by a jet of water propelled through the shed. These looms operate at high speeds of ~600 ppm. These looms can produce superior quality fabrics.

(4) Air-jet looms: a jet of air is used to propel the filling yarn through the shed at a relatively high speed of ~600 ppm.

## 2.5 KNITTED FABRICS

Knitting is a process whereby fabrics are formed by the interlacing of neighboring yarn loops. The fabric manufactured by knitting has distinctly different properties than those of the woven structures. The knitted structure may be formed either (a) by weft knitting, in which one or more individual weft supply yarns are laid across beds of needles so that loops of yarns are drawn through previously made loops, or (b) by warp knitting, in which the fabric is formed by looping together parallel warp yarns as they are fed collectively from a warp beam. In a knitted fabric, the yarn density is denoted by wales and courses per cm. The wales are a series of loops in successive rows lying lengthwise in the fabric; they are formed by successive knitting cycles and the intermeshing of each new loop through the previously formed loop. It gives an indication of needles per cm in the machine. Courses are the horizontal ridges in the weft direction that give an idea of the stitch length. A stitch is made when a loop of yarn is drawn through a previously made loop. Due to fewer manufacturing steps, knitted fabrics are easy to produce compared to woven fabric. Moreover, the changeover from one structure to the other can be readily done. Knitted fabrics have the following important characteristics:

- high extensibility
- shape retention on heat setting
- crease and wrinkle resistance
- pliability
- better thermal insulation property
- better comfort property

These fabrics find wide application in casual wear, sportswear, and undergarments. In the coating industry, they are widely used for making upholstery fabric and leather cloth.

### 2.5.1 WEFT-KNITTED STRUCTURES

Weft knitting process is the method of creating a fabric via the interlocking of loops in a weftwise or crosswise direction. The three most popular and fundamental structures of weft-knitted structures are jersey (plain), rib, and purl.

In jersey-knit fabrics, the vertical component of the loops appears on the face side, and the horizontal component is seen on the reverse side of the fabric. The face side of jersey usually has a softer hand than the reverse side. The fabric is characterized by a smooth, regular surface with visible wales on the face side, and a series of semicircular loops on the reverse side. The drawback to these fabrics is that a cut fabric easily ravels in knitting and reverse directions. Jersey fabrics can be made in circular or flat knitting machines with a set of needles in circular or linear positions.

Rib structure differs from the jersey fabric in that it has identical appearance in both directions. The rib fabric is produced when stitches intermesh in opposite directions on a walewise basis. When opposite interlocking occurs in every other wale, the fabric is known as 1 × 1 rib. Similarly, when the interlocking occurs at every three wales in one direction to every two wales in the opposite direction, the fabric is termed as 3 × 2 rib. The rib fabric can be produced on a simple circular knitting or on a flat knitting machine using additional attachments.

Purl fabrics are produced on machines with needles that have hooks at both ends. Purl structures have one or more wales that contain both face and reverse loops.

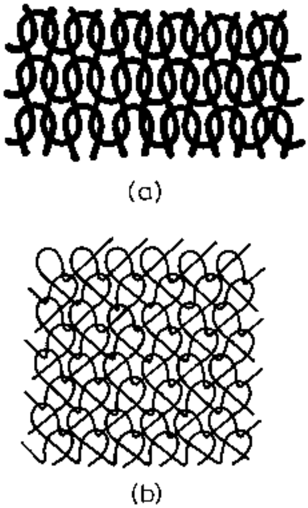
### 2.5.2 WARP-KNITTED STRUCTURES

In warp knitting, each yarn is knitted by one needle. The needle bar that carries the needle moves sideways as well as up and down, so that the yarns are carried vertically and, to a limited extent, diagonally. This diagonal motion is needed to assure that the yarns interlace not only with the stitch directly below but also with stitches to the side. The fabric is formed by the intermeshing of parallel warp yarns that are fed from a warp beam. Here, the warp yarns move in a zigzag motion along the length of the fabric which results in a loop at every change of direction as individual yarn is intermeshed with neighboring yarns. Compared to weft-knit fabrics, warp-knit fabrics are flatter, closer, less elastic, and dimensionally more stable, as parallel rows of loops are interlocked in a zigzag pattern. They have a higher production rate and can be produced in a wider width. Warp-knit fabrics can be of different types of construction, i.e., tricot, Raschel, simplex, and milanese. Among these, tricot and Raschel are commonly used in industrial textiles.

In warp knitting, guide bars are used to guide sets of yarns to the needles. The pattern potential of the knitted fabric is controlled by these devices. Tricot fabrics are classified according to the number of guide bars used. Thus, one-bar tricot uses one guide bar, and two-bar tricot uses two guide bars for production. Tricot fabrics are known for softness, wrinkle resistance, and drapability. They possess higher bursting and tear strength.

Compared to tricot warp-knit fabrics, Raschel fabrics are generally coarse gauge. However, the machines used for producing Raschel fabrics are more versatile, and they have a very large pattern area for ornamentation. Typical products made from this fabric include dressware, laces, powernets, swimwear, curtain nets, etc.

The majority of tricot fabrics are knitted from smooth filament yarns in lightweight construction. On the other hand, the Raschel machines are capable of producing heavier fabrics using spun yarns. Patterns of some important knits are given in Figure 2.3.



(a)

(b)

**Figure 2.3** Patterns of some important knits: (a) jersey knit and (b) warp-knit tricot.

## 2.6 NONWOVEN FABRICS

Nonwoven fabrics are constructed directly from a web of fibers without the intermediate step of yarn manufacture as is necessary for woven, knitted, braided, or tufted fabric. These fabrics are extensively used in disposable and reusable goods because of their low cost and suitability for several specialized applications, as in fusible interlinings, filter media, surgical wear, sanitary goods, diapers, and wipers, etc. In the coating industry, they are widely used in synthetic leather, poromorics, upholstery backing, and protective clothing. Nonwovens may be classified by the type of fiber used, method of web formation, nature of bonding, and type of reinforcements used. The fibers commonly used are cotton, nylon, polyester, rayon, acetate, olefins, and combinations. There are two distinct steps in the manufacture of nonwovens. The first step is the manufacture of a web of fiber. The laid fibers, known also as a batt, do not possess adequate strength. The second step involves entanglement or bonding of the fibers to develop adequate strength.

### 2.6.1 WEB FORMATION

There are various methods for laying the web. In mechanical methods, compressed fibers are passed over rotating wire-covered cylinders (carding machine). The wires pick up the fibers and deposit them in sheet or batt form. A single layer of the web produced from the card is too thin, as such, multiple layers are often stacked to achieve the desired thickness. If the web layers are laid in parallel, they are known as parallel-laid web. These webs have higher strength in the machine direction than in the cross direction. If the webs obtained from the card are cross lapped (changing the orientation from direction of web travel to cross direction), the ratio of strength between the machine direction to cross direction is reduced. Such webs are known as cross-laid webs.

An effective way to minimize the fiber alignment is to sweep the opened fiber coming out of a carding machine by a stream of air and then condense the fiber on a slow moving screen or perforated drum. Such webs are known as air-laid webs. Webs can also be produced by a wet process similar to the one used in the making of paper. In this process, the fibers are suspended in water. The suspension is passed over a moving screen to remove the water. The remaining water is squeezed out of the web, and the web is dried. Webs produced by this method are denser than those produced by the air-laid process. The fiber alignment is also more random.

The spunbonded method is especially used for the manufacture of a nonwoven from continuous filament fibers. In this process, continuous filament extruded through spinnerettes is allowed to fall through a stream of air on a moving conveyor. The desired orientation of the filaments in the web is achieved by controlling the stream of air, speed of conveyor, and rotation of the spinnerette.

If the fibers are thermoplastic, the batt can be thermally bonded by passage between the nip of the heated calender roll. Fusion of the fibers occurs at the intersections.

### 2.6.2 WEB BONDING

There are two types of bonding for the batt: entanglement of fibers and bonding by adhesives.

#### 2.6.2.1 Entanglement of Fibers

(1) Needle punching process: this is one of the most common mechanical bonding processes. In this process, an array of barbed needles is pushed through the web. The barbs hold the fibers at the surface and push them into the center, densifying the structure and leading to an increase in strength. The machine consists of a bed plate to support the web as the set of needles penetrates the web and a stripper plate to strip the fabric off the needles. The number of penetrations per unit area controls the density, thickness, and permeability of the nonwoven fabric. Most needle-punched fabrics are reinforced by a scrim.

(2) Hydroentanglement: in this process, a fine jet of water is used to push fibers from the surface toward the interior of the batt. During impingement, the web is supported on a bed. The force exerted by the jet is less than that

exerted by needling, and as such, the hydroentangled structure is less dense and more flexible than that obtained by the needling process. The method is useful for bonding relatively thin webs. Such fabrics are often termed spunlaced fabrics.

#### 2.6.2.2 Bonding by Adhesives

The bonding of fibers of the web can be achieved by using a variety of adhesives, both in liquid and solid forms. Liquid adhesives can be solutions, emulsions, or pastes. They are applied on the web by dipping and squeezing, spraying, or kiss coating. After application of the adhesives, the solvent is evaporated, and the adhesive is cured by passage of the web through a heated chamber using heated air or IR heaters.

Solid adhesives can be applied as hot melt by spraying or by using the gravure/rotary printing process and subsequently cooling the web. Solid powder adhesives can be applied on the web by scatter coating; the adhesive is activated by passage through a heated chamber. If the web contains a mixture of low melting fibers along with high melting or nonmelting fibers, e.g., rayon and polyester, passage of the web through a heated chamber or hot calender rolls melts the thermoplastic fiber, leading to bonding. These are known as thermobonded fabrics.

The distribution of adhesive in the web is very important, because unlike in paper, movement of fibers in a nonwoven fabric is necessary to produce its textile-like properties. Adhesives interfere with fiber movement. Small bonded areas separated by unbound areas constitute the textile property of the fabric. If the adhesive fills the void between the fibers completely, the product becomes similar to fiber-reinforced plastic.

The strength of a web can be enhanced by the incorporation of yarn in the web. In the stitch-bonded process, the web is passed through a sewing or knitting machine. The stitched structure holds the fibers of the web together. Thus, the fabric is an open-mesh yarn structure with interstices filled with nonwoven fibers. The technology is known as the “Arachne” stitch bonding process.

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CHAPTER 3

# Coating Methods

## 3.1 GENERAL FEATURES

**COATING** a layer of polymeric material on a textile imparts new characteristics to the base fabric. The resultant coated fabric may have functional properties, such as resistance to soiling, penetration of fluids, etc., or have an entirely different aesthetic appeal, such as finished leather. There are various coating methods used to apply polymer to textiles. They can be classified on the basis of equipment used, method of metering, and the form of the coating material. The various methods are given below.

(1) Fluid coating: the coating material is in the form of paste, solution, or latices.
   *a.* Knife coaters, wire wound bars, round bars, etc.: these are post-metering devices.
   *b.* Roll coaters, reverse roll coaters, kiss coaters, gravure coaters, dip coaters, etc.: these are premetered application systems.
   *c.* Impregnators: material to be coated is dipped in the fluid, and the excess is removed by squeeze roll or doctor blades.
   *d.* Spray coaters: the material is sprayed directly on the web or onto a roll for transfer.
(2) Coating with dry compound (solid powder or film):
   *a.* Melt coating: extrusion coating, powder coating, etc.
   *b.* Calendering: for thermoplastic polymers and rubber compounds, Zimmer process, etc.
   *c.* Lamination

The choice of a coating method depends on several factors. They are as follows:

- nature of the substrate
- form of the resin and viscosity of the coating fluid
- end product and accuracy of coating desired
- economics of the process

### 3.1.1 COMMON FEATURES OF FLUID COATING UNITS

A fluid coating operation basically involves applying the coating fluid onto the web and then solidifying the coating. There are common features in all coating operations. The different modular sections of a coating machine are illustrated in Figure 3.1 and described below.

(1) Fabric let-off arrangement. Here, the base fabric is unwound and drawn through the machine under uniform tension. Many machines have accumulator sections, where the rolls are temporarily sewn together for continuous operation, without interruption due to changeover of the rolls. A typical accumulator is shown in Figure 3.2.

(2) A coating head. It may be knife, roll, or any of the methods of fluid coating.

(3) Drying oven. All of the solvents are evaporated, and the film is solidified, dried, and cured. The oven may be steam heated, air heated (oil/forced air), or electrically heated. For rubber-coated fabrics, vulcanization is carried out separately after removal of solvents by evaporation. For other polymers requiring higher temperature, drying and curing can be done by IR heaters, gas-fired units, heater strips, etc. To prevent volatiles from forming an explosive mixture, fresh air is continuously circulated throughout the oven. In the case of organosols, the drying rate is carefully controlled to prevent blister formation or cracking. To properly control solvent evaporation, it is necessary to divide the oven into several zones, increasing the temperature of each zone in order to remove the solvent without blisters.

(4) Winding section. The fabric coming out of the oven is passed over cooling drums to make it tack free. The fabric is then wound up in rolls.

In addition, there is a drive unit that transports the substrate web through the

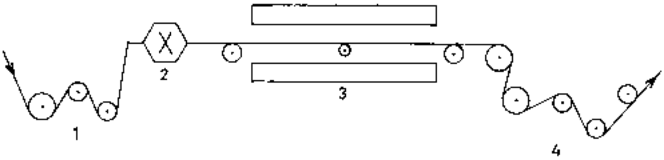


**Figure 3.1** Layour of direct coating line: (1) fabric let-off arrangement, (2) coating head, (3) drying oven, and (4) winding section. (Adapted with permission from G. R. Lomax, *Textiles*, no. 2.1992, ©Shirley Institute U.K. [1].)

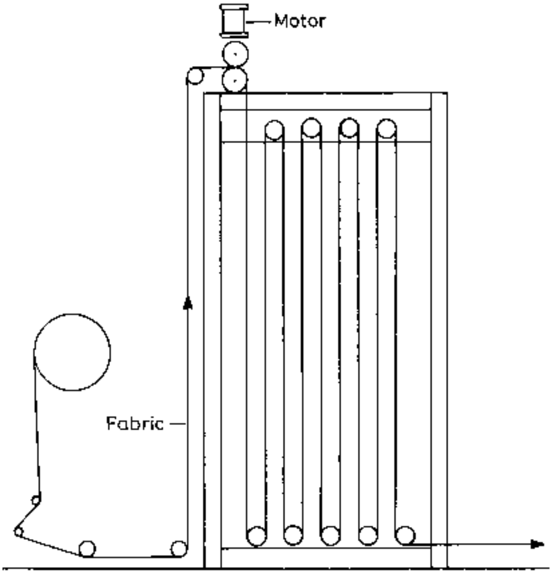


**Figure 3.2** Line diagram of a fabric accumulator. Courtesy Sanjay Industrial Engineers, Mumbai, India.

coating head under constant tension. At times, the drive unit incorporates a stenter frame to minimize shrinkage during the drying process. Coating thickness can be measured by a $\beta$-ray gauge or from the web speed and flow rate of the coating fluid [1,2]. A general view of a coating plant is shown in Figure 3.3.

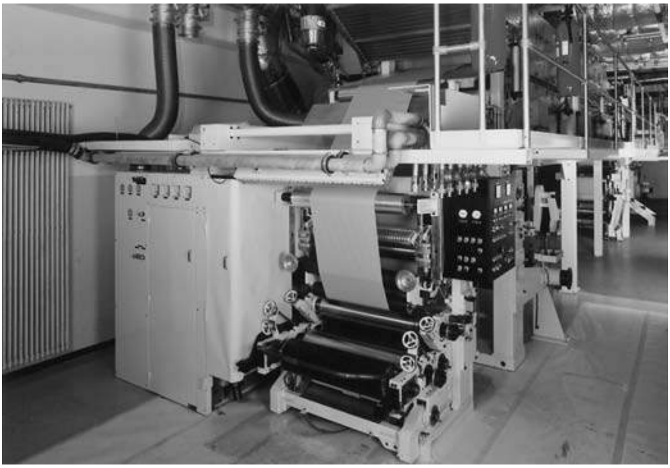


**Figure 3.3** General view of a fluid coating plant. Courtesy Polytype, U.S.A.

### 3.1.2 POST- AND PREMETERING METHODS

The coating process can be classified on the basis of stages of metering, i.e., (a) process where the material is applied on the substrate and then metered and (b) process where the material is metered prior to application. A combination of these methods uses application of premetered excess followed by further metering for more accurate coating. A discussion of the advantages and disadvantages of the methods is presented below.

The first category, i.e., postmetering processes, is considered to be effective for coating noncritical weights on the substrate. As has been described earlier, in this class are the common knife coaters, wire wound (Mayer rod) coaters, single-roll squeeze coaters, etc. Here, excess coating is initially applied on the textile substrate. After the substrate is wetted, a coating device meters the coating to a predetermined thickness. The parameters necessary for consistency in coating add-on are as follows:

*a.* Substrate tension
*b.* Viscosity of the coating material
*c.* Substrate uniformity and porosity

Any variation in these parameters may lead to a nonuniform coating. Coating accuracy is poor. The coating range is limited to about 0.02 to 0.2 mm thickness. However, the major advantage is their low investment cost and fast product changeover.

In the second category, a premetered quantity of material is applied onto the textile. The processes include roller coatings, gravure coatings, extrusion coatings, and lamination. These methods are much more accurate and give highly reproducible add on. The coating range is wider, 0.1 to 0.5 mm. However, the initial investment cost is higher [3].

The common methods of coating are described below.

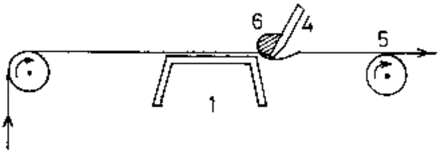
## 3.2 KNIFE COATING

Also known as spread coating, this is one of the oldest coating methods. A dry, smooth fabric is fed over the bearer roll under a knife known as a knife or doctor blade. The coating material is poured in front of the knife by a ladle or by a pump over the entire width of the web. As the web is transported under the knife, the forward motion of the fabric and the fixed knife barrier give the viscous mass of the material a rotatory motion. This is known as the rolling bank that functions as a reservoir of coating compound in front of the knife. To prevent the fluid from spilling over the edges of the fabric, two adjustable guard plates known as dams are also provided. Proper tension is applied on the fabric as it is unwound, so that the fabric is taut under the knife. Most machines can coat fabric widths up to 1.5–2.0 m, but specially designed machines can accommodate up to 4 m widths. Special care is taken that the material has adequate viscosity so that it does not strike through the fabric. The coated fabric then passes through the drying oven. The rate of evaporation of the solvent determines the rate of transport of the fabric, and thus, the coating rate. The coating thickness is mainly controlled by the gap between the knife and the web [4].

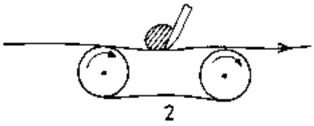
### 3.2.1 ARRANGEMENTS OF KNIFE COATING

There are three distinct arrangements of knife coating. They are knife on air, knife on blanket, and knife on roll. These arrangements are given in Figure 3.4.

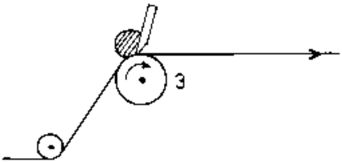
In the floating knife [Figure 3.4(a)] or knife-on-air coating, the knife is positioned after a support table and rests directly on the fabric. In this arrangement, compressive force applied on the coating material is greater, and as such, the coating compound enters the interstices of the fabric. This technique is useful for applying very thin, lightweight, impermeable coatings (as low as 7–8 g/m$^2$) suitable for hot air balloons, anoraks, etc. [5].



(a) Floating knife



(b) Knife over blanket



(c) Knife over roll

**Figure 3.4** Different types of knife coating: (1) support table, (2) rubber blanket, (3) rubber or steel roll, (4) knife, (5) web, and (6) coating material. (Adapted with permission from *Encyclopedia of Chemical Technology*, Vol. 6, 3rd Ed. 1979; and *Encyclopedia of Polymer Science & Engineering*, Vol. 3, 2nd Ed. 1985. Both ©John Wiley & Sons.)

Web tension, viscosity, percent solids, and specific gravity of the coating compound play a significant role in the amount of coating deposited. The higher the viscosity of the compound, the greater will be its tendency to force the web away from the knife, resulting in a higher weight add on. On the other hand, it can be easily visualized that the coating weight will be less if tension on the fabric is greater. The method is suitable for both closely woven and open fabrics, because strike through does not affect the coating operation [6].

In the knife-on-blanket arrangement [Figure 3.4(b)], the web is supported by a short conveyor, in the form of an endless rubber blanket stretched between two rollers. Because the tension applied on the blanket results in a uniform pressure between the knife and the substrate, the fabric is not subjected to stretching in this arrangement. It is possible to coat dimensionally unstable substrates with this technique. The amount of coating is dependent on the tension of the blanket, which is adjusted by the rollers. Care should be taken that there is no damage to the blanket and that no foreign matter is adhered on the inside of the belt, as this will result in an irregularity in coating weight.

The knife-on-roll system [Figure 3.4(c)] is the most important and widely used technique for its simplicity and much higher accuracy. In this configuration, a suitably designed doctor blade is properly positioned on top of a high-precision roller. The gap between the bottom of the blade and the thickness of the fabric that passes over the roller controls primarily the coating weight. The roll may be rubber covered or chromium-plated steel roll. The hardness of the rubber-covered roll may vary from 60 to 90 shore A, depending upon the type of fabric [4]. The advantage of a rubber-covered roll is that any fabric defects, such as knots and slubs having thickness greater than the fabric thickness, are absorbed by the roll surface, allowing free passage of the fabric through the coating knife. However, rubber rolls are not as precise as steel rolls and may cause variation in the wet coating weight up to ±30 g/m$^2$. Rubber rolls also have the disadvantage of swelling on prolonged contact with solvents and plasticizers. Steel rolls, on the other hand, can give more precise coating [5]. The gap between the knife and the roll can be adjusted by the screws provided on the mounting rod of the knife. In modern machines, the gap is controlled by pneumatic arrangement. Besides pneumatic, quick lifting is also provided to release lumps, splices, torn edges, etc. Materials with a wide viscosity range (up to 40,000 cps) can be coated by the knife-on-roll technique. It can also impart heavy coatings on fabric using a solventless system like plastisols. The coating method is better suited for dimensionally stable fabrics, which will not easily distort due to tension applied on the fabric while pulling through the coater. Care is always taken that the coating material does not strike through. In case of a strike through, steel rolls are easier to clean. A knife-on-roll coating plant is shown in Figure 3.5.

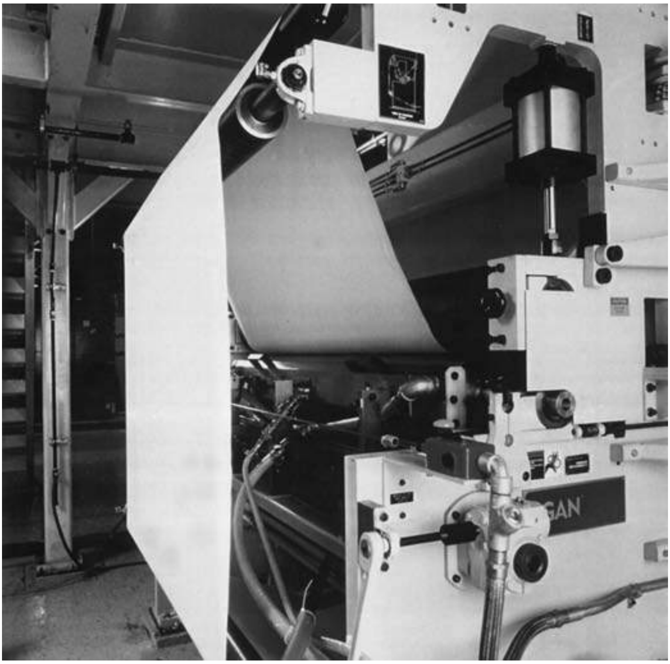


**Figure 3.5** A knife on roll coating plant. Courtesy Egan Davis Standard Corp., and U.S.A.

### 3.2.2 COATING KNIVES

The profile of the coating knife and its positioning over the roll are important parameters affecting coating weight and penetration. Numerous knife profiles are used in the trade, however, some common types are shown in Figure 3.6.

The knife profile [Figure 3.6(a)] is normally used for lightweight coating. The base of the knife may vary from 0.5 to 4 mm wide. The knife is chamfered on the other side of the rolling bank. The sharper the base of the knife, the lower the coating weight. If the blade is chamfered on both sides, that is the V-type profile [Figure 3.6(b)] a wedge effect is produced during coating,

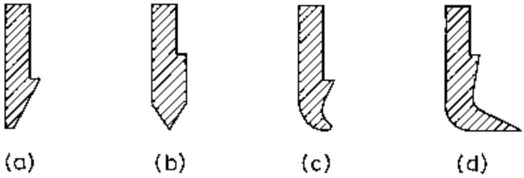


**Figure 3.6** Profiles of knives: (a) knife type, (b) V type, (c) bull nose, and (d) shoe. (Adapted with permission from F. A. Woodruff. *J. Coated Fabrics*, Vol. 21, April 1992. ©Technomic Publishing Co., Inc. [5].)

which puts considerable pressure on the coating material, resulting in much greater penetration of the material into the interstices of the fabric. This type of profile is used where a high degree of penetration is required for good mechanical adhesion. Multiple coats are applied to achieve the desired coating weight of the end product, such as for tarpaulins, hoses, etc. A bull-nosed knife [Figure 3.6(c)] imparts heavy coating weights with little penetration into the weave and is suitable for easily damaged fabrics. The shoe [Figure 3.6(d)] knife is so named because of its resemblance to a shoe. The front of the knife may be straight or rounded. The base dimension may vary from 2–30 mm. The toe of the blade is nearest to the substrate. By varying the angle between the blade and the roll, the elevation of the heel of the knife and the web can be altered. A wedge of coating compound is formed between the web and the heel of the knife. The greater the elevation, the more material will be available in the wedge, leading to greater penetration [5].

During the coating process, many compounds, because of their surface tension properties, rise up the back of a knife, accumulate, and drop on the coated surface in an unsightly fashion, called spitting. In the shoe knife, due to the design of the toe, this is completely prevented. For PVC pastes and breathable PU coatings, shoe knife is the preferred type [6].

Proper positioning of the knife and the roll are other important considerations for proper coating. The rolls should be true to knife surface, without eccentricity. It is also vital that the knife be aligned horizontal to the axis of the roll, otherwise, wedge-shaped coating will result. The angle of the knife over the roll affects penetration. The greater the angle at which the knife meets the moving fabric, the greater the penetration. If the position of the blade is at a point behind the crown of the roll, the blade will be directly pressing the fabric, and a situation similar to floating knife is created [5].

Instead of a single knife fitted over the roll, modern machines have a knife supporting beam fitted with two or three different types of knives mounted 180° or 120° apart. A twin knife arrangement is shown in Figure 3.7. This facilitates easy changeover of the blades.

### 3.2.3 THE ROLE OF ROLLING BANK AND WEB TENSION

As has been described earlier, the coating compound is pumped or ladled over the substrate in front of the blade in knife coating, forming a rolling bank that acts as a reservoir for the coating material. The viscosity and the amount of rolling bank also contribute to the penetration and coating weight of the end product. The rolling bank (Figure 3.8) exerts a pressure on the web, as such, if the height of the roll bank is greater at the center, heavier coating will be produced at the center. Similarly, if the height is more at the sides, the coating will be more in the sides. In case of a pump pouring fluid over the web across the width, its traverse also results in variation of coating in an “S” pattern.

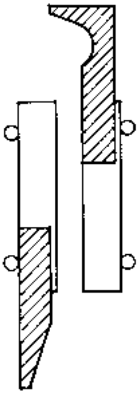


**Figure 3.7** Twin knife arrangement.

Harrera has described Mascoe's patented trough system (Figure 3.9) for better control of the conditions prevailing in the rolling bank [7]. The coating compound is fed into a trough in front of the blade. The gap between the trough and the blade is adjustable, but it is fixed during the coating process.

In this device, because the opening of the trough is constant, the exposure to fabric is controllable and is much shorter than the rolling bank. It is claimed that greater accuracy and repeatability can be obtained by this system, however, cleanup of the trough is a problem.

Fabric tension plays an important role in the final add on of the coated product and is thus dependent on the stretchability of the fabric. A higher tension in warp direction opens up the weave, exposing more surface, and thus, the coating weight add on is heavier when the fabric is excessively stretched. This is true if the weave pattern is regular. In case of an irregular pattern, application of uniaxial tension results in uneven tension in the filling yarn, causing uneven coatings. Mascoe has developed a tensioner that maintains a uniform force across the substrate width, which is not altered by the changing speed of the web [7].

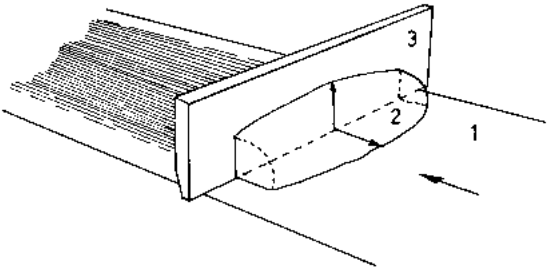


**Figure 3.8** Rolling bank: (1) web, (2) rolling bank, and (3) knife. (Adapted with permission from A. Harrera. *Journal of Coated Fabrics*, Vol. 20, April 1991. ©Technomic Publishing Co., Inc. [7].)

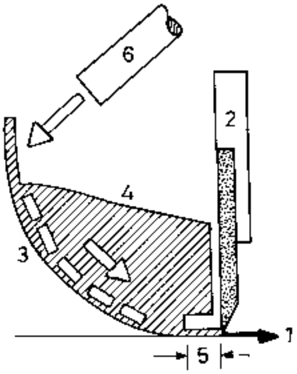


**Figure 3.9** Mascoe's trough: (1) web, (2) knife, (3) trough, (4) coating compound, (5) adjustable gap, and (6) feeder. (Adapted with permission from A. Harrera. *Journal of Coated Fabrics,* Vol. 20, April 1991. ©Technomic Publishing Co., Inc. [7].)

## 3.3 ROLL COATING

### 3.3.1 MAYER ROD COATING

In this method, compound is applied on the web by a single-roll applicator. The coating is postmetered by a wire wound rod, known as the Mayer rod, that removes excess coating (Figure 3.10).

The Mayer rod is a small, round stainless rod, wound tightly with a fine wire also made of stainless steel. The grooves between the wire determine the precise amount of coating that will pass through. The coating thickness is directly proportional to the diameter of the wire. The most common core rod diameter varies from 4–6 mm, although sizes up to 25 mm are used. To prevent deflection of the Mayer rod due to web pressure, it is mounted on a rod holder. The simplest rod holder is a rectangular steel bar with a "V" groove machined to it. The rod is placed on the groove, and the holder is mounted between the side frames of the coating machine. During coating, the rod is slowly rotated

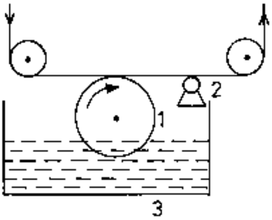


**Figure 3.10** Mayer rod coater: (1) applicator roll, (2) Mayer rod with holder, and (3) feed pan. (Adapted with permission from *Encyclopedia of Polymer Science & Engineering*, Vol. 3, 2nd Ed. 1985, ©John Wiley & Sons.)

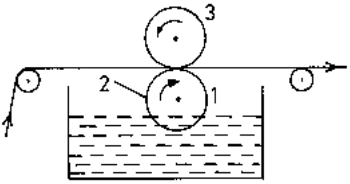


**Figure 3.11** Direct roll coater: (1) applicator roll, (2) doctor blade, and (3) backup roll.

in the opposite direction of the web. The rotation removes the coating material between the wires, keeping the wire surface wet and clean. The rotation also increases the life of the rod due to reduced wear.

The thin lines formed during coating smooth out due to surface tension. The uniformity of the coating is maintained if the viscosity of the compound, speed, and tension of the web are properly controlled. This method is used for low solid, low viscosity (50–500 cps), thin coatings (2–3 g/m$^2$). It is suitable for silicone release papers and as a precoater [8].

### 3.3.2 DIRECT ROLL COATING

In direct roll (or squeeze roll) coating, a premetered quantity of the coating is applied on the fabric by controlling the quantity on the applicator roll by the doctor knife (see Figure 3.11.) The fabric moves in the same direction as the applicator roll. This method is also restricted to low viscosity compounds and is suitable for coating the undersurface of the fabric. The coating thickness depends on nip pressure, coating formulation, and absorbency of the web [2].

### 3.3.3 KISS COATING

A typical arrangement of kiss coating is shown in Figure 3.12.

The pickup roll picks up coating material from the pan and is premetered by the applicator roll. The coating is applied on the web as it kisses the applicator roll. The pickup roll may be rubber covered, and the applicator roll may be made of steel. The metering is done by nip pressure, and consequently, the

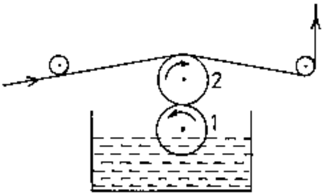


**Figure 3.12** Kiss coater: (1) pickup roll and (2) applicator roll. (Adapted with permission from *Encyclopedia of Polymer Science & Engineering*, Vol. 3, 2nd Ed. 1985, ©John Wiley & Sons.)

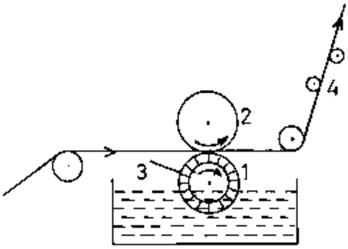


**Figure 3.13** Gravure coater: (1) gravure roll, (2) backup roll, (3) doctor blade, and (4) smoothening rolls. (Adapted with permission from *Encyclopedia of Polymer Science & Engineering*, Vol. 3, 2nd Ed. 1985, ©John Wiley & Sons.)

amount of material coated on the web is dependent on nip pressure, speed of the operation, roll hardness, and its finish. The coating weight and splitting of the film as it leaves the roll are also dependent on web tension.

### 3.3.4 GRAVURE COATING

Engraved rollers are utilized in gravure coatings to meter a precise amount of coating on the substrate. The coating weight is usually controlled by the etched pattern and its fineness on the gravure roll. There are a few standard patterns like the pyramid, quadrangular, and helical. For lighter coating weight, a pyramid pattern is used. In a direct two-roll gravure coater (Figure 3.13), the coating material is picked up by the gravure roll and then transferred to the web as it passes between the nip of the gravure and the backup roll. The pattern may be self-leveling or the coated web may be passed between smoothening rolls.

In offset or indirect gravure coater, a steel backup roll is added above the direct gravure arrangement. The coating compound is first transferred onto an offset roll and then onto the substrate (Figure 3.14).

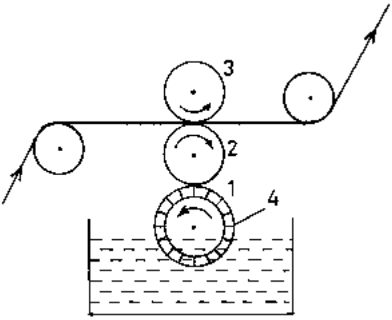


**Figure 3.14** Offset gravure coater: (1) gravure roll, (2) rubber-covered offset roll, (3) steel backup roll, and (4) doctor blade. (Adapted with permission from *Encyclopedia of Polymer Science & Engineering*, Vol. 3, 2nd Ed. 1985, ©John Wiley & Sons.)

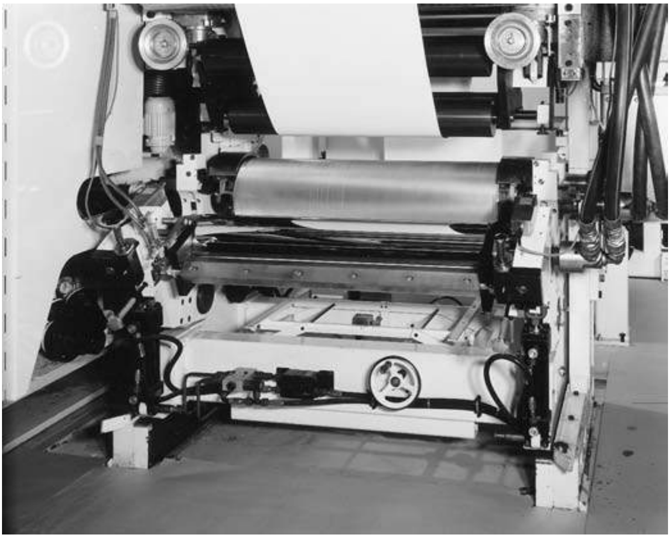


**Figure 3.15** A gravure coating plant. Courtesy Polytype, U.S.A.

The speed and direction of the gravure and offset rollers can be varied independently. The arrangement is suitable for an extremely light coating (as low as 0.02 g/m$^2$) and minimizes the coating pattern. This offset process can handle a higher viscosity material (~10, 000 cps.) than the direct process. By heating the feed pan, the process can coat hot melt compounds. Gravure coating is used for applying laminating adhesives or a topcoat on a treated fabric. A gravure coating plant is shown in Figure 3.15.

### 3.3.5 REVERSE ROLL COATERS

Reverse roll coating is one of the most versatile and important coating methods. It can be used for a wide range of viscosities and coating weights. The accuracy of the coating is very high. Reverse roll coaters apply a premetered coating of uniform thickness, regardless of the variations in substrate thickness, and are therefore known as contour coaters. The coating is also independent of substrate tension. There are two basic forms of reverse roll coaters: three-roll nip and pan fed. Figure 3.16 shows the arrangement of a nip-fed coater.

The applicator and the metering rolls are precision-ground chilled cast iron or stainless steel rolls, finished to a high degree of precision. The two rolls are set at an angle, and the coating material is kept in a reservoir, at the nip, bound by the applicator roll and coating dams on each side. The gap between the applicator and metering roll can be precisely controlled. The backup roll is to bring the moving web in contact with the applicator or transfer roll. A film

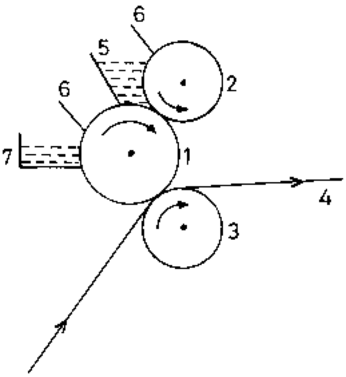


**Figure 3.16** Nip-fed reverse roll coater: (1) applicator roll, (2) metering roll, (3) backup rubber roll, (4) web, (5) coating pan, (6) doctor blades, and (7) drip pan. (Adapted with permission from *Encyclopedia of Polymer Science & Engineering*, Vol. 3, 2nd Ed. 1985, ©John Wiley & Sons.)

of the coating compound is metered between the applicator and the metering roll. The applicator roll then carries the coating material to the coating nip where the compound is transferred to the web moving in the opposite direction. The opposite direction of the applicator roll and the web creates a high level of shearing action. The criteria of a reverse roll coater are the opposite direction (a) of the applicator and the metering roll and (b) of the applicator roll and the web. A scraper or doctor blade cleans the metering roll to prevent dropping of material on the web. The coating material remaining on the applicator roll after contact with the web is also scraped off, collected in a pan, and recycled. This helps to clean the roll of dirt and dried coating material, which would cause inaccuracy in coating.

The thickness of the coating is controlled by the gap between the applicator and the metering roll, the rotational speed of the applicator roll, and the amount of material transferred on the web, which in turn is dependent on the web pressure on the applicator roll adjusted by the backup roll. Thus, a reverse roll coater has greater flexibility in adjusting the coating thickness compared to the knife-on-roll, where coating is controlled only by gap of knife and the roll. In direct roll coating, where the web and applicator roll move in the same direction, nonuniform coating occurs with the formation of ribbing due to the film split phenomenon, while in reverse roll, the coating is smooth [6].

One challenge when using the nip-fed coater is to prevent leaks from the coating reservoir, particularly with low viscosity compounds. The pan-fed coater operates using the same principle as the nip-fed coater, but it is more suited for low viscosity materials (Figure 3.17).

Greer [9] has recently reviewed studies on the fluid mechanics of reverse roll coating. The reasons for nonuniformity of coating have been discussed. The two common defects are ribbing and cascading, i.e., formation of a wavy pattern. To

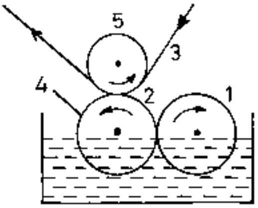


**Figure 3.17** Pan-fed reverse roll coater: (1) metering roll, (2) applicator roll, (3) web, (4) doctor blade, and (5) backup roll. (Adapted with permission from *Encyclopedia of Polymer Science & Engineering*, Vol. 3, 2nd Ed. 1985, ©John Wiley & Sons.)

explain the reasons for these defects, a dynamic wetting line has been defined. This is the point from which the coating pulls away from the metering roll as it leaves the metering nip and moves along with the applicator roll. If the wetting line is at the center of the nip, the coating is smooth. If the wetting line is at the outlet side, ribbing occurs; if it is on the inlet side, cascading occurs. An important criterion governing the position of the wetting line is the ratio of metering to applicator roll speeds. In addition, surface tension and viscosity of the coating compound also play important roles.

## 3.4 DIP COATING

This is also known as impregnation or saturation. The substrate web is immersed in a tank of the coating material for a certain period of time, known as the dwell time. The excess material is then squeezed out by passing through nip rolls or a set of flexible doctor blades precalibrated to give a fixed net pickup of the resin. There are various arrangements for the dip process. A simple arrangement is shown in Figure 3.18. Sometimes, a prewet station precedes the dipping to remove air from the interstices and promote penetration. The factors that are to be considered in designing an impregnated fabric are the solid content of the impregnant and the absorption capacity of the fabric. In dip coating, the pickup is quite low, and penetration occurs into the interstices of the fabrics as well as in the yarns. Moreover, because the fabric is not stressed,

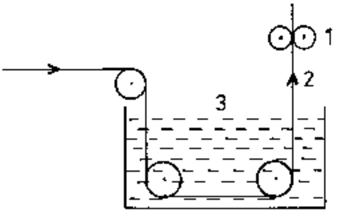


**Figure 3.18** Dip coating: (1) squeeze rolls, (2) web, and (3) dipping tank. (Adapted with permission from *Encyclopedia of Polymer Science & Engineering*, Vol. 3, 2nd Ed. 1985, ©John Wiley & Sons.)

no damage or distortion to the yarn occurs. The process is mainly used for finishing processes like flame retardant treatments and application of adhesive primer.

## 3.5 TRANSFER COATING

In principle, transfer coating consists of applying polymeric coating on the surface of a support, usually paper, laminating the textile substrate to be coated to the polymeric layer, and removing the paper, to yield a transferred polymeric layer on the textile.

The process of applying coating material directly on the textile is known as direct coating. The direct coating process has certain limitations. They are as follows:

- It is applicable to closely woven, dimensionally stable fabrics that can withstand machine tension, and it is not suitable for excessively stretchable knitted fabrics.
- Penetration occurs in the weave of the fabric, increasing adhesion and lowering tear strength and elongation, resulting in a stiff fabric.

Transfer coating overcomes these limitations. Because no tension is applied during coating, the most delicate and stretchable fabrics can be coated by this process. Fabric penetration and stiffening is significantly low. Moreover, with proper processing, the appearance of the textile substrate can be altered to give a much better aesthetic appeal, like artificial leather for fashion footwear. A schematic diagram of the process is given in Figure 3.19.

The steps involved are as follows [1]:

- A layer of coating is applied on a release paper in the first coating head and is then passed through the first oven, where it is dried and cured. This forms the top surface of the coated fabric. The release paper is

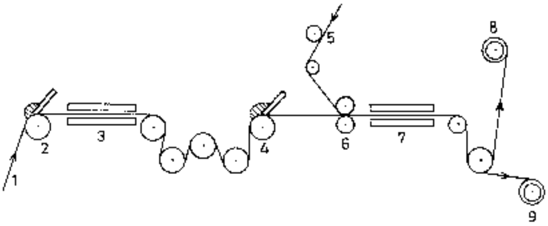


**Figure 3.19** Layout of transfer coating process: (1) release paper, (2) first coating head, (3) first oven, (4) second coating head, (5) textile substrate, (6) laminating nip rolls, (7) second drying oven, (8) coated fabric takeoff roll, and (9) release paper wind roll. (Adapted with permission from G. R. Lomax, *Textiles*, no. 2. 1992. ©Shirley Institute U.K. [1].)

usually embossed. The pattern of the paper is thus transferred on the coating. This is known as the top coat.

- In the second coating head, an adhesive layer known as the tie coat is applied on the dry top coat, previously laid on the release paper. The release paper thus has two layers, the dry top coat and the tacky adhesive tie coat.
- The textile substrate is then adhered to the release paper containing the top and the tie coats, while the tie coat is still tacky. The lamination is done by a set of nip rolls. The composite layer is then passed through the second oven to dry and cure the tie coat.
- The release paper is finally stripped, leaving the coated textile.

The release papers are calendered to uniform thickness and are coated with a thin layer of silicone. The property of release paper should be such that it is able to grip the top coat during the processing and able to release the fabric without damaging the top coat. Various grades are available. Normally, paper can be reused about eight to ten times.

The coating head in a transfer coating unit is typically knife over rubber-backing roll. The rubber roll has the advantage in that it does not damage the release paper. The laminator rolls are steel rolls. The setting of the coating knives and gap between the laminating rolls can be set and maintained fully automatically.

Transfer coating is used for PVC pastes and for polyurethane coating. Although the basic transfer process involves a two-coat operation, the top and the tie coat, a three-coat process is becoming quite popular. The first two heads apply the top coat in two thin layers. This permits faster line speeds due to greater efficiency of solvent removal from thinner films, and it prevents pinholing, where waterproofness is important. The third coating head applies the tie coat. In polyurethane transfer coating, this affords an option of using two different types of PU for the two layers of top coats for special properties, as required for artificial leather [10].

## 3.6 ROTARY SCREEN PRINTING

This method is common for coating and printing textiles. The coating head is a screen that is a seamless nickel cylinder with perforations. This screen rests on the web. A squeegee is mounted in the screen, serving as supply and distribution pipe of the coating paste. The squeegee blade, which is mounted to this pipe, pushes the paste out through the perforations of the screen. A whisper blade smooths the applied coating. A backup roll is provided for counterpressure (Figure 3.20). After coating, the coated material is sent to an oven for fusion of the polymers. The amount of coating applied is determined mainly by the

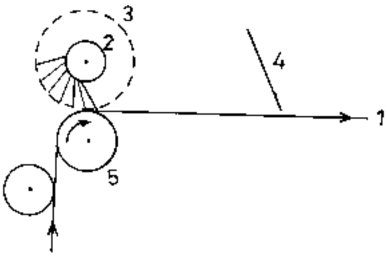


**Figure 3.20** Rotary screen coating: (1) web, (2) squeegee, (3) screen, (4) whisper blade, and (5) backup roll.

mesh number of the screen, the squeegee pressure, i.e., the angle between the blade and the screen, and the viscosity of the paste.

Depending on the mesh size and design of the screen, continuous coating, coating of complex pattern, and dot coating can be done. In continuous coating, the coating can be up to 200 g/m$^2$, by proper choice of the screen. Dot coating is useful for making fusible interlinings for woven and nonwoven fabrics. In this process, the screen, the web, and the counterpressure roller all have same speed. The coating is, therefore, done without tension and friction. Consequently, delicate and stretchable fabrics can be coated without difficulty. The coating is accurate, and the penetration can be controlled [8].

A relatively new development by Stork (Stork-Brabent, Holland) is the screen-to-screen technology (STS). Basically, the process consists of two screen-coating heads, back to back, each with its own coating feed system, squeegee roll, and whisper blade to smooth out the applied compound. The substrate travels between the screens either in a horizontal or a vertical position (depending on the model), and the compound is gelled (or cured) with IR heaters. With STS technology, it is possible to coat (different colors) or print both sides of a substrate in one pass.

## 3.7 CALENDERING

Calendering is a versatile and precise method of coating and laminating polymeric material onto a fabric. The equipment consists of a set of heated rolls also known as bowls. Fluxed, precompounded stock is fed between the roll nips, which comes out as a sheet as it passes through consecutive roll nips. The sheet so produced is press laminated to the fabric with another pair of mating rolls, which may be in the same calender machine. A variety of thermoplastics can be processed on the calender, however, it is extensively used for coating rubbers and vinyls.

For continuous operation of a calender, different equipment is arranged in line and functions in tandem to produce the coated fabric. This is known as

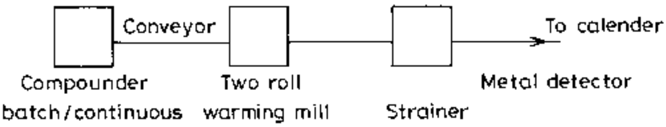


**Figure 3.21** Precalender train.

the calender train. The train has three distinct sections, viz, the precalendering section, the calendering itself, and the postcalendering section.

### 3.7.1 PRECALENDERING SECTION

The task of the precalender section is to deliver fused polymer stock to the calender in a thoroughly compounded, homogenized, degassed condition that is free from impurities. The compounding can be done either in a batch process, using an internal mixer such as the Banbury mixer, or continuously, in an extruder. The compounded material is then fed to a two-roll mill to impart uniformity of temperature to the stock. Frequently, the material is next passed through a strainer. The strainer is a heated short-barreled extruder with a screen orifice. It masticates the compound further and prevents impurities, particularly metal particles, from entering the calender. The compounded material is then fed into the calender by a conveyor. The feed is a thick and narrow strip of material. Metal detectors are provided in the feed line to prevent any metal particle from entering the calender and damaging the rolls. If the material is conveyed a distance of more than 2 m, the feed is heated by IR heaters. The stages of this section are shown in the block diagram given in Figure 3.21.

### 3.7.2 CALENDER

The equipment consists of a stack of rolls mounted on bearing blocks, supported by a side frame. It is equipped with roll drive, nip adjusting gear, and heating arrangement. The rolls are made of chilled cast iron. The number of rolls and their arrangements are varied. Three- and four-roll calenders are the most popular.

Thinner coating can be achieved by increasing the number of rolls, but they increase the complexity of the equipment, the cost, and the space required. The sizes of the rolls vary from 45–120 cm diameter and 90–300 cm width [6,11,12].

Some common configurations of the rolls are given in Figure 3.22.

Vertical arrangements of the rolls in the stack were used in early machines. They suffer from the problem of adjusting the nips independently and of feeding the calender [13]. The feeding is easier if the top roll is offset, in an inverted “L”-type configuration, for instance, the feed bank is horizontal.

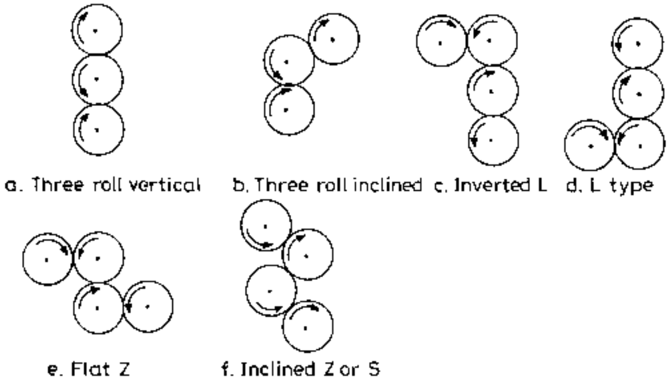


**Figure 3.22** Configurations of rolls.

The selection of the configuration of rolls is dependent on its end use. The most suitable configuration for plasticized vinyl compounds is the inverted "L", the most suitable for rubbers is the three-roll inclined, and the most suitable for two-sided coating is the "Z" type [14].

The rolls are individually driven, which provides wide flexibility in the variation of the roll speeds and the corresponding friction ratio. For proper control of process temperature, the rolls are heated. The rolls are provided with either a hollow chamber or they have peripheral holes located close to the roll surface. The heating is done by circulation of hot water or special heat exchange liquid. Temperature control in the peripheral holes is far superior due to better heat transfer. The two factors, viz., the friction ratio and temperature, enable the calender to process a wide range of compositions differing in rheological properties. End dams are fitted in the rolls to constrain the compound in an adjustable span for coating fabrics of different widths [6,12].

The compound is fed into the feed nip of the calender. In the case of an inverted "L" type, it is the nip between the top two rolls. The rolls rotate in opposite directions at the nip and at different speeds. The material is pushed forward by the friction of the rolls and adheres to the faster roll. The material then passes through the successive rolls where it is resurfaced and metered and comes out of the calender in the form of a sheet. Calendering can, therefore, be regarded as sheet extrusion. During operation, rolling banks are formed at each nip. It is thick and narrow at the feed nip but becomes thin and wide in successive nips. The passage of the material from the feed to outlet is known as the sheet path and is controlled by the adherence of the material to a particular roll. The material adheres to the faster roll and the one having a higher temperature.

Separating forces on the rolls are produced when the viscous material is passed through the nip. These forces are highest at the center of the roll, therefore, the sheet is thicker in the middle. The separating force is dependent on several factors: the viscosity of the material, the gap between the rolls, the speed of the rolls, the size of the rolling bank, etc. In older machines, this was corrected by contouring the rolls in such a way that the center of the rolls had a slightly larger diameter, known as roll crowning. However, this is only suitable for specific compounds and operating conditions [15]. The methods adopted at present are roll bending and roll crossing. In roll bending, a hydraulic load is applied to the roll journal ends. This force exerts leverage on the rolls that makes them slightly concave or convex depending on the direction of the applied load. In roll crossing, an angular shift is given to one or both rolls at the nip. Although the rolls remain in the horizontal plane, their axes are no longer parallel but form a slight angle. This increases the end clearance between the rolls, resulting in thickening at the edges of the sheet produced. For proper operation, the material should be fed at a steady rate at uniform temperature. Any variation results in roll deflection and consequent variation in the thickness of the product.

### 3.7.3 COATING AND LAMINATION

A calender is used for coating polymer directly onto the fabric or for making unsupported film that may be subsequently laminated to a fabric. There are various ways of coating and lamination which are discussed below [6,11].

*a.* Nip coating: here, the coating is done at the bottom nip of the calender. The mechanical setup is simpler. The fabric pulls the sheet off the calender. The method is suitable for heavy impregnation. The extent of penetration is dependent on the gap at the nip and the friction ratio (Figure 3.23).

*b.* Lamination against calender roll: in this setup, the fabric is laminated against the last calender roll by means of a rubber backup laminating roll that is hydraulically operated—known as a squeeze roll. The conditions of penetration and takeoff of the sheet from the calender are similar to those in nip lamination (Figure 3.24).

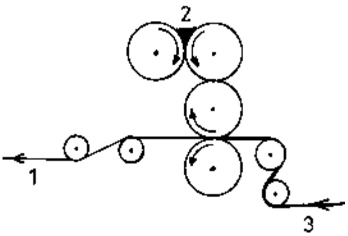


**Figure 3.23** Nip coating: (1) fabric, (2) rubber bank, and (3) coated fabric. (Adapted with permission from *PVC Plastics* by W. V. Titow. ©Kluwer Academic Publishers, Netherlands, 1990.)

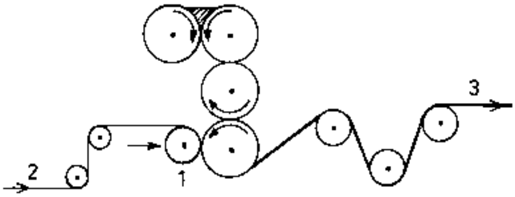


**Figure 3.24** Lamination against calender roll: (1) squeeze roll, (2) fabric, and (3) coated fabric. (Adapted with permission from *PVC Plastics* by W. V. Titow. ©Kluwer Academic Publishers, Netherlands, 1990.)

*c.* In-line lamination: the sheet produced from the calender is laminated to the fabric outside the calender by laminating rolls. This arrangement is convenient for heat-sensitive substrates. The sheet coming out of the calender may cool and have to be heated prior to lamination for proper bonding to the fabric (Figure 3.25).

*d.* Another method of laminating multiple sheets of polymer and textile is given in Figure 3.26. Here, two or more sheets of polymer and textile are laminated by pressing them between a steel belt and a hot roll. The heat and pressure laminate the webs. The steel belt (1) is pressed against a hot drum (2) by means of a tension roll (3) and guide rolls (4 and 5). The fabric and the sheets are heated by IR heaters prior to being fed between the gap of the steel belt and the hot roll. The configuration is similar to the rotocure system used in continuous vulcanization.

*e.* Coating of elastomers: as mentioned earlier, the rolls rotate in the opposite direction at the nip with different speeds. The higher the friction ratio, the greater the penetration. Thus, if the rolls run at even or near even speeds, the penetration is low, and the coating thickness is high. For rubberized fabrics requiring thick coatings with high degrees of penetration for better adhesion, a friction coating is applied first, followed by top or skim coating. The frictioning is done at a higher temperature and at a friction ratio of

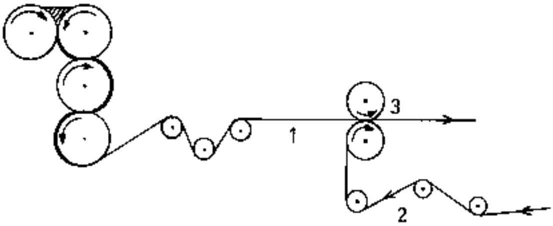


**Figure 3.25** In-line lamination: (1) sheet, (2) fabric, and (3) hydraulically operated laminating roll. (Adapted with permission from *PVC Plastics* by W. V. Titow. ©Kluwer Academic Publishers, Netherlands, 1990.)

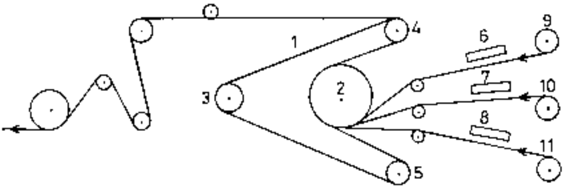


**Figure 3.26** Lamination against steel belt: (1) steel belt, (2) hot roll, (3) tension roll, (4, 5) guide rolls, (6, 7, 8) IR heaters, (9, 11) polymer sheets, and (10) textile sheet. (Adapted with permission from D. Zickler. *Journal of Coated Fabrics*, Vol. 8, Oct. 1978. ©Technomic Publishing Co., Inc. [16].)

1:1.5 to 1:2; for skim coating, the friction ratio is 1:1.1 to 1:2. The operating temperature of the calender depends on the polymer, however, it is generally between 60° to 150°C. For rubber coating, the temperature required is lower to prevent scorching. A three-roll inclined calender is suitable for rubber coating (Figure 3.27) [14].

Simultaneous coating on both sides in a "Z"- type inclined calender is shown in Figure 3.28 [14].

### 3.7.4 POST-CALENDERING SECTION

A block diagram of the post-calender section is given in Figure 3.29.

Embossing consists of a pair of rolls, one of them is a metal engraved roll to impart the pattern, and the other is a rubber-covered roll. The coated fabric from the calender is passed through the nip of the rolls for embossing. The diameter of the roll is determined by the size of the repeat pattern. The rubber roll may have the same diameter or be larger than the metal roll.

The thickness of the sheet is measured by $\beta$-ray gauge. The feed from the gauge is used to automatically control roll bending or crossing to correct the thickness variation.

The finished product is then passed over cooling cans to lower the temperature and reduce tack. The train consists of a set of cans that is cooled by circulating

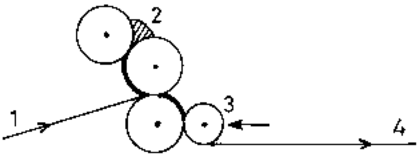


**Figure 3.27** Three-roll inclined calender for rubberized fabric: (1) fabric, (2) rubber bank, (3) laminating roll, and (4) coated fabric. (Adapted with permission from J. I. Nutter. *Journal of Coated Fabrics*, Vol. 20, April 1991. ©Technomic Publishing Co., Inc. [14].)

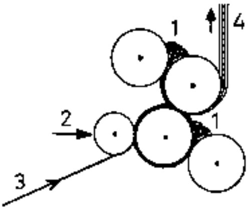


**Figure 3.28** Coating on both sides in a "Z" calender: (1) rubber bank, (2) laminating roll, (3) fabric, and (4) double-sided coated fabric. (Adapted with permission from J. I. Nutter. *Journal of Coated Fabrics*, Vol. 20, April 1991. ©Technomic Publishing Co., Inc. [14].)

cold water through its inner shell. The number of cans depends on the sheet thickness and the speed of operation [6,11].

The fabric is then wound up in rolls.

### 3.7.5 COATING DEFECTS

One of the major problems of processing vinyl compounds is plate-out. It is the transfer of a sticky deposit that sometimes appears on the rolls of the calender. The calender rolls, embossing rolls, and cooling rolls require frequent cleaning in order to prevent loss of output and surface defects. Plate-out occurs from hot PVC stocks due to an incompatibility of some the constituents of the compound, particularly certain lubricants and stabilizers.

Other surface defects, like discoloration, surface roughness, crowfeet marks, bank marks, etc., are caused by diverse factors, such as excessive heat on the compound, nonuniformity of the stock temperature, improper dispersion of particulate additives, and undergelation of PVC [11,15].

### 3.7.6 COMPARISON WITH OTHER COATING METHODS

The calendering process imparts an even coating within a range of about 0.1–1.5 mm. The upper limit is restricted by the formation of blisters on the coated fabric due to entrapment of air in the rolling bank. For lower thickness, the load requirement on the calender is heavy, moreover, at lower thickness, void formation takes place. An extruder can produce thicker gauges suitably; but, in

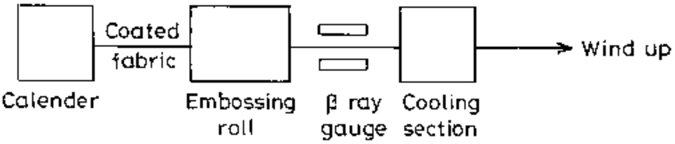


**Figure 3.29** Post-calender section.

thinner gauges, there is abrupt variation in thickness [6,13]. The advantage of the calender over an extruder is its (a) high production rate, (b) better product thickness control, and (c) suitability for continuous operation. Compared to fluid coating by spreading, calender coating is a much cleaner process, does not require removal solvents, and uses raw materials that are lower in cost, particularly for vinyl compositions. The cost of calender equipment is, however, higher than either extrusion or spreading [6,14].

### 3.7.7 ZIMMER COATING

The Zimmer coater (Zimmer Plastics GmbH, Germany) and Bema coater (A. Manrer, Switzerland) are calender-like machines that have been specifically designed for coating fabrics. Thermoplastic polymers in the form of granules, dry powder, or plastic stock are the feedstock for these machines. These machines are less expensive and require lesser manpower and space than a calender.

The Zimmer coater (Figure 3.30) consists of two melt rolls (1) and(2). The rolls are made of diamond-polished, deep-hardened high-grade steel. The gap between the two rolls is adjusted hydraulically. The material is fed at the nip of the rolls, the temperature of which is about 200°C. The coating material melts and adheres to roll (2) which runs at a higher speed and is maintained at a higher temperature. After heating by passage through one or more preheater rolls and IR heaters, the textile substrate is fed between the nip of roll (2) and the backup roll (3). After coating, the hot laminate is either smoothened or embossed by

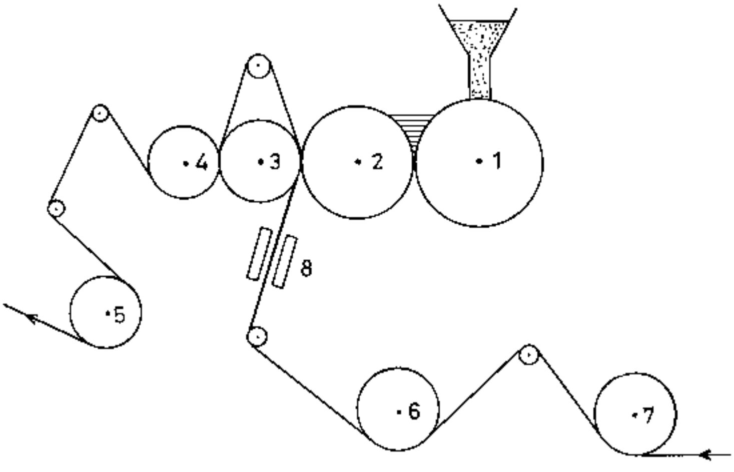


**Figure 3.30** Zimmer coater: (1, 2) melt rolls, (3) backup roll, (4) embossing roll, (5) cooling roll, (6) substrate preheat roll, (7) fabric roll, and (8) IR heaters. (Adapted with permission from D. Zickler. *Journal of Coated Fabrics*, Vol. 8, Oct. 1978. ©Technomic Publishing Co., Inc. [14].)

an embossing roll (4). The coated material is then cooled by cooling drums and wound [16].

## 3.8 HOT-MELT COATING

### 3.8.1 EXTRUSION COATING

In this process, an extruder converts solid thermoplastic polymers into a melt at the appropriate temperature required for coating. This melt is extruded through a flat die vertically downward into a nip of the coating rolls (Figure 3.31).

The two rolls at the nip are a chromium-plated chill roll and a soft, high-temperature-resistant elastomer-coated backup roll. The chill roll is water cooled. The heat transfer should be adequate to cool the coated fabric so that it can be taken out of the roll smoothly. Means are provided to adjust the position of the die and the nip in three directions. The chill roll may be polished, matt finished, or embossed. Lamination can be accomplished by introducing a second web over the chill roll. The molten resin acts as an adhesive. Extrusion coating is especially suitable for coating polyolefins on different substrates. Because polyolefins can be brought down to low viscosity without risk of decomposition, very high coating rates are achieved, and as such, the process is highly economical. For other polymeric coatings like PVC, PU, and rubber, this process does not yield uniform coating across the width, particularly at thickness below 0.5 mm.

In this method, the coating width can be adjusted by reducing the aperture of the die by insertion of shims. Thus, it is possible to coat different widths for a given die, however, the coating width cannot be changed while coating. Moreover, the process does not permit easy changeover of material. This restricts its use for coating industrial fabrics [16]. A view of an extrusion coating plant is shown in Figure 3.32.

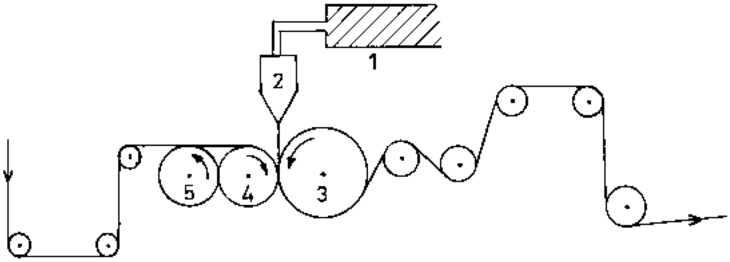


**Figure 3.31** Extrusion coating: (1) extruder, (2) die, (3) chill roll, (4) backup roll, and (5) pressure roll. (Adapted with permission from *Encyclopedia of Polymer Science & Engineering*, Vol. 3, 2nd Ed. 1985, ©John Wiley & Sons.)

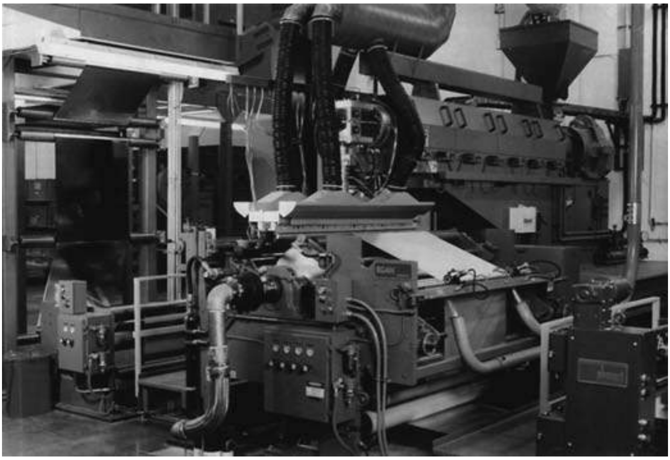


**Figure 3.32** Extrusion coating plant. Courtesy Egan Davis Standard Corp., U.S.A.

## 3.8.2 DRY POWDER COATING

There are two processes in this category, scatter coating and dot coating [17,18]. These processes are used for coating fusible polymer powder. They are polyethylene, polyamide, polyester, and EVA. The products are used for fusible interlinings, carpet backcoating, especially in the automotive industry for contoured car carpets, and for lamination. The process lends itself to the lamination of two different types of webs, e.g., textiles to foam. Laminates produced by this process retain their flexibility and porosity. Scatter coating is also used for fiber bonding of nonwovens.

In the scatter coating process, polymer powder of 20–200 $\mu$m size is spread uniformly onto a moving textile substrate. The web is then passed through a fusion oven and calendered. The method of scattering the powder may be a vibrating screen or a hopper with a rotating brush arrangement, the latter being more accurate. The coating weight is dependent on feed rate and web speed (Figure 3.33).

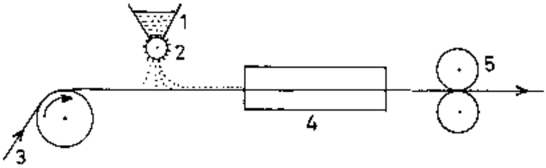


**Figure 3.33** Scatter coating: (1) hopper, (2) rotating brush, (3) fabric let off, (4) IR heater, and (5) two-roll calender. (Adapted with permission from *Encyclopedia of Chemical Technology*, Vol. 6, 3rd Ed. 1979, ©John Wiley & Sons.)

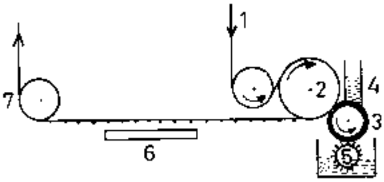


**Figure 3.34** Powder dot coating: (1) fabric, (2) oil-heated drum ~200°C, (3) engraved roll, (4) powder feed, (5) cleaning brush, (6) IR heaters, and (7) chilled drum. (Adapted with permission from C. Rossito. *Journal of Coated Fabrics*, Vol. 16, Jan. 1987. ©Technomic Publishing Co., Inc. [18].)

In the powder dot coating process, a heated web having a surface temperature slightly less than the melting point of the polymer is brought in contact with an engraved roller embedded with dry powder. The web is thus coated with a tacky polymer powder in a pattern dependent on the engraving. The engraved roller is kept cool to prevent the polymer from sticking to the roll. A schematic diagram is shown in Figure 3.34 [18].

A new method for printing a hot-melt on a web has been recently described by Welter [19]. In this process, hot molten polymer contained in a trough attached to an engraved roller is picked up by the latter and is pressed into a running web, with the pressure coming from a backup roll. Lamination can also be achieved with another web in the same machine. Various patterns can be printed on the web, including the conventional dot and computer dot printing (Figure 3.35).

Hot-melt coating offers certain advantages over fluid coating. These are as follows [20]:

(1) It does not pollute the environment as no volatiles are emitted.
(2) The rate of production is higher, as it is not dependent on rate of drying/curing.
(3) The plant space requirement is smaller as drying ovens are not required.
(4) The energy consumption is low.
(5) It has better storage stability than fluids.

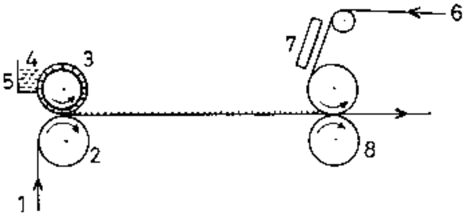


**Figure 3.35** Engraved roller melt printing: (1) fabric, (2) backup roll, (3) engraved roll, (4) polymer melt, (5) trough, (6) second web, (7) preheater, and (8) calender. (Adapted with permission from C. Welter. *Journal of Coated Fabrics*, Vol. 24, Jan. 1995. ©Technomic Publishing Co., Inc. [19].)

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