CHAPTER III

PVA SPONGE TECHNOLOGY

3.1 PVA SYNTHETIC SPONGE

Foamed plastics differ in their density, that is, in amount of gaseous "filler" . The denser foams are stronger and the lighter ones weaker but more compressible. They differ in the nature of the polymer matrix and in their cell structure. So called expanded polymers have closed cells, that is, the cells of gas are discrete. Sponges are open celled and have predominantly interconnecting cells[3]. Many foams can be produced in both forms. In general, open cell structures are flexible while closed cell structure are rigid, but there are many exceptions.

The form actually depends on cross-link density which is defined as the molecular weight per cross-link. A cross-link density of 800 - 2000 yields a semi rigid foam, and a density of 300 - 800 is needed for a rigid foam[3].

The cell structure is largely determined by the method of expansion and the point in the curing of the polymer when gas bubbles form. If the polymer is foamed while in the liquid state, gas can migrate easily and homogeneously through the mixture, creating open cell structure.And open cells also result from mechanical frothing and from other less widely used techniques. If the polymer is partly cured, however, the gas bubbles lose their mobility and a closed cell structure results.

PVA synthetic sponges or PVA foams are rigid, open cell materials that possess good strength properties at low densities. Their abrasion resistance and resiliency when wet make them excellent sponges. The supersoft, low density polyvinyl alcohol-formaldehyde condensate foam has been suggested for various applications, such as

synthetic sponges or chamois, skins, mops, and washcloths. The strong, resilient, hydrophilic material has been investigated as surgical pads ((National Institutes of Health), bandage pads for treatment of burns (Johnson & Johnson), and surgical implants (National Institutes of Health). Polyvinyl - formal reported in a British patent issued to Revertex Ltd.; the foaming technique was later refined in the United States.

As with the other condensation foam systems, the mechanical properties depend on (a) the structure of the resin, (b) the density of the composite, and (c) the cell structure. The PVA sponge can be made in a variety of densities, from 0.019 to 0.2 g/cm^3. The foams have the capacity to accept large quantities of fillers (800-1200 wt %) without extensive collapse. This characteristic is in keeping with the behavior of the original resin.

The uses of PVA sponges include intake filters for compressors, engines and air conditioners, and filters for all kinds of industrial oils and chemical, water and paints. Other uses are as domestic washing sponges and other absorbent cloths, industrial dehydrating rollers, pant rollers and acoustic filters.

These sponge materials are prepared by reacting the formaldehyde with polyvinyl alcohol so that only a portion of the hydroxyl groups of the alcohol esters into the reaction.

3.1.1 PHYSICAL PROPERTIES

PVA sponge is a synthetic essentially composed of polyvinyl alcohol. It possesses a three dimensional open cell structure similar to that of natural sea sponges. All of its cells are interconnected, not independent. Major advantages of this physical structure are its high filtering efficiency, its ability to be reused after cleaning, and its impressive retention and wicking properties.

PVA sponge will absorb up to12 times its dry weight in water. When saturated with water, it becomes flexible and soft like natural sea sponge. The wet volume is

about 20% greater than the dry volume. PVA exhibits mechanical strength and abrasion resistance equal to or greater than any other synthetic sponge material. Pore size and shape can be vary to meet specific applications. Wet PVA sponge will withstand temperatures to 90°C without plastic deformation. PVA is pure white. It can be pigmented in any color and to a high of color-fastness.

3.1.2 CHEMICAL PROPERTIES

During the manufacture of PVA sponge, a water-soluble porous structure is chemically insolubilized. The material will withstand the action of dilute acids, strong alkalis and solutions of common detergents. Organic solvents do not, as a rule, effect the sponge unless they are water-miscible and are applied mixed with 30-60% water. In that case the sponge will swell and be weakened. Thorough washing in water will return the sponge to its original state. PVA is also not compatible with Nikel Sulphate solutions.

PVA sponge behaves in water as a negatively charged colloid and will strongly adsorb metallic cations such as copper or ion. In fact, it acts like an ion exchange resin in this respect. It also has strong affinity for cationically charged organic ions of the quaternary ammonium type. PVA sponge, itself, will neither support the growth of bacteria nor molds, nor will it destroy those organisms. Foam packaged wet should be treated chemically to bacteria or mold growth. Rust stains may be removed in the same way as they are from cotton using a solution of oxalic acid or citric or tartaric acid. Sodium hypochlorite solution (domestic bleach) degrades the sponge.

3.2 METHOD OF PREPARATION

PVA sponges can be prepared by condensation or by dispersion. In condensation process the final gas phase of the composite is present initially as a

separate species which agglomerates to form bubbles. Two common methods of foaming by condensation are used extensively in the industry : (a) the solvated gas process, which depends upon pressure differential for dissolution of gases in liquids, and (b) the gas-releasing agent process.

PVA sponges can be prepared by both methods. Typical examples of the latter process are (a) the generation of CO_2 or H_2 by the chemical reaction of carbonates or metal powders with the acidic condensation catalysts[4] and (b) the use of chemical blowing agent that liberate the expanding gas under the influence of heat.

Polyvinyl-formal foams have been prepared using dipotassiumdiazomethionate [5], N-nitroso-β-amino ketones, and sodium borohydride[6] as blowing agents. In all these cases, long-term foam stability depends on the viscosity of the polyvinyl alcohol aqueous solution and the polyvinyl alcohol - formaldehyde condensate. The main function of the blowing agent is that of pore former.

In the dispersion method of producing PVA sponges the gas initially exists as a bulk phase. Volumes of gas are introduced into the aqueous system containing polyvinyl alcohol, surfactant, formaldehyde, and strong acid, by the use of high speed stirrers. Although monodisperse foams (i.e. bubbles of identical structure) can be made by forcing gas through a capillary into the liquid and by using special equipment, the most economical method of generating a PVA sponge before cure is to beat air into the reaction mass with a high speed stirrers or propeller[4][7].

3.2.1 METHODS OF DISSOLVING POLYVINYL ALCOHOL

The solubility of polyvinyl alcohol are depends on the degrees of polymerization and hydrolysis[8]. The solubility of partly hydrolyzed grades of polyvinyl alcohol is less dependent on temperature than that of completely hydrolyzed grades. The formation of lumps when polyvinyl alcohol is added to water should be prevented as far as possible. The basic operations for each grade are as follows.

A. Fully hydrolyzed grades

The concentration of fully hydrolyzed grades of polyvinyl alcohol that can be dissolved in water and effectively frothed to maximum volume is limited by the viscosity that can be handle in mixing and application equipment rather than by a saturation point [7].

Polyvinyl alcohol is added to water at room temperature (about 15-25°C) with continuous stirring. Since fully hydrolyzed grades of polyvinyl alcohol dissolve hardly at all at room temperature, no lumps will be formed. The mixture is then heated, and by the time the temperature reaches 97-98 $^\circ$C, the polyvinyl alcohol is completely dissolved. However, with poor stirring equipment, continual agitation at these temperature may be required to achieve solution.

B. Partly hydrolyzed grades

Partly hydrolyzed grades of polyvinyl alcohol are liable to form lumps when they are added to water ; grades with high degrees of polymerization are especially prone to this. To avoid this, and obtain rapid and easy solution, water temperature during addition, the rate of addition and the stirring must be carefully controlled, especially with high concentrations :

(a) The water temperature should be 25°C or less when the polyvinyl alcohol is added.

(b) The charging rate should be as low as possible, within the permissible time of the operation.

(c) The polyvinyl alcohol slurry should be agitated for 10 -15 min without raising the temperature.

(d) The temperature should be increased to about 95 $^\circ$C to reduce the dissolving time. However, polyvinyl alcohol of a low degree of polymerization dissolves at lower temperature.

3.2.2 METHODS OF MAKING PVA SPONGE

The PVA sponge is formed by a plurality of steps wherein the process conditions such as reaction time, temperature, reactant ratios, mixing procedure, etc. are carefully controlled. Polyvinyl alcohol and formaldehyde are reacted in aqueous system having air bubbles uniformly dispersed therein in the presence of an inorganic acid catalyst. The reaction is carried out in the presence of a non-toxic surfactant which is added in order to aid in forming and stabilizing the gas bubbles formed uniformly throughout the reaction system. The reaction is carried out in two stages.

In the first stage, the polyvinyl alcohol catalyst and wetting agent are combined and are subjected to agitation to entrap air bubbles uniformly throughout the reaction system and to form a froth having a volume between 150 - 400% of the volume of the reactants in an unfrothed condition. During the second stage, reaction between the polyvinyl alcohol and the formaldehyde is carried out while mixing is maintained during the polymerization to achieve a more fibrous thin walled cell geometry and uniform pore distribution. In this stage, reaction is effected until a stiff, pourable, or easily extrudable froth, which is sufficiently stable as to substantially retain the size and distribution of gas bubbles, is formed as a result of the agitation. After forming the froth, the reactants are cure in a mold at elevated temperature in the second stage.

3.3 CHEMISTRY OF FOAM FORMATION

The standard recipe for preparing sponges from polyvinyl alcohol-aldehyde condensation reactions involves four major reactants in an aqueous medium :

1. Polyvinyl alcohol resin

2. Formaldehyde

3. Acid

4. Surfactant

3.3.1 PVA RESIN

Polyvinyl alcohol (PVA) is a water sensitive polymer that is white to yellow in color . PVA is an unusual polymer in that it is not manufactured from the vinyl alcohol monomer. The theoretical monomer, $CH_2=CHOH$, rearranges to acetaldehyde, $CH_3CH=O$. Consequently, the polymer, which is shown below, is obtained by the hydrolysis of polyvinyl acetate[9].

$$-(- CH_2CHOH -)_n-$$

The properties of PVA are primarily determined by the molecular weight of parent polyvinyl acetate and the extent of hydrolysis of polyvinyl alcohol. The molecular weight of PVA ranges from a few thousand to almost one million. The degree of hydrolysis, or how many of the acetate groups are hydrolyzed to hydroxyl groups, determined the properties of the resulting resin.

Polyvinyl alcohol with a small percentage of the acetate groups hydrolyzed has greater flexibility, dispersing power, water sensitivity, and adhesion to hydrophobic surface when compared to the highly hydrolyzed polymer. Similarly, polyvinyl alcohol with a small percentage of hydroxyl groups has increased to tensile strength, solvent resistance, solubility in water with resistance to additional hydrolysis, and adhesion to hydrophilic surfaces in contrast to the properties of the polymer with less than 80 percent hydrolysis.

Polyvinyl alcohol reacts with aldehydes, in the presence of an acid catalyst, chiefly forming six-membered intramolecular acetal rings between the adjacent intramolecular hydroxyl groups, as shown in Figure 3.1(a). However, there is also the possibility of forming intermolecular cross linking, as shown in Figure 3.1(b). The formation of the five-members rings shown in Figure 3.1(c) is also possible.

$-CH_2CHCH_2CHCH_2-$
      | |
    OH   OH

$-CH_2CHCH_2CHCH_2-$
      | |
    O H O
     \ | /
      C
      |
      R

(a)

$-CH_2CHCH_2CHCH_2-$
      | |
    OH   OH

OH   OH
 | |
$-CH_2CHCH_2CHCH_2-$

+ RCHO

$-CH_2CHCH_2CHCH_2-$
      | |
    OH   O
           |
    RCH
      |
    OH   O
     | |
$-CH_2CHCH_2CHCH_2-$

(b)

$-CH_2CH\text{-}CH\ CH_2CH_2CH-$ + RCHO
    | | |
  OH OH   OH

$-CH_2CH\text{-}CHCH_2CH_2\text{-}CHCH_2-$
    | | |
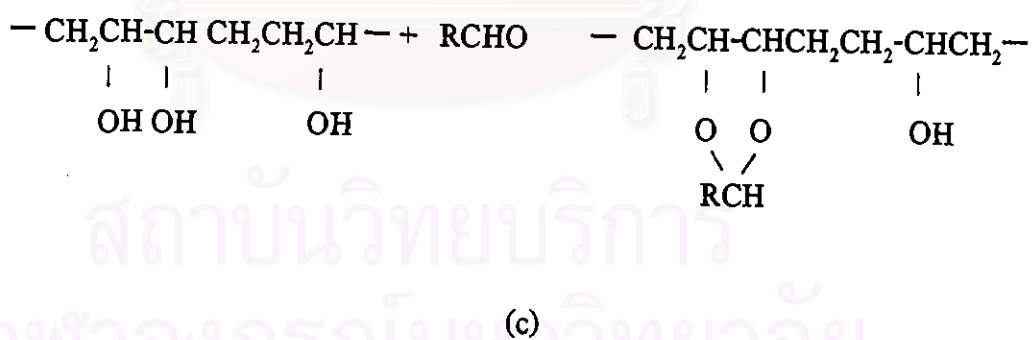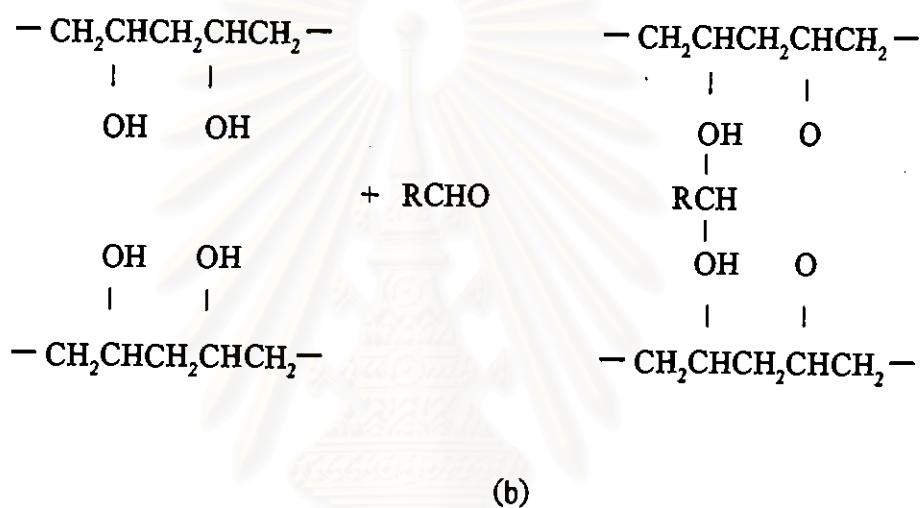   O O   OH
     \ /
    RCH

(c)
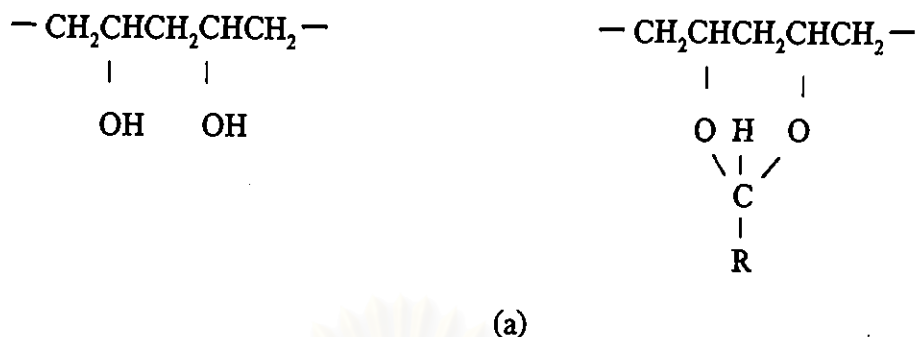
Figure 3.1 Acetalization of polyvinyl alcohol[10]:

    (a) Intramolecular acetalization of 1,3 glycols in polyvinyl alcohol

    (b) Intermolecular acetalization

    (c) Intramolecular acetalization of 1,2 glycols in polyvinyl alcohol

Commercial polyvinyl alcohol contains not only the 1,3 glycol bonds, but also 1-2 percent of 1,2 glycol bonds.

3.3.2 FORMALDEHYDE

Formaldehyde is preferred because it is very reactive and can produce a cured foam in a relatively short time. Also, it is water soluble and can be easily removed by simple washing techniques. The formaldehyde employed herein comprises aqueous solutions of formaldehyde. It has been found that other sources of formaldehyde, e.g. paraformaldehyde or hexamethylenetetramine, residues of which are toxic, and they are more difficult to remove from the sponge product prior to use.

The materials that form the basic structure of polyvinyl - formal polymers are condensates having the following general structure[4] :

$$\left[\begin{array}{c} CH_2CHCH_2CH \\ | \quad\quad | \\ OH \quad OH \end{array} \right]_n + nCH_2O \xrightarrow{H^+} \cdots$$

This reaction represents the simplest case. The polyvinyl alcohol is cross linked with formaldehyde to convert the water-soluble resin into a strong, cross linked network insoluble in aqueous solution but extremely hydrophilic. The basic stoichiometry of the polyvinyl alcohol - formaldehyde reaction requires 2 equivalents of vinyl alcohol to react with 1 mole of formaldehyde to produce complete cure.

3.3.3 ACID

Any primary acid can be used as the acid catalyst. The main requirement is that the acid catalyst have a dissociation constant of at least 10^{-2} and that it does not react or interfere with the reaction and foam stability[10].

Any inorganic acid catalyst employed in the process to effect reaction of the formaldehyde and the polyvinyl alcohol. Organic acids are not useful in the process because they are more difficult to remove from the sponge product and if present in the sponge product would present a serious toxicological problem.

3.3.4 SURFACTANT

Surfactants do not only help foaming, they control bubble size, uniformity, and configuration and stabilize the foamed liquid polymer for short period until the polymer solidifies, gels, or cross-links and can support itself. They do this by lowering the surface tension, by causing liquid to draw towards thinning point on a bubble wall, by lending resilience and surface plasticity to the bubble wall, and by reducing the natural migration of liquid from the thin cell walls to the cell struts [3].

The main requirements of a surfactant are that it functions effectively in strong acid media and is a high former. The surfactants employed herein are those which promote formation of a stable froth in small quantities and do not present a serious toxicological hazard.

The wetting agent or surfactants that can be used in the preparation of PVA sponges are presented in Table 3.1.

Table 3.1 The wetting agent used in the preparation of PVA sponges[11].

Surfactant	Manufacturer	Chemical Name
Renex 31	Atlas Chemical	Polyoxyethylene tridecyl ether
Ultra Wet 40K	Arco Chemical	Alkyl aryl sulfonate
Orvies WA	Proctor & Gamble	Sodium lauryl Sulfate
Igepon	Antara Chemical	Sodium N-methyl-N-oleoyl taurate
Triton X – 100	Rohm & Haas	Alkyl aryl poly oxyethylene alcohols

The main requirements of a surfactant are that it functions effectively in strong acid media and is a high former. The surfactants employed herein are those which promote formation of a stable froth in small quantities and do not present a serious toxicological hazard.

3.4 EFFECT OF PROCESS VARIABLES ON FOAM PROCESS

Within the polyvinyl formal sponge process each of the component fits into a special category. Each part of the recipe has a particular function ; for example, the concentration and structure of the surfactant play a major role in determining froth volume (primarily by lowering the surface tension of the composite solution). The molecular weight and elasticity of the polyvinyl alcohol is major factor in determining the ultimate density of the foam, the degree of shrinkage, etc. Since the degree of cross-linking of polyvinyl alcohol with formaldehyde depends on formaldehyde concentration, temperature, and concentration of acid catalyst, one would also expect these components to influence degree of shrinkage between froth and finished foam, final foam density, and strength final product.

3.4.1 <u>ROLE OF SURFACTANT</u>

In the Polyvinyl alcohol-formaldehyde foam system the foam must be stabilized for a critical time period until the condensation reaction increases the molecular weight of the polymer to point where the resin is in soluble and the foam is self-supporting. The initial step in PVA sponge processing is to produce a stable froth by whipping or beating air into the mixture. Stable froths cannot be produced without the use of highly surface active agents. On the basis of published reports and reviews, one would predict that the volume of a froth would be determined by the surface tension of the solution and the elasticity and viscosity of the film or lamella within the foam composite.

This evidence emphasizes that the concentration and structure of the surfactant play the major role. Therefore, the dominant physical phenomenon that controls froth volume is one of surface tension. Data have been presented that a given resin formulation can be foamed to a maximum froth volume. If adds more water or surfactant to go beyond the maximum volume the froth collapses after a short time. Froths made at or below the maximum volume lead to stable structures ; larger-volume froths show extensive collapse and shrinkage.

3.4.2 <u>ROLE OF PVA RESIN</u>

Once maximum froth volume has been attained, the phenomena of film drainage and foam aging proceed. The rate of drainage depends on viscosity and, in the special PVA-CH$_2$O case, on solubility. This means that the more viscous solutions should be able to maintain froth stability and therefore produce the lowest density foams with least shrinkage. One would, therefore, predict that foam stability depends on the rate and degree of cross linking.

Processing and foam stability (as measured by lowest density), therefore, are a result of the molecular weight of the starting resin. As the molecular weight (solution

viscosity) of the resin increases, the froth is more stabilized and produces the lowest density foams (less collapse).

3.4.3 ROLE OF CROSS-LINKING AGENT

The cross-linking agent, formaldehyde, maybe supplied as a gas, a water solution of a gas, paraformaldehyde, hexamethyllenetetramine, etc. Any reactant that yields formaldehyde (i.e. methylal) under the conditions of the reaction in order to react with polyvinyl alcohol is acceptable.

Other aldehydes or dialdehydes can be used in similar manner. For example:

$$2 \text{---CH}_2\text{CH--CH}_2\text{CH ---} \quad \overset{O}{\underset{\parallel}{}} \quad \text{--- CH}_2\text{CH -- CH}_2\text{CH ---}$$

$$\underset{\text{OH}}{|} \quad \underset{\text{OH}}{|} + O = C(CH_2)_n\text{--CH} \longrightarrow \quad \underset{O}{|} \quad \underset{O}{|}$$

$$n = 1\text{-}6$$

$$\begin{array}{c} \text{CH} \\ | \\ (CH_2)_n \\ | \\ \text{CH} \\ \diagup \quad \diagdown \\ O \qquad O \\ | \qquad | \\ \text{--- CH}_2\text{CH} \qquad \text{CH ---} \\ \diagdown \qquad \diagup \\ CH_2 \end{array}$$

The stiffness of the froth will determine its volume to some degree. This is a minor effect as long as the mole ratio of cross linking agent to polymeric alcohol is kept above 0.5. This phenomenon could be attributed to solubility because the lower molecular weight resins require more formaldehyde to react to produce insoluble gel than the higher molecular weight resins. Therefore, at low concentrations of formaldehyde the low molecular weight resins itself is being drained off during foam aging.

3.4.4 EFFECT OF WATER AND ACID

The most stable froth is one which is as viscous as possible. Increasing the amounts of water or acid or both causes an increase in froth volume. If the froth volume is increased too greatly, the froth may either give rise to weak product or partially collapse before cure.

3.5 EFFECT OF PLASTICIZERS

Polyvinyl alcohol forms tough, tear-resistant foams with good abrasion resistance. The tensile strength of the parent polymer and the expanded structure is high in relation to other plastics and especially good when compared to other water soluble polymers. The tensile strength, elongation, hardness, and tear resistance of the composites vary with plasticizers content and relative humidity.

When the sponge material are dry, however, they partially shrink and become hard and rigid. As soon as water is reintroduced into the structure, the foam softens. In these cases, the water is acting as a migratory plasticizer. Although the process is completely reversible and involves no less in properties, the hardness of the dry foam for many sponge applications is not desirable.

The use of non-migratory plasticizers has been suggested as a method for improving and extending the flexibility range of the foam. Foams containing non-migratory plasticizers can be maintained in a soft and resilient state at low humidifies. The finished foam can be soaked in any high molecular weight or high boiling polyhydroxy compound, such as glycerine or polyethylene glycol. The foam is subsequently spin dried. The deficiency of these materials is that invariably they are at least slightly soluble in water or detergent mixtures. Therefore, the longevity of their effect is limited.