agrimer™ VA

vinyl pyrrolidone/ vinyl acetate copolymers

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vinyl pyrrolidone/ vinyl acetate copolymers

- binder
- film former
- seed coatings

this brochure is divided into two main segments

These case studies highlight the use of Agrimer™ VA as an excellent material for seed coatings amongst other applications

general properties and uses

Agrimer™ VA series include linear random copolymers that form hard, glossy, thermoplastic films. The films are oxygen permeable with good water holding properties, appropriate for seed coatings and leaf adhesion. Agrimer™ VA copolymers have good adhesive, cohesive, and binding properties for several substrates and a host of active ingredients. Can be used as a co-dispersant in enhancing solubility/ dispersibility of complex active ingredients for improved bio-availability.

Provides excellent survivability of biological materials / living organisms such as rhizobia.

- linear, random copolymers of vinyl pyrrolidone (VP) and vinyl acetate (VA)
- family includes both hydrophobic and hydrophilic, thermoplastic, oxygen permeable polymers
- solubility varies with the proportion of vinyl acetate
- insoluble in ethers and aliphatic hydrocarbons
- soluble in water if VP content is greater than 50%
- increased VA content gives increased hydrophobicity and decreased hygroscopicity, Tg

benefits

- forms films with a wide range of water resistance properties
- dusting reduction in coatings
- uniform films that enhance survival rate of rhizobia
- adhesive and cohesive properties
- can enhance hydrophobic active ingredient solubility / dispersibility
- effective at reducing surface tension of water
- effective at reducing oil/water interfacial tension

suggested applications

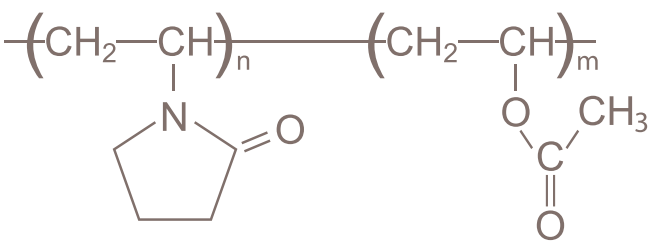
- seed coatings
- binders for water dispersible granules
- film forming agent
- co-stabilizers in water-based flowable formulations
- controlled release via co-precipitation with polybasic acids
- binders in thermal extrusion

regulatory status

Agrimer™ VA grades are exempt from the requirements of a tolerance for use in food and non-food applications both pre and post harvest.

nomenclature

The identity of these products can quickly be discerned through the product's suffix. The suffix number indicates the percentage of pyrrolidone moiety in the backbone (for example, Agrimer™ VA 6 copolymer is 60% ethylene pyrrolidone). The number suffix is often followed by a letter designation indicating product availability as either a 50% solution in ethanol (E), isopropanol (I), water (W), or as a solid (no letter suffix).



physical and chemical properties

As can be seen in Table 1, Ashland offers a full range of these copolymers. The Agrimer™ VA family offers the formulator products with molecular weights from about 13,000 to 57,000. Note that the products in ethanol generally have about twice the molecular weight of their counterparts in isopropanol. The product family has vinyl pyrrolidone: vinyl acetate ratios ranging from 30:70 to 70:30.

table 1: physical properties

property	Agrimer™ VA 3E	Agrimer™ VA 5E	Agrimer™ VA 6E	Agrimer™ VA 7E	Agrimer™ VA 5E	Agrimer™ VA 3I	Agrimer™ VA 5I	Agrimer™ VA 7I	Agrimer™ VA 7W	Agrimer™ VA 6
appearance	clear viscous liquid	clear viscous liquid	clear viscous liquid	clear viscous liquid	clear viscous liquid	clear viscous liquid	clear viscous liquid	Aqueous viscous liquid	white powder	Aqueous viscous liquid
% ash	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	<0.3
brookfield viscosity @ 25°C – as is (cps)	1340	–	–	2670	1080	–	–	1740	670[c]	1800
cloud point (°C, 5% aq.)	cloudy to °C	cloudy to °C	12	58	12	10	19	66	–	68
color (APHA) – as is	100 max.	60 max.	100 max.	150 max.	40 max.	60 max.	80 max.	80 max.[a]	60 max.[b]	20 max.[a]
film adhesivity[d]	85.2	51.8	no data	54.0	94.8	70.4	117.2	no data	no data	no data
film pencil hardness	4H	4H	no data	3H	H	4H	3H	no data	no data	no data
intrinsic viscosity [n] @ 25°C (dl/g)	0.265	0.363	0.330	0.429	0.176	0.222	0.261	0.265	0.424	–
K-value (1% in EtOH)	25-35	30-50	30-45	35-50	20-30	25-35	28-36	25-35	32-45	26-34
% moisture	0.5 max.	0.5 max.	0.5 max.	0.5 max.	0.5 max.	0.5 max.	0.5 max.	48-52	5 max.	48-52
approximate Mw	28,800	36,700	38,200	56,700	12,700	19,500	22,300	27,300	51,000	51,000
% nitrogen	3.5 – 4.5	5.8 – 6.8	7.0 – 8.0	7.5 – 9.4	3.9 – 4.9	6.0 – 6.9	8.0 – 9.0	8.0 – 9.0	7.8 – 8.8	7.0 – 8.0
saponification number (mg KOH/g) – as is	204	151	126	95	201	160	112	92	241	131
% solids	48 – 52	48 – 52	48 – 52	48 – 52	48 – 52	48 – 52	48 – 52	48 – 52	95 – 100	48 – 52
specific gravity @ 25°C	0.0945 – 0.965							1.110	1.081	1.113
Tg (°C)	69	96	106	117	71	89	108	114	110	99
VP/VA ratio	30/70	50/50	60/40	70/30	35/65	50/50	70/30	70/30	60/40	60/40

(a) 10% Solids. (b) 5% Solids in EtOH. (c) Measured at 38% solids @ 30°C in H2O. (d) IMASS slip/peel Tester – Force (g) to separate parafilm.

hydrophilic-lipophilic balance

The hydrophilic:lipophilic ratios (HLB) shown in Table1 suggest that as the percentage of vinyl pyrrolidone moieties increases there is a corresponding increase in the copolymer's HLB making it more water soluble. Conversely, increasing amounts of vinyl acetate content lowers the HLB and increases hydrophobicity. This is shown graphically in Figure 1.

interfacial tension

Figure 2 shows that the Agrimer™ VA copolymers reduce the petroleum oil-water interfacial tension. Table 2 shows that this interfacial tension reduction is greatest when the monomer ratios are equal (50% vinylpyrrolidone and 50% vinyl acetate). This data is in full conformity with the HLB's given in Figure 1 since it would be expected that the polymer most effective in reducing oil-water interfacial tension would be the one having the most hydrophobicity while remaining water soluble. The emulsification of octanol in water was observed at 1% level for all of the Agrimer™ VA copolymers.

figure 1: molecular weight, PVP VA ratio and HLB relationship

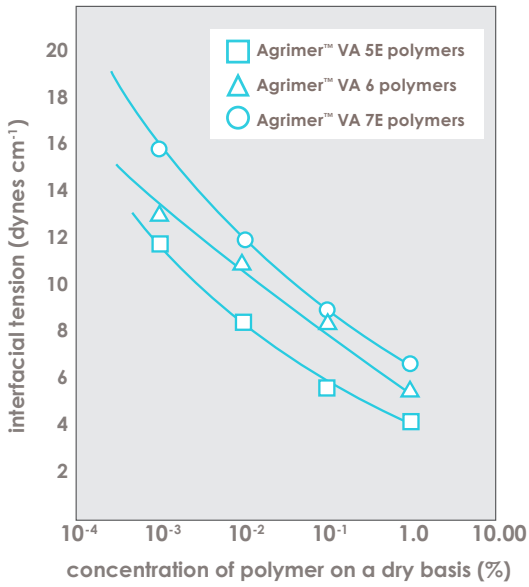
Mn, Mw are values reported by GPC using H_2O/MeOH as solvent in 0.1 m $LiNO_3$.

Filled points represent number average molecular weights (Y2 axis)

Open points represent weight average molecular weights (Y1 axis)

Solid Ethanol solution Isopropanol solution

figure 2: interfacial tension of Aromatic 150 and Aqueous Agrimer™ VA copolymers



Interfacial tension without copolymer = 36.4 dynes cm-1

table 2: surface tension and partition coefficients

polymer properties	Agrimer™ VA 7E[a]	Agrimer™ VA 5E[a]	Agrimer™ VA 3E[a]	Agrimer™ VA 7I[a]	Agrimer™ VA 5I[a]	Agrimer™ VA 3I[a]	Agrimer™ VA 6
surface tension of aqueous solutions (1.0%) 23°C	37.18	43.00	not soluble in water	44.80	39.25	not soluble in water	44.71
interfacial tension between aromatic 150/H_2O (23°C) ɣ, dynes cm-1 (1%)	6.00	3.77	-	similar to E series		-	4.99
octanol/water partition coefficient	at 1% polymer level, all emulsified						

[a] Solids obtained after removing the solvent

table 3: solubilities

solvent	Agrimer™ VA 7E[a]	Agrimer™ VA 5E[a]	Agrimer™ VA 3E[a]	Agrimer™ VA 7I[a]	Agrimer™ VA 5I[a]	Agrimer™ VA 3I[a]	Agrimer™ VA 6
Aromatic 150	< 0.1%	< 0.1%	< 0.1%	< 0.1%	< 0.1%	< 0.1%	< 0.1%
Aromatic 200	< 0.1%	< 0.1%	< 0.1%	< 0.1%	< 0.1%	< 2.5%	< 0.1%
AgsolEx™ 8	< 1%	> 1%	> 5%	2-5%	2-5%	2-5%	> 1%
AgsolEx 1	> 50%	> 50%	> 50%	> 50%	> 50%	> 50%	> 50%
AgsolEx BLO	> 50%	> 50%	> 50%	> 50%	> 50%	> 50%	> 50%
ethanol	> 50%	> 50%	> 50%	> 50%	> 50%	> 50%	> 50%
mineral oil	< 0.1%	< 0.1%	< 0.1%	< 0.1%	< 0.1%	< 0.1%	< 0.1%
soybean oil	< 0.1%	< 0.1%	< 0.1%	< 0.1%	< 0.1%	< 0.1%	< 0.1%
water	> 50%	> 50%	< 0.1%	> 50%	> 50%	< 0.1%	> 50%

[a] Solids obtained after removing the solvent

solubility

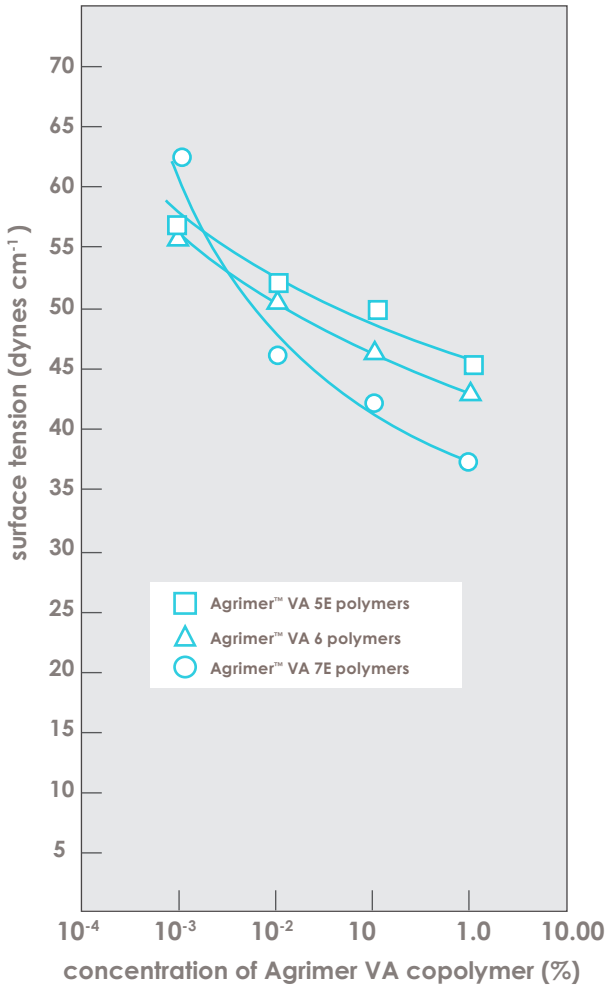
HLB is directly related to solubility, as shown in Figure 1 and expanded upon in Table 3. When the amount of vinyl acetate in the copolymer exceeds 50%, its solubility in water drops but its solubility in hydrophobic solvents such as Ashland's AgsolEx 8 increases. Only Agrimer™ VA3 copolymer is water insoluble and generally restricted to sticker adjuvants or dispersants in water-in-oil systems. The remaining copolymers are water soluble and suitable for applications in water-based formulations and in oil-in-water emulsions.

surface tension

Oil-in-water emulsion stability, including bloom and robustness upon dilution, can be enhanced by reducing the surface tension between the oil and water phases. Figure 2 shows that at concentrations as low as 0.1% the water soluble Agrimer™ VA copolymers reduce interfacial tension between water and Aromatic 150 from 36 dynes cm-1 down to 8 dynes cm-1.

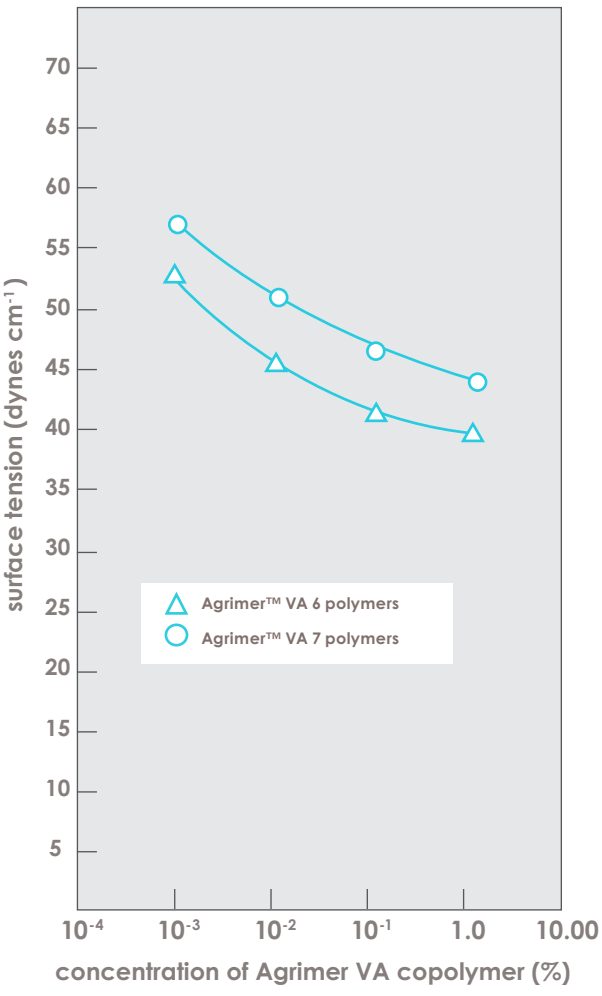
Figures 3 and 4 show that the Agrimer™ VA copolymers will reduce the surface tension of water by 25-40% at concentrations of 0.1-1.0%. There is little difference in the ability of these copolymers to reduce surface tension, although those with a greater portion of vinyl pyrrolidone (and those having higher molecular weights) tend to provide the most reduction in surface tension.

figure 3: surface tension of aqueous solutions of Agrimer™ VA series copolymers



surface tension of water = 73.14 dynes cm-1

figure 4: surface tension of aqueous solutions of Agrimer™ VA series copolymers



surface tension of water = 73.14 dynes cm-1

adhesivity

The Agrimer™ VA copolymers are better adhesives than the vinylpyrrolidone homopolymers. Agrimer™ VA 6 and Agrimer™ VA 7I copolymers are the best water soluble adhesives of the family, as shown in Table 4.

Table 4 also shows that the trend is toward better copolymer adhesivity as the percentage of vinylpyrrolidone increases. Agrimer™ VA 6 and Agrimer™ VA 7I copolymers are nearly twice as effective as the homopolymers in their adherence to leaf-like surfaces. If you are looking strictly for adhesive and interfacial film properties, Ashland recommends that you also look into its Agrimer™ AL family of alkylated vinyl pyrrolidone polymers.

table 4: adhesivity

Product	Adhesivity (g peel force on parafilm)
Agrimer™ VA 3E	85
Agrimer™ VA 5E	52
Agrimer™ VA 6	129
Agrimer™ VA 7I	117
Polyvinylacetate	73
Agrimer™ PVP	65

agricultural case studies

seed coating

Agrimer™ VA 6 copolymer is one of the most used polymers in seed treatments because of its adhesivity, water and air permeability, and complexing capabilities. Compared to a standard formulation, the inclusion of Agrimer™ VA 6 copolymer was shown to quadruple the number of rhizobia adhering to a variety of seeds after simulated packaging and transportation. Further, as a result of its complexing ability, Agrimer™ VA 6 copolymer has been shown to significantly enhance the survivability of rhizobia bacteria on legume seeds (Table 5).

table 5: improved survival of biologicals (rhizobia and soybeans)

Treatment	0	3 months	6 months
dry inoculation	85,000	0	0
plus Agrimer™ VA 6 slurry	3,400,000	190,000	760
plus gum arabic slurry	3,100,000	94,000	0

solubility enhancement

A solution containing both Agrimer™ VA 6 copolymer and prodiamine, a fluorinated dinitroaniline derivative, was mixed at 10% each and heated to 50°C. The solvent was then evaporated. The resulting solid co-precipitate had apparent water solubility 30 times greater than the active ingredient alone.

dispersion enhancement

Agrimer™ VA 6 copolymer and a hydrophobic fluorinated phenyl urea insecticide were co-precipitated from a common solvent. The dispersibility of the resulting solid was enhanced by about 100 times.

dissolution rate

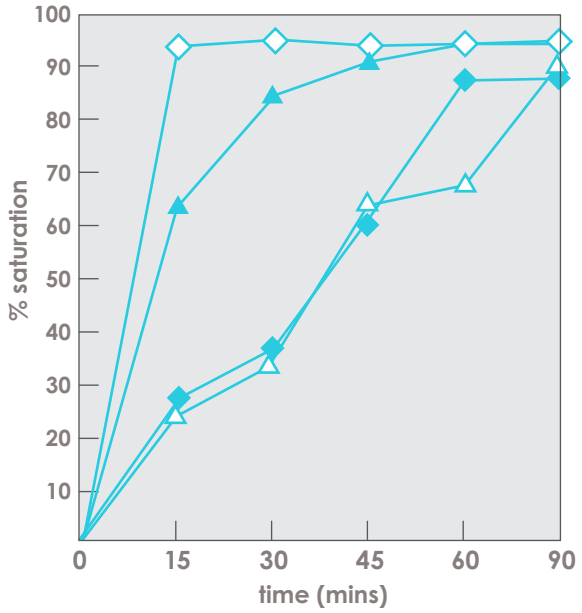
Figure 5 shows that Agrimer™ VA 6 copolymer significantly enhanced the dissolution rate of cypermethrin relative to the Agrimer™ 30 PVP homopolymer. The dissolution rates can be further enhanced by co-precipitation with citric acid (CA). The dissolution rate of cypermethrin granules was quadrupled if the polymeric binders were co-precipitated with citric acid prior to granulation.

granule binders

Agrimer™ VA 6 copolymer has been shown to be a significantly better granule or tablet binder than the more commonly used Agrimer™ 30 copolymer or lignosulfonate. Comparatively, the Agrimer™ VA 6 copolymer generally enhanced such important parameters as product yield and suspensibility. It also decreased granule friability, reducing dustiness, and reduced the amount of foam the granules generated when dissolved in a spray tank having agitation. The polymeric alloy made by using a combination of Agrimer™ VA 6 and Agrimer™ AL 10LC copolymers (butene alkylated PVP), was a superior binder in almost all measured parameters as compared to any of the other binders used alone (Table 6).

The dispersion of the copolymer, hence the granule, can also be enhanced by either co-precipitating it with citric acid or by adding a small amount of a wetting agent. Naphthalene sulfonate formaldehyde condensate type dispersants may be used as the starting dispersants when developing formulations containing Agrimer™ VA 6 copolymer.

figure 5: dissolution rate of 10% cypermethrin granules



Agrimer™ 30 is a PVP homopolymer
CA is citric acid

◇ Agrimer™ VA 6 polymers + CA
◆ Agrimer™ VA 6 polymers
▲ Agrimer™ 30 polymers + CA
△ Agrimer™ 30 polymers

extrusion

Table 1 shows the Tg for the various Agrimer™ VA copolymers. These copolymers have Tgs that are in a suitable range for the preparation of granules through the formation of solid solutions during hot melt extrusion. Further, their more hydrophobic nature makes them more suitable in this process than the Agrimer™ homopolymers. Ashland recommends using the appropriate plasticizers to obtain the appropriate size range of the extruded granules.

table 6: binder effect on yield and suspendibility of Atrazine

Binder	Granulation moisture %	Powder granule conversion %	Filter sed. susp. %	Cone sed. index
Agrimer™ 30	8	75	88	8.0
Agrimer™ VA 6	10	84	95	8.0
Agrimer™ AL 10LC	8	88	85	6.7
Agrimer™ AL 10LC + VA 6	8	86	86	6.0
Lignosulfonate	15	60	78	13.0

Representative data from large and small batch experiments.
The friability and foam index were best with the system containing both Agrimer™ VA 6 and AL 10LC.

aqueous flowables

Increased suspensibility can often be optimized by using Agrimer™ VA 6 copolymer as a co-dispersant with anionic polymeric dispersants, (for example, naphthalene sulfonate formaldehyde condensate). In comparisons against chlorothalonil and carbaryl formulations, percent active ingredient suspended at 1:100 dilution from a 40% SC were doubled by adding Agrimer™ VA 6 copolymer as co-dispersant in the formulation compared to identical formulations without the Agrimer™ VA 6 copolymer.

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