

David Vanaken, Lan Nguyen, and Zegui Yan, Hexion Inc, report on a cost-effective option that matches and can even outperform the current products for elastomeric roof coatings

Highly branched vinyl ester-based binders for elastomeric roof coatings

Elastomeric roof coatings have been used for many years to extend the useful life of many types of roofing substrates.

The roof coatings market has seen significant growth, driven by the “cool roof” movement. By using a white roof coating, the underlying building and surroundings can be protected from excessive heat build-up. A proper white reflective elastomeric coating offers reduction in temperature and hence a reduction in cooling costs.

The strength of elastomeric coatings lies in their elasticity. Because these coatings are normally used at temperatures above their glass transition temperatures (T_g) they usually exist in a rubbery state. In this state, elastomeric coatings can be deformed by stress, but they will return to their original state once the stress is removed¹. Elastomeric roof coatings need to have very good water barrier properties. High water resistance is required so that the elastomeric coating can withstand ponding water, which can occur on low slope roofs. Good adhesion to the substrate and good weatherability are some of the other factors that contribute to a long service life of the roof coating.

The majority of elastomeric roof coatings are based on acrylic latices, with silicones, urethanes, and epoxies accounting for the remainder. Acrylic and styrene/acrylic latex coatings typically last for 5–10 years¹. The properties of latex polymers such as barrier properties, adhesion, flexibility, hydrophobicity, and other can be varied by manipulating the latex monomer composition.

Traditionally acrylates and styrene have been used as main monomers in the emulsion polymerisation process to make latex binders for elastomeric coatings. This paper describes the use of the very hydrophobic highly branched VeoVa™ vinyl esters⁵ for high performance binders for elastomeric coatings.

■ MINIMUM REQUIREMENTS FOR ELASTOMERIC ROOF COATINGS

Some of the most important tests for elastomeric roof coatings are tensile strength, elongation and water absorption. Other tests often performed are peel adhesion, low temperature flexibility, accelerated weathering, water vapour

permeability and recovery after elongation.

Norms and standards as well as test methods differ per region. Often, different test methods are used, and also minimum requirements do vary between countries. ASTM D6083, “Standard Specification for Liquid Applied Acrylic Coating Used in Roofing”, is one of the most well-known standards².

■ MONOMERS FOR ELASTOMERIC BINDERS

Latex polymers for elastomeric roof coatings are prepared by emulsion polymerisation. In this process, different monomers are polymerised in water through free-radical polymerisation. A polymer needs to have a low T_g to be flexible at low temperatures. Therefore, latex polymers for elastomeric roof coatings typically consist of a combination of low T_g and high T_g monomers to obtain the desired balance between elongation and tensile strength.

Besides flexibility, water resistance is one of the most important properties of a roof coating. The water resistance of a coating is mainly governed by the composition of the polymeric binder and therefore by the monomer used. If one takes water solubility of the monomers as an indication of hydrophobicity, it becomes clear that the vinyl ester of neodecanoic acid (VeoVa monomer) has a much higher hydrophobicity than other monomers commonly used in emulsion polymerisation (Table 1)³. In addition, the homopolymer T_g of the VeoVa vinyl ester of (-3°C) is rather low, between those of hard monomers such as styrene and methyl methacrylate (MMA) and those of softer monomers such as butyl

Table 1. Water solubility and T_g of some commonly used monomers

Monomer	Water solubility at 20°C (g/100g)	Homopolymer T _g (°C)
VeoVa monomer	<0.001	-3
2-ethylhexyl acrylate	0.01	-65
Styrene	0.03	+90
Butyl acrylate	0.16	-40
Methyl methacrylate	1.5	+100
Vinyl acetate	2.5	+32

acrylate (BA) and 2-ethylhexyl acrylate (2-EHA).

The very high hydrophobicity of the VeoVa monomer combined with a Tg suitable for the preparation of low-Tg polymers makes it a very interesting candidate to develop novel, high-performance binders for elastomeric coatings.

HIGHLY BRANCHED VEOVA™ VINYL ESTERS

VeoVa vinyl ester is an ideal vinyl monomer for the production of latices for high quality water-based elastomeric coatings. It finds its principal use as a hydrophobic co-monomer in vinyl and acrylic polymerisation. This vinyl ester molecule has a unique highly branched tertiary substituted α -carbon structure. Therefore, this alkyl neodecanoate group is resistant to degradation in alkaline conditions as there is no hydrogen on the α -carbon and in addition the bulky alkyl structure protects the ester function of the molecule. The branched tertiary structure with bulky and hydrophobic hydrocarbon groups provides the VeoVa vinyl ester (**Figure 1**) with a highly hydrophobic nature and a low surface tension. Furthermore, VeoVa vinyl ester exhibits strong resistance to hydrolysis and does not degrade under the influence of UV light.

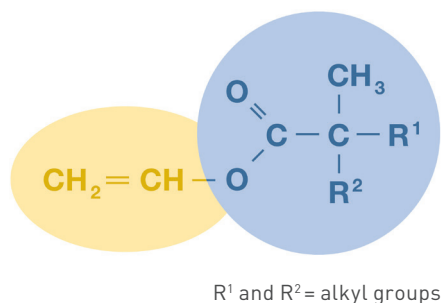


Figure 1. Chemical structure of VeoVa monomer

VeoVa monomer polymerises with various other monomers through its vinyl ester functional group. In this way the specific properties of the monomer can be imparted to its copolymers. VeoVa monomer enhances the performance of vinyl acetate-based latices, significantly upgrading key properties such as water and alkali resistance.

The manufacture of these vinyl acetate/ VeoVa vinyl ester latices is characterised by ease of production with low reactor fouling and high batch reproducibility. VeoVa vinyl ester-based polymers exhibit the required polymer

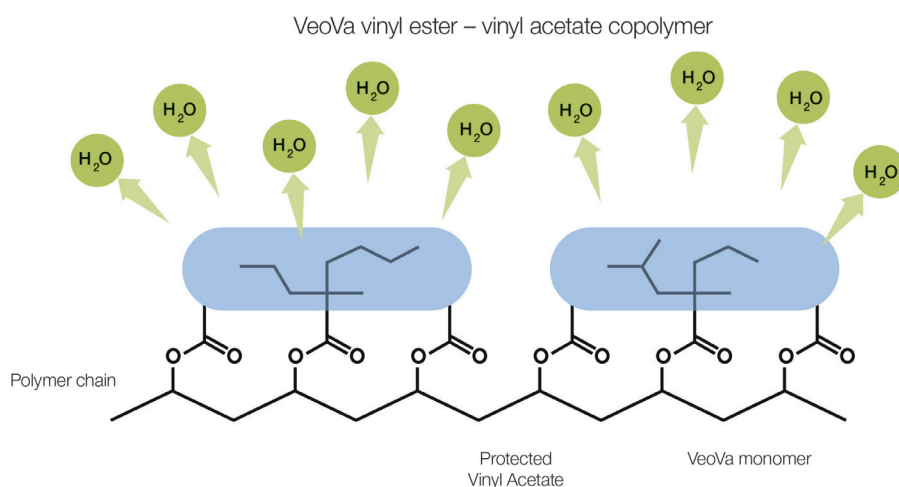


Figure 2. Protection of the acetate groups by adjacent VeoVa 10 groups

Table 2.

Description	Solid(%wt)	Particle size (nm)	Homopolymer Tg (°C)
Market-leading all-acrylic system	55	360	-32
VA/VV/BA vinyl-modified acrylic system	54	160	-13

hardness and flexibility balance for the formulation of a range of high-performing elastomeric coatings.

PROTECTIVE EFFECT OF VEOVA MONOMER

VeoVa monomer and vinyl acetate exhibit very similar reactivities in free-radical emulsion polymerisation, which yields polymers with monomer units randomly distributed along the chains. This is important because it allows the key performance characteristics of VeoVa monomer to be fully utilised. The unique, highly branched, carbon-rich structure of VeoVa monomer sterically protects its ester group from hydrolysis. More importantly, it also protects neighbouring acetate groups (**Figure 2**), thus improving the hydrolytic stability of the polymer. This protection is called the “umbrella effect” and enables such polymers to be successfully used as paint binders even on very alkaline substrates. The umbrella effect of the highly branched carboxylate groups is supported by experimental data⁴.

VEOVA/VA/ACRYLATE EMULSIONS

Soft, plasticising, acrylate monomers such as BA (Tg -40°C) and 2-EHA (Tg -65°C) can be used to improve the flexibility of vinyl acetate-based polymers. Unlike VeoVa monomer, these acrylates do not

protect the adjacent acetate groups from chemical attack and therefore such systems have the major disadvantage of low hydrolytic stability leading to poor outdoor durability. The addition of VeoVa monomer to such polymers to form terpolymers with vinyl acetate and acrylates substantially upgrades the hydrolytic stability, while allowing to retain a low minimum film formation temperature (MFFT) and good flexibility. In addition, outstanding water resistance and outdoor durability, good elongation and tensile strength can be achieved for elastomeric roof coatings. Terpolymers can be prepared with a combination of vinyl acetate, acrylic and VeoVa vinyl ester providing great formulation latitude with options to modify Tg, MFFT, hydrophobicity and hydrolytic stability to meet specific requirements for cold to tropical climates. The incorporation of VeoVa 10 monomer in the polymer backbone offers a novel and innovative route to formulate very cost-efficient high-performance vinyl acetate based elastomeric coatings.

EVALUATION IN ELASTOMERIC ROOF COATINGS

Hexion developed a vinyl-modified acrylic resin based on vinyl acetate, VeoVa 10 vinyl ester (VV), and butyl acrylate. This resin was tested in a formulated elastomeric roof coating against a leading all-acrylic emulsion. See **Table 2**.

■ RESULTS

The performance of these systems against the reference is summarised in **Figure 3**.

■ CONCLUSIONS

Veova monomer significantly upgrades the overall performance of the binders used in roof coatings. Production of vinyl acetate/Veova vinyl ester polymers is easy due to the favourable reactivity characteristics of the Veova monomer and vinyl acetate. Combining Veova monomer with acrylate monomers offers an additional tool to formulate a various very versatile polymers for use in elastomeric coatings.

Roof coatings based on Veova vinyl ester terpolymers combine very high elongation with high tensile strength. The very hydrophobic Veova monomer also imparts very low water absorption, often superior to commonly used acrylic polymers. Since these terpolymers are based on a relatively low-cost vinyl acetate based monomer, high quality vinyl ester-based polymers offer the formulator a cost-efficient option to design coatings that match and even outperform the current products for elastomeric roof coatings.

More detailed information on producing Veova vinyl ester polymer latices and formulating coatings can be obtained from the authors.

PPCJ

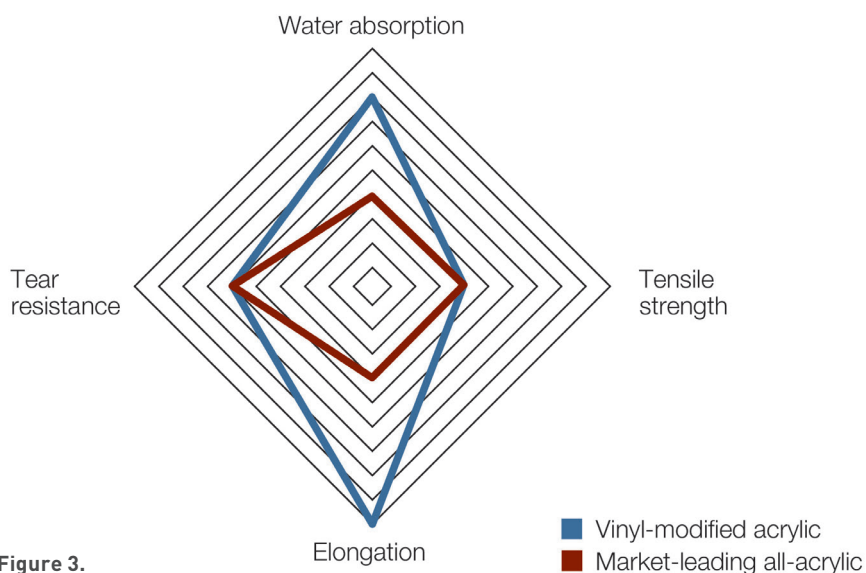


Figure 3.

References

1. Leo Procopio, "Elastomeric acrylic coatings for use on commercial structures", Proceedings of SSPC 2013, January 2013.
2. ASTM D6083 "Standard specification for liquid applied acrylic coating used in roofing".
3. D. Basett, "Hydrophobic coatings from emulsion polymers", *Journal of Coatings Technology*, 2001, pp. 43.
4. D. Vanaken, V. Arriaga, "Branched vinyl ester monomers for hydrophobic emulsion polymers", Proceedings of the 40th Annual International Waterborne, High Solids, and Powder Coatings Symposium, February 2013, pp. 117-131.
5. © and ™ denote trademarks owned by or licensed to Hexion Specialty Chemicals Inc.

Authors: David Vanaken, Lan Nguyen, Zegui Yan, Hexion Inc.
Contact: David Vanaken
Email: david.vanaken@hexion.com
Website: <https://veovahouse.hexion.com/>