Novel polymer systems

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ABSTRACT: Traditional emulsion polymer systems have a variety of limitations in the marketplace. The copolymerization of monomers is largely controlled by reactivity ratios, thereby limiting what may be the optimum combination of monomers either from a cost or performance criterion. Also, common polymer systems utilizing N-methylol acrylamide as a crosslinker to achieve performance release formaldehyde as they cure. Formaldehyde poses a health, environmental, and regulatory concern. Several unique polymer systems have been developed which address the limitations of traditional systems. Interpenetrating polymer networks allow for virtually any combination of monomers. Additionally, starch and polyvinyl alcohol have been used as reactive materials to produce a series of specialized grafted latex systems for the high performance durable nonwoven sector. These substrates have been grafted with a wide range of monomer systems and have further been reacted with novel crosslinking compounds resulting in surfactantless systems which do not evolve formaldehyde and exhibit an extremely wide range of properties. Preparation and application of both technologies are discussed.

KEYWORDS: Addition polymers, aldehydes, chemical reactions, cross linking, formaldehyde, glucans, monomers, natural polymers, polysaccharides, polyvinyls, preparation, starch, substrates, thermoplastics, utilization.

There are numerous limitations including cost, performance, and environmental restrictions when traditional emulsion polymers are used for commercial purposes. As cost competitiveness increases, performance criteria become more demanding, and regulatory standards are tightened, new polymers must be introduced to fulfill the ever changing needs.

Various monomers are known to exhibit specific properties when they are part of a polymer system. A partial listing is shown in **Table I**. However, the copolymerization of monomers in traditional polymer systems is restricted, under normal circumstances, to monomers which have similar reactivity ratios. The reactivity ratios of vinyl acetate *(1, 2)* with some common monomers are presented in **Table II**.

By way of example, vinyl acetate would react readily with ethylene but copolymerization with styrene, methyl methacrylate, or acrylonitrile to produce a hard copolymer is not chemically feasible under normal commercial conditions. These limitations, at times, do not allow for the optimum combination of monomers for either cost or performance. Interpenetrating polymer networks (IPN) can be used to overcome these shortcomings.

Interpenetrating polymer network

An IPN *(3,4)* is defined as a combination of any material containing two or more polymers, each in a network form, at least one of which is synthesized and/or crosslinked in the immediate presence of the other. These latexes differ both in structure and synthesis from core shell latexes. Both systems begin similarly but have significant differences in the later stages of polymerization. Core shell latexes are normally synthe-

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I. Monomer properties.

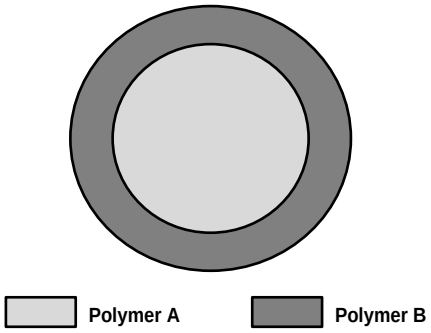
Monomer	*Feature*
Styrene	Hard, glossy, water resistant
Vinyl acetate	Film forming, low cost
Acrylonitrile	Solvent resistant
Vinyl chloride	Fire resistant, low cost
Vinylidene chloride	Fire resistant, moisture vapor transmission resistance
Butadiene	Rubber elasticity
Ethylene	Soft, low cost

II. Reactivity ratios of vinyl acetate with common monomers

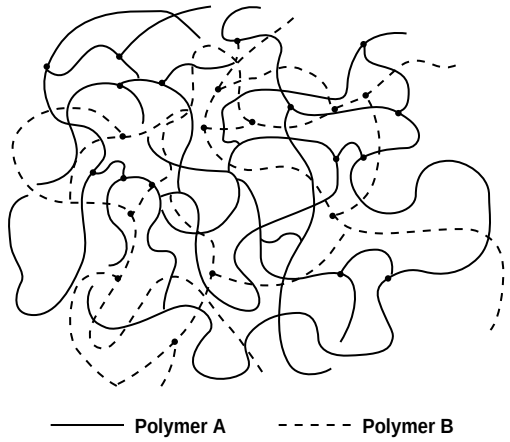
Vinyl acetate	r_1	r_2
Acrylonitrile	0.07	6
Ethylene	1.00	1.00
Methyl methacrylate	.03	26
Styrene	0.01	55

r_1 = self reaction; r_2 = cross reaction

1. Ideal core shell polymer



2. Ideal interpenetrating polymer network



sized by the continuous addition and subsequent polymerization of a second monomer on to a first stage latex. They exist as a structured particle in which the core consists of one polymer and the shell is a different polymer (**Fig. 1**). On the other hand, when employing IPN technology the first stage latex is swelled for various lengths of time with the second monomer(s) and polymerized within the interstices of the first network. An IPN is a polymer system which can be thought of as a mixture on a molecular scale as represented in **Fig. 2**. The polymer networks are intertwined and cannot be demixed without breaking covalent bonds. Due primarily to domain size, IPNs exhibit vastly different properties than pure physical mixtures.

Graft latexes

N-methylol acrylamide (NMA) is commonly used as a crosslinking agent in polymer systems. It is extremely reactive under acidic conditions with heat, is relatively cheap, is commercially available, and the final cured polymer properties are very good. In an attempt to address the concern of evolved formaldehyde on curing from latexes containing N-methylol acrylamide, monomer grafts of polyvinyl alcohol (PVOH)*(5,6)* and starch *(7,8)* were studied.

Polymer grafting of starch and polyvinyl alcohol substrates has been known for decades; however, the restrictions posed by some of the reactants (i.e., ceric ammonium nitrate catalyst, etc.) and the limited success in achieving the desired end use performance properties has inhibited large-scale commercialization. A major modification of the catalyst package coupled with novel crosslinking technology in which the grafting substrate is part of the

III. VAE/S IPN vs physical blends

Sample	*Tensile strength[a], Dry, kg*	*Wet, kg*
VAE	6.7	3.4
80/20 VAE/S blend	7.6	3.3
80/20 VAE/S IPN	8.1	4.1
60/40 VAE/S blend	8.1	3.8
60/40 VAE/S IPN	9.2	4.2

[a]TAPPI Method 656

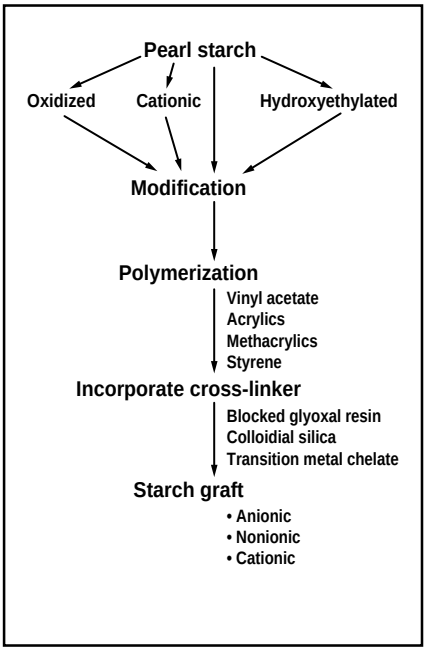
IV. Solvent swelling

	%Swell			
	PS	*PVAc*	*Blend*	*IPN*
MEK[a]	200	1200	1100	200
Xylene	1000	100	200	200

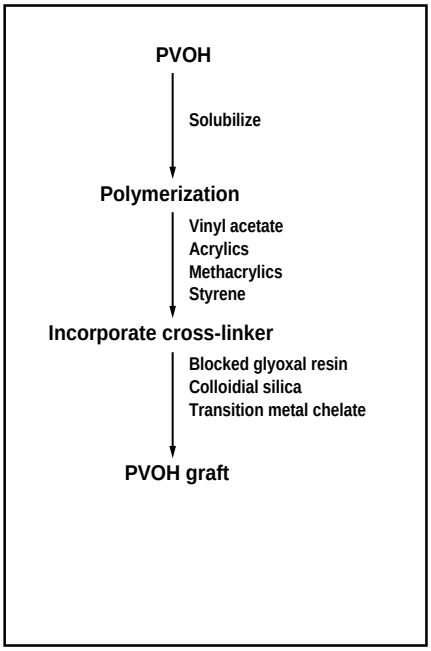
[a]Methylethyl ketone

crosslinking system, has allowed for vastly improved rheological properties and the flexibility to design systems to fit various performance criteria. High levels of polyvinyl alcohol and starch are reacted with acrylic or vinyl monomers and an internal crosslinking agent if desired. The latex system may also be externally crosslinked with a non-formaldehyde crosslinking agent under normal cure temperatures to afford a highly water resistant, surfactantless, formaldehyde free, high strength binder suitable for high temperature applications.

3. Synthesis routes for starch grafts



4. Synthesis routes for polyvinyl alcohol grafts



Synthesis

Interpenetrating polymer network

Two very different routes are used to synthesize IPNs and the graft latexes. When preparing IPNs, a first-stage or precursor polymer (30–50% total solids) is prepared by a semi-batch process. Monomer(s) and crosslinker(s) are emulsified in water using appropriate surfactant(s). A portion of this emulsion is added to the reactor, which was previously charged with water and surfactant(s) and the reaction is begun by the addition of an initiator. The reaction is controlled at the appropriate temperature while the remainder of the monomer emulsion and initiator are added to the reactor normally over a 1- to 3-h period. When the precursor is completed, a mixture of the second monomer is prepared and is added to the reactor in either neat or emulsion form. The precursor polymer is allowed to swell with the second monomer from 30 min to several hours. Additional surfactant may be added to the reactor and the polymerization is driven to completion.

Graft latexes

The molecular weights of starch and PVOH are critical when preparing starch grafts. Low molecular weights of PVOH are preferred. Most any type of starch (corn, potato, maltodextrin, ethoxylated, cationic, oxidized, etc.) can be used as the backbone for these polymer systems as long as the dextrose equivalent is between one and ten. A generic synthesis follows. A reactor is charged with deionized water and polyvinyl alcohol or starch is added slowly with stirring. A slow nitrogen purge is started and the mixture is heated to 90°C for 30 min. A neat (not emulsified) monomer mix is prepared in a second vessel containing all monomers and internal crosslinkers. A third vessel is charged with a solution of deionized water and catalyst. After the polyvinyl alcohol or starch is solubilized, the mixture is cooled to 80°C and the monomer and cata-

V. IPN urethane results

	Tensile, g/cm²	*Elongation, %*
Urethane no.1	97	991
IPN no.1	150	1171
Urethane no.2	13	676
IPN no.2	50	737

VI. Roofing mat results

Product	*A*	*B*	*C*	*D*
MD tensile (kg) RT[a]	27.3	30.0	30.7	31.3
CD tensile (kg) RT	19.6	19.7	21.3	19.6
% Stretch, 5 kg	5.5	4.9	4.3	4.8
at 180°C, 10 kg	14.9	15.1	10.2	14.5

[a]Room temperature
A & B: Commercial NMA latexes
C: Polyvinyl alcohol/monomer 1/4
D: Polyvinyl alcohol/monomer 1/5

lyst are added over a period of 3 h. A finishing catalyst is then added and held at 80°C for 1 h. The batch is cooled to room temperature and a biocide can be added if desired. The solid portion of the graft copolymer contains approximately 25% polyvinyl alcohol or starch and 75% vinyl or acrylic monomer. The system can be further crosslinked by the use of novel crosslinking technology such as blocked glyoxal resin, colloidal silica, or salts of transition metals. Various synthesis routes (**Figs. 3 and 4**) can be taken to synthesize polymers with specific end-use properties.

Results and discussions

Interpenetrating polymer network

The tensile strength of vinyl acetate-ethylene (VAE) should theoretically be increased if styrene (S) could be incorporated into the system. To illustrate the difference in a physical blend and an IPN, several samples were made. IPNs of 80/20 and 60/40 VAE/S were prepared and tested for tensile strength versus 80/20 and 60/40 physical blends of VAE and S. The results are listed in **Table III**.

It can be seen that in each case the IPN is superior in tensile strength to both the VAE copolymer and the corresponding physical blends. This can almost assuredly be attributed to the mixing of IPNs on a molecular scale resulting in small domain size when compared to pure physical mixtures.

In most instances when a physical blend of materials is prepared, the resultant properties are only as good as the limiting value of the individual components. However, by employing IPN technology, the design of the system can allow for optimization of properties as illustrated in **Table IV**.

It can again be noted that the IPN system is vastly superior (less swell) to either the individual latex systems or a physical blend when exposed to both solvent systems.

In a further example of the diversity of this technology, samples were made using a water based urethane system. The results are presented in **Table V**. Normally, elongation of a polymer system is achieved only at the expense of tensile strength. However, it can be seen that when correctly designing a system with IPN technology an increase in both tensile and elongation can be obtained.

Graft latexes

Polyvinyl alcohol/acrylate grafts (with 1% transition metal crosslinker) and samples of commercial acrylic and vinyl acrylic N-methylol acrylamide crosslinked latexes were applied to nonwoven polyester roofing mat in the laboratory. Polymer add-ons of approximately 20% were achieved. The results are given in **Table VI**. It can be noted that both polyvinyl alcohol grafts exhibit machine and cross directional tensile strength equivalent to or better than commercial latexes. Additionally, the polyvinyl alcohol based products also exhibit less high temperature stretch.

Several samples were also run on a polyester roofing mat pilot machine (**Table VII**). All samples achieved a 31% add on. Once again it can be noted that the polyvinyl alcohol grafted product is superior to the commercial product containing N-methylol acrylamide, NMA, and the properties can be further improved by the addition of a crosslinking agent. This is accomplished without the use of surfactants and the latexes do not emit formaldehyde.

The starch-graft technology was applied to polyester roofing mat as a replacement for acrylic latexes containing NMA as a crosslinking agent. At comparable add-on, the non-formaldehyde emitting starch grafts afford equal tensile strength, equal or better resistance to wicking and superior elongation resistance at el-

evated temperature. The acrylic starch graft was crosslinked by incorporation of a blocked glyoxal resin. The acrylic control was a latex containing NMA that is commercially used as a binder for polyester roofing mat. Results are shown in **Table VIII**. The tensile strength of the starch graft system compares well with that of the commercial latex while, additionally, being superior at 180°C at both 5 kg and 8 kg.

VII. Pilot trial results

Sample	*A*	*B*	*C*
MD tensile (kg) RT	29.5	32.5	35.3
CD tensile (kg) RR	19.2	25.4	27.8
% Stretch, 5 kg	5.8	5.3	5.1
at 180°C, 10 kg	12.1	10.5	9.7

[a]Room temperature
A : Commercial available latex—contains NMA
B: Polyvinyl alcohol/monomer 1/4
C: Sample B crosslinked with colloidal silica

VIII. Acrylic starch graft vs acrylic latex on polyester mat

	Starch graft	*Conventional latex*
Add-on, %	22.8	22.1
Wicking, mm	3.0	5.0
Tensile (kg) RT[a]	28.5	28.2
Stretch,% 5 kg	2.6	3.4
180°C, 8 kg	7.0	9.0

[a]Room temperature

Conclusions

Nontraditional polymer systems, exhibiting a wide range of properties, can be produced by using interpenetrating polymer networks (IPNS) or polymer grafts with either a starch or polyvinyl alcohol substrate. These methods allow for expanded versatility in designing a variety of polymers to meet a large number of end-use criteria. IPNs can be prepared with virtually any monomer combination and the network can be designed to be cost effective, achieve properties in a single latex system superior to conventional blends, or to modify traditional polymer properties. Additionally, both starch and polyvinyl alcohol grafts, when used with novel crosslinkers, result in performance equal or superior to conventional crossslinking polymers without use of surfactants and do not contain formaldehyde. TJ

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