CHEMICAL BINDERS AND AUXILIARIES

Michèle Mlynar
Rohm and Haas Company
Specialty Polymers
Spring House, PA

Abstract

Nonwoven fabrics are utilized in a wide range of end use applications: disposable, durable, and industrial. While the use of non-chemical bonding has grown in recent years, the application of a latex binder remains a popular bonding method for imparting integrity, strength, and durability to nonwoven fabrics. There are many types of emulsion polymers used in the nonwoven industry due to their diverse nature. In this paper, we will attempt to introduce the various types and offer reasons for their use in this industry.

Introduction

Although the use of binderless technologies has increased in recent years, the use of chemical binders remains one of the most versatile and useful ways of manufacturing nonwoven webs. There are many different classes of chemical binders to choose from which allows the manufacturer to tailor make a nonwoven web to meet the desired performance characteristics. Because of this, chemical bonding is used to make nonwoven webs for myriad applications.

Latex Binder Market for Nonwovens

The market for chemical or latex binders (emulsion polymers) used in the production of nonwoven fabrics is very large. By one estimate, the binder consumption for nonwoven fabrics is approximately 600 MM wet pounds for conventional and highloft nonwovens. Binder reinforced nonwoven fabrics are utilized in a variety of end use applications including:

Conventional Nonwovens	Highloft Nonwovens
Wipes and	Furniture
Roofing	Bedding
Medical Nonwovens	Apparel
Interlinings	Filtration
Filters	Automotive Trim
Cover Stock	Pillows
Carrier Fabrics	
Coated Fabrics	
Automotive Trim	

There is a host of other small applications for both types of nonwoven fabrics that are not included on this list. In addition, this does not take into account the fiberglass insulation nonwoven market which is huge. It also requires a reinforcing chemical binder to obtain desired performance properties.

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Alternative Nonwoven Bonding Technology

There are many ways to bond nonwoven fabrics. In the case of thermally bonded nonwovens, heat is used to cause the melt fusion of fibers which then holds the nonwoven web together. With spunbonded and meltblown nonwovens, molten resin is sprayed onto a conveyor to produce a nonwoven web. Hydroentangled or spunlaced nonwovens rely on high pressure water jets to entangle fibers thereby forming a web with good strength and soft hand. Powder bonding is still another method for producing nonwovens. With powder bonding, a powdered adhesive is applied to the unbonded web and then the web is heated so that the powder adhesive melts and bond the fibers together.

With chemical bonding, a latex is applied to the unbonded web and then the web is heated to remove the water. The latex tends to orient itself where the fibers touch one another and so a strong bond is formed between fibers at the crossover points.

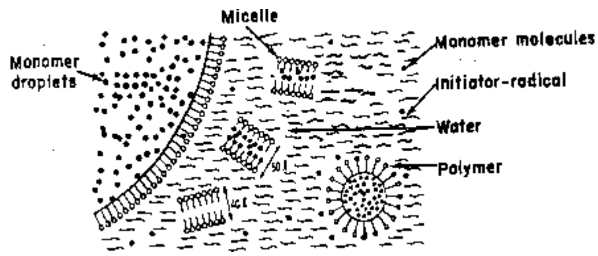
Reasons for Latex Binders

The popularity of latex binders used to impart integrity and strength to nonwoven fabrics has its foundation built on four cornerstones:

Low viscosity - ease of application
High molecular weight - toughness
Binder variety and versatility
Low cost and economy of use

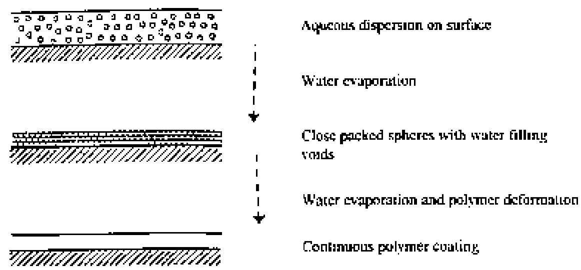
What Is a Latex Binder?

Simply, a latex binder is the polymerization product of monomers and initiators, which is stabilized in water through the use of surfactants [2]. It is a colloidal polymer dispersion (also called an emulsion polymer).



Schematic Representation of an Emulsion Polymerization H.Gerrens, Ber. Bunsenges. Physik. Chem. **67**, 741 (1963).

As the water is driven off, the polymer particles coalesce to form a tough film. An idealized model of the film formation process was depicted by Zdanowski and Brown in 1958.[3.]



Types of Latex Binders

Variety is key in nonwoven production. As indicated, the nonwoven fabric industry is diverse with many different applications. Each application has its own specific functional requirements for the latex binder. As a result, there are many types of binders used in the industry, including the following major classes:

- Acrylic
- Styrene acrylates
- Vinyl acetate
- Vinyl acrylic
- Ethylene vinyl acetate
- Styrene butadiene rubber
- Polyvinyl chloride
- Ethylene vinyl chloride

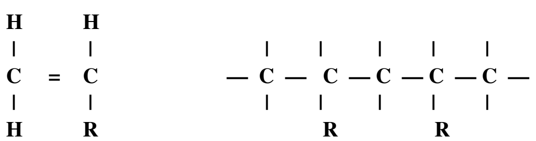
To completely understand why there are so many polymer types used in bonding nonwoven fabrics, we must consider the factors which differentiate binder performance. These are as follows:

- Polymer Composition
- Functional Groups
- Surfactant
- Polymerization Process

Polymer Composition

A vinyl monomer unit is the basic building block of all polymers and copolymers used in bonding nonwoven fabrics. The basic vinyl monomer unit consists of two carbons joined by a double bond capable of a free radical polymerization. The result is a high molecular weight polymer dispersed in water and stabilized by a surfactant. Vinyl monomers are differentiated by the "R" group which is bonded to one or more of the carbon atoms.

Basic Monomers/Polymers

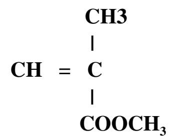


Vinyl Monomer **Vinyl Polymer**

Monomer/Polymer Differences

Name	**R**
Ethylene	**H**
Styrene	C_6H_5
Vinyl Acetate	**O** ‖ **O – C –** CH_3
Vinyl Chloride	**Cl**
Ethyl Acrylate	**O** ‖ COC_2H_5
Butyl Acrylate	**O** ‖ COC_4H_9
Acrylonitrile	**CN**

Methyl Methacrylate



The selection of monomer units influences the glass transition temperature (Tg) of the resultant polymer or copolymer. Simply, the lower the Tg, the softer the polymer is. Some of the common monomers used in the latex binders used for nonwovens include:

	Tg (°C)
Ethylene	-125
Butadiene	-78
Butyl acrylate	-52
Ethyl acrylate	-22
Vinyl acetate	+30
Vinyl chloride	+80
Methyl methacrylate	+105
Styrene	+105
Acrylonitrile	+130

Backbone composition also influences dry strength, wet strength, elasticity, solvent resistance and long term aging characteristics. We can illustrate how the selection of monomer can affect the wet strength of the polymer is by comparing their hydrophilic/hydrophobic nature.

Hardness versus Hydrophobic/Hydrophilic Nature

Monomer		**Tg (°C)**
Styrene	Most Hydrophobic	+105
2-Ethyl Hexyl Acrylate		- 85
Butyl Acrylate		- 52
Methyl Methacrylate		+105
Ethyl Acrylate		- 21
Methyl Acrylate		+ 8
Acrylonitrile		+130
Vinyl Acetate	Most Hydrophilic	+ 29

Ideally, when designing a binder for maximum wet strength you would select styrene over vinyl acetate. However, when you are considering solvent resistance, acrylonitrile would be the choice because of its oleophobic nature.

Elasticity is generally related to the softness of the polymer and its molecular weight. Therefore, binders containing butadiene, butyl acrylate and 2-ethyl hexyl acrylate would be more elastic than a polymer containing vinyl chloride and methyl methacrylate. An example of a very elastomeric copolymer is the combination of acrylonitrile and butadiene, commonly called nitrile rubber.

Long term aging properties are a concern in many nonwoven fabric applications. Butadiene, chlorinated monomers, and vinyl acetate all have a tendency to degrade or yellow with age or on exposure to heat and light. SBR latices, for example, require the addition of an antioxidant to reduce the aging phenomenon caused by oxidation of the residual double bond in the polymer backbone. Bluing agents, pigments or dyes are common additives to mask yellowing tendencies.

Functional Groups

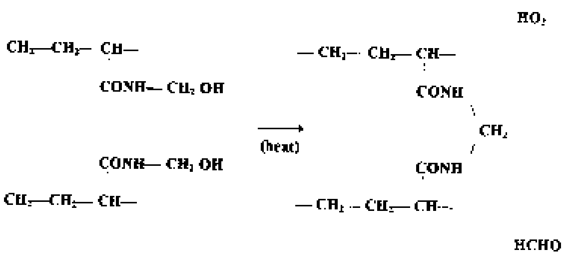
While the backbone composition of the polymer is the key component in determining latex binder performance, the incorporation of functional groups can enhance the performance by improving the following properties:

Durability
Solvent Resistance
Adhesion
Elasticity
Tack
Mechanical and Emulsion Stability

Some of the common functional groups included in latex binders used for nonwoven fabrics are:

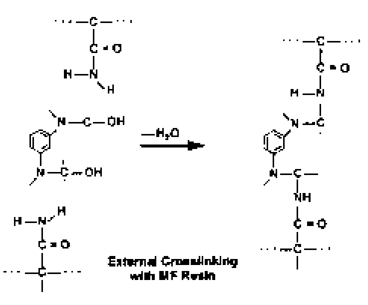
Acrylic Acid
Itaconic Acid
Methacrylic Acid
Acrylamide
N-Methylol Acrylamide

The addition of carboxylic acid to the polymer improves mechanical and emulsion stability, aides adhesion, reduces tack and provides a reaction site for external crosslinking resin additives. The addition of acid can also impart self-thickening properties to the latex binder.



Crosslinking Mechanism

Self-reactive latex binders are produced by incorporating n-methylol acrylamide (shown above). When subjected to sufficient heat (300-320°F) under acid conditions, this functional group will self condense to form a strong three-dimensional structure bridging polymer chains and greatly increasing molecular weight. Crosslinking improves the performance of the binder by imparting wash durability and improving wet strength, solvent resistance and resiliency.



External Crosslinking with MF Resin

Polymers containing acid or acrylamide functionality can react with external crosslinkers including melamine formaldehyde resins to improve durability and toughness (see above). Both n-methylol acrylamide and melamine crosslinking processes occur during the final step in the production of bonded nonwovens. It is called the curing step. While the oven could be set at temperatures for crosslinking, it is extremely important that the actual latex binder "dried" films reach the temperatures required to crosslink. The cure temperature for self-reactive emulsions can be reduced to 280°F by adding a latent acid catalyst, such as ammonium nitrate. The melamine formaldehyde reaction requires 260-280°F. The disadvantage of both reactions is the generation and release of formaldehyde, a known carcinogen.

This has caused binder manufacturers to develop latex binders with lower levels of free-formaldehyde in the latex and binders which release less formaldehyde during the curing process. Nonwoven manufacturers are also redefining finishing formulations, reducing or eliminating the use of melamine formaldehyde resin in their finishes. There are also a growing number of latex binders which do not contain or generate formaldehyde which perform as well as conventional formaldehyde-containing latexes. As a result, latex binders are sometimes categorized by reactivity.

Non-Crosslinking - No functional groups to crosslink
Crosslinkable - Contain acid or amide functional groups.
Self Crosslinking - Will self condense.
Thermosetting - Has a high level of curing resin incorporated in latex.

Surfactant and Polymerization Process

The surfactant type and level used to stabilize the polymer emulsion has an effect on adhesion, stability, hydrophilicity/hydrophobicity, dermatological properties and foaming tendencies. There are two major classes, nonionic and anionic. Latex binders stabilized with nonionic surfactants, i.e., alkyl/aryl polyether alcohols, are very compatible and have good mechanical stability. Those anionically stabilized, i.e., sodium lauryl sulfate, have good compatibility, excellent mechanical stability and improved salt tolerance.

The polymerization process utilized dictates molecular weight and particle size. Higher molecular weight polymers are more resilient, stronger, more elastic and exhibit less tack than those produced at lower molecular weight. The particle size of the polymer has an effect on colloidal and mechanical stability.

Latex Binder Comparison

Now that we have an understanding of what impacts on the performance properties of latex binders, we should now compare the different classes to gain an understanding of the advantages and disadvantages of each class.

100% Acrylic binders offer the ultimate in durability, color stability and dry/wet performance. Acrylic binders have the widest hand range. They vary from very soft (Tg=-40°C) to extremely hard (Tg=+105°C). They can be used in most, if not all nonwoven applications.

Styrenated Acrylics are tough, hydrophobic binders. Their hand range (Tg) varies from -20°C to 105°C, so it is slightly reduced versus acrylics. These binders can be used in applications where there is a need for some wet strength without crosslinking. When using this type of latex binder, you sacrifice some UV and solvent resistance.

Vinyl Acetate binders (PVA) are firm, (Tg=+30 to +40°C) low cost binders. They offer good dry strength and toughness but tend to be hydrophilic and have a tendency to yellow when subjected to heat.

Vinyl Acrylics are more hydrophobic than vinyl acetate binders, and maintain excellent toughness, flexibility, and better color stability. They are the compromise between PVAs and acrylics and compete on a cost performance basis. The hand range is limited to soft/intermediate (Tg=-10°C) to firm (Tg=+30°C).

Ethylene Vinyl Acetate latex binders (EVA) have a Tg Range of -20°C to +15°F which is equivalent to a moderate soft to an intermediate hand. They exhibit high wet strength coupled with excellent absorbency[4] and are less costly than acrylics. They do have a tendency to be more aromatic than other binders.

Styrene Butadiene Rubber (SBR) binders offer an excellent combination of flexibility and toughness. They range in hardness from very soft (Tg=-30°F) to very firm (Tg=+80°C). However, the Tg of SBRs do not compare well with other classes of nonwoven binders. The styrene to butadiene ratio (S/B ratio) is the common method of describing relative hand[5]. When crosslinked, this class of binder is very hydrophobic and durable. As previously mentioned, SBRs are adversely affected by heat and light because of their tendency to oxidize.

Polyvinyl Chloride homopolymer (PVC) is a very hard, rigid polymer (Tg=+80°C) which must be plasticized to promote flexibility and film formation. Generally, the PVC binders used in nonwovens are internally softened by copolymerizing PVC with softer acrylic monomers,. The hand range of most of these copolymers is still firm (Tg>+30°C). This type of polymer is more thermoplastic thus performs will in heat and dielectric sealing applications. The chlorine in the polymer promotes flame retardency, the primary benefit for utilizing this class of binder. However, the chlorine also gives the polymer a tendency to yellow upon heat aging due to dehydrohalogenation.

Ethylene Vinyl Chloride binders are a class of chlorinated low flame response polymers which have a slightly broader hand range (Tg=0 to +30°C) without external plasticization. They exhibit good acid resistance, fair water resistance and excellent adhesion to synthetic fibers. This type of binder also has a tendency to yellow upon aging.

Latex Binder Application

Latex binders are applied to dry laid nonwovens by four methods: saturation (padding), print bonding, froth bonding or spraying. There have been number of papers presented at INDA functions which described each method in detail. An excellent reference document is the Principles of Nonwovens available from INDA[6]. Simply saturation is a process by which the binder is applied to the web from a formulated dilute bath by dipping the web in the mix and removing the excess by passing the saturated web through squeeze rolls.

In the print bonding operation, the binder is metered onto the web in a discrete pattern by a gravure roll or a rotary screen. The web may be pre-wet with surfactant prior to entering the print station to limit delamination or linting.

The advantages of froth bonding are improved migration resistance and the dilution of the higher solids binder with air rather than water resulting in reduced drying requirements. The aerated mix can be applied at the nip or through a slot followed by a vacuum extractor. In each case, the foam is unstable, collapsing into the substrate during application or upon drying.

Spray bonding is employed where the retention of bulk or loft is important. The diluted binder is sprayed onto the moving web to obtain spot welds at the fiber crossover points.

Following application of the binder, the treated nonwoven fabric must be dried and possibly cured, if the application requires durability. This is accomplished by in-line gas fired ovens or dry cans, steam heated or gas fired. In some cases infra-red panels are utilized.

Formulating Nonwoven Binders

Latex binders are seldom applied straight from the drum or storage tank. They are generally formulated with various ingredients to "fine-tune" the binder for a particular end-use. Types of additives utilized in nonwoven applications include:

Defoamers to eliminate foam,
Surfactants to improve adhesion or foam,
External crosslinkers to improve performance,
Thickeners to control rheology,
Flame Retardant Salts to impart low flame response properties,
Durable LFR Additives to impart low flame response,
Catalysts to facilitate cure,
Ammonia to raise the pH of the latex,
Dyes and Pigments to color the fabric,
Fillers to reduce tack and reduce cost,
Optical brighteners to enhance whiteness,
Sewing Aids to lubricate during fabrication,
Water Repellents.

Defoamers. While it is important to design storage and handling equipment to minimize latex foaming, most baths will tend to foam at the applicator unless a defoamer is used. Defoamers are divided into two categories, those which contain silicone oils and those which do not. The former (example: Dow H-10) are more efficient defoaming agents but can cause poor wet-out if you later plan to coat the surface of the fabric. An example of non-silicone is Nopco NXZ. Latex binder suppliers will have defoamer recommendations for their particular latex.

Surfactants. Surfactants, or wetting agents are added to enhance binder penetration, modify the binder hydrophobicity and increase the stability of the bath. Typically, they are either nonionic or anionic. Nonionics assist in wetting hydrophobic fibers such as polyesters or polypropylene. Nonionics are the surfactants of choice to promote chemical stability, for example when adding a cationic water repellent to an anionic latex. Nonionics also tend to act as plasticizers for acrylic latex polymers at higher concentration. Anionic surfactants are also excellent for wetting hydrophobic fibers and are particularly useful for imparting rewet characteristics to the nonwoven. Anionics have a greater tendency to foam, because lower surface tension more effectively. Thus the level of anionic surfactants should be held to a minimum.

Flame Retardants. One of the more commonly used chemicals used to flame retard nonwovens are the flame retardant salts, including diammonium acid phosphate (DAP). Normally 50-100 parts of salt are added per 100 parts of polymer on a dry, or solids basis. This large amount of DAP requires s special, “salt-stable” latex where chemical stability has been enhanced. DAO is a so-called non-permanent flame retardant – it can be washed out. A decabromophenyl oxide/antimony oxide mixture is widely used in the textile and nonwoven industries as a permanent flame retardant. The predispersion can be added to most lattices without concern.. It is significantly more expensive than DAP however.

Thickeners. The topic of thickeners for latex binders in all applications merits a separate seminar. For nonwoven binders, thickeners are not so much utilized for thickening action, because baths are normally low in solids and viscosity. Rather they function as water-holding agents to promote stability, prevent drying on the applicator roll or as a suspending agent to keep high density ingredient, such as flame retardant or filler, from settling. Thickeners also come into play for coating bonded nonwovens, where rheology is important, Thickeners can be classified in two categories: the alkali soluble type and acid soluble type:

- Alkali soluble thickeners require neutralization with a base, such as ammonium hydroxide, and thicken only at high pH. These thickeners generally are very efficient and yield pseudoplastic or shear thinning rheology.
- Acid soluble thickeners can be used at any pH, are generally less efficient and yield more Newtonian or shear rate - independent viscosity. This type of rheology is useful for gravure or rotary screen printing for nonwovens.

Catalyst. Catalysts are used to facilitate cure at reduces temperature or increase cure speed at high temperature. With conventional self-crosslinking binders which use n-methylol amide chemistry, latent acid catalysts such as ammonium nitrate (NH_4NO_3) or ammonium chloride (NH_4Cl) are recommended because they decompose during drying to form strong acid catalysts (nitric or hydrochloric, respectively). Organic acid catalysts, such as oxalic acid or citric acid, are weaker and must be used at a pH less than 7 because salts of these acids are very poor catalysts.

Ammonia. Ammonia may be used to raise the pH of an acrylic latex to maximize the stability during application. With self-thickening binders, ammonia can be used to raise viscosity without the need of external thickeners. This technology is useful in printing bonding of nonwovens. The ammonia is driven off during the initial stages of drying.

Dyes, Pigments, Fillers. Dyes and pigments are frequently added to a binder to color a nonwoven fabric, such as the familiar blue for medical/surgical gowns and drapes. Fillers are less frequently used, while they are lower in cost, they generally detract from binder properties at levels where real savings occur. Small amounts of clay can serve to detackify a softer binder to facilitate unwiding.

Optical Brighteners. Optical brighteners are incorporated to enhance whiteness and brighteness through a bluing action.

Sewing Aids. Sewing aids are lubricant agents added to prolong sewing needle life when bonded nonwovens are fabricated in apparel such as interlinings.

Water Repellents. At this stage of the formulation, a water repellent may be added, either to an anionic or a nonionic latex which has been stabilized to accept it, or to a cationic latex which generally will accept it without additional stabilization.

The order in which the formulation ingredients are added in preparation of the bath is important. Generally, most materials are added to the dilution water prior to adding the latex in order to see that they are properly incorporated before the latex obscures in compatibility with its milky whiteness. Exceptions are the thickener which is added to the mix to adjust viscosity, catalyst which is normally left out until just before application to insure stability, ammonia to adjust pH and dye or pigment to color the mixture. Additional water is added last to a final desired solids following the solids check.

Binder Use: Specific Applications

The following list describes some of the specific end-use application for nonwovens.

Conventional Nonwovens

Wipes and Towels
EVA - cost, wet strength and absorbency
Acrylic
SBR

Roofing
Acrylic - long term weatherability
PVA
Vinyl Acrylate
SBR

Medical Nonwovens
Acrylic - versatility and strength
Styrenated acrylic
EVA

Cover Stock (Feminine hygiene)
Styrenated acrylic - wet strength and ultra low formaldehyde

Interlinings
Acrylic - hand range and durability
Vinyl acrylic

Filters
PVC copolymers and EVCl - LFR characteristics
PVA

Coated Fabrics
Acrylic - versatility

Automotive Trim
PVC copolymers - LFR and sealing performance
Acrylic

Highloft Nonwovens

Furniture
PVA - cost/performance
Acrylic - excellent color and outdoor durability

Bedding
Acrylic - durability
PVA

Apparel
Acrylic - durability

Filtration
PVC Copolymers/EVCl - LFR and sealing
PVA
Acrylic

What I hope to have left you with, is a better understanding of the reason latex binders are used, the types of binders available, the compositional factors which affect performance, and the art of formulation which fine-tunes the latex binder for end-use.

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