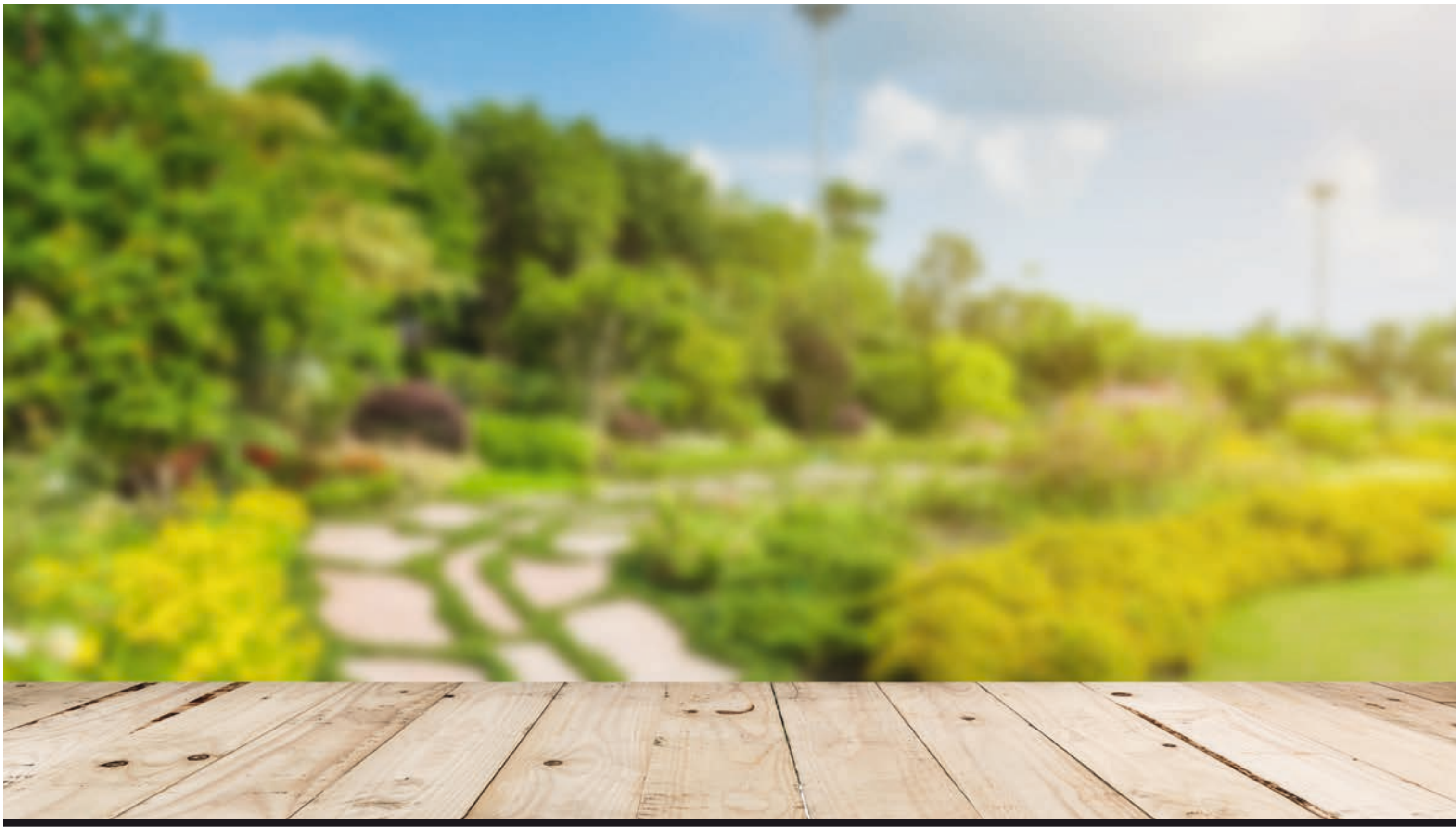

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ON THE ROAD TO A MORE NATURAL FINISH

Partially plant-based polymers evaluated in exterior and furniture coatings. By Tijs Nabuurs and Maud Kastelijn, DSM Coating Resins, the Netherlands.

Several plant-based alternatives to fossil fuel-based (meth) acrylate monomers are described. Both exterior wood finishes and furniture finishes using binders containing 40% plant-derived carbon showed performance at least equal to that of the fossil-based control formulations.

Polymeric binders containing (meth)acrylic copolymers have long been used in the coatings market. With increasing awareness of the earth's depleting natural resources and climate changes, there is growing pressure on industry to find plant-based alternatives for its raw materials. Since the turn of the century, much research has been done to develop renewable alternatives to current polymers as used in paints and coatings. Most of this research has been aimed at using vegetable oils or sugars, and modifying wood structures to obtain lignin structures [1]. Although polymers obtained like this have their merits, they do not provide alternatives for modern coatings used in, for instance, the interior furniture or exterior industrial wood markets.

Renewable monomers that do provide a means of producing (partially) plant-based polymer binders for use in paints and coatings have been suggested using various approaches [2], but so far, no commercial plant-based binders based on these monomers have been reported.

In this study, it will be shown that it is currently feasible to produce partially plant-based polymer binders via emulsion polymerisation for use in industrial paints or coatings for wood. Following an overview of the various plant-based monomers available, some paints prepared from partially plant-based polymer compositions will be compared with their fossil fuel alternatives.

For the sake of this study, polymer synthesis was restricted to emulsion polymerisation. Many detailed overviews of this technology have been published over the years [3].

TECHNICAL BACKGROUND AND COMMERCIAL STATUS

To replace polymer binders that can be used in coatings with plant-based types, suitable plant-based monomers must be commercially available. The common acrylate and methacrylate monomers are not yet commercially available from renewable resources.

In the past decade, routes have been developed to produce acrylic and methacrylic acid from plant-based sources. Acrylic acid, for instance, can be derived from 3-hydroxy propionic acid [4], or alternatively from glycerol [5].

Methacrylic acid can be prepared, for instance, from syngas (a mix-

RESULTS AT A GLANCE

→ Several plant-based alternatives to fossil fuel-based (meth) acrylate monomers are available. Most promising types include the diesters of itaconic acid and esters of (meth)acrylate monomers prepared with plant-based alcohols.

→ Other plant-based monomers show issues with either too slow, or too high reactivity, or are not currently commercially available.

→ Both self-crosslinking exterior wood finishes and 2K isocyanate crosslinking furniture finishes were prepared with binders containing 40% plant-derived carbon. Preliminary tests on these coatings showed performance at least equal to that of the fossil-based control formulations.

→ At this point in time, polymeric binders with plant-based contents of around 40% can be achieved (calculated on total carbon content). New developments with even higher plant-based contents are, however, expected to be available within five years from now.

Table 1: Clear and pigmented formulations for exterior coatings based on self-crosslinking binders.

	Clear formulation	Pigmented formulation
Binder*	70.6	55.6
Water	18.6	5.3 **
Butyl diglycol	2.2	2.5
“Thixol 53L” (1:10 in water)	7.2	5.0
“Dapro DF7580”	0.6	0.4
“Borchigel L75” (1:1 in water)	0.8	0.6
“Disperbyk 2015”		1.5 **
“Tego Foamex 810”		0.3 **
“Kronos 2190”		24 **
Ammonia (25%)	***	***

* Used at a solids content of 44%
** Part of the pigment paste premix
*** To raise pH to 8.9

ture consisting primarily of hydrogen and carbon monoxide) [6]. This syngas is currently obtained from fossil fuel based sources, but can, obviously, also be obtained from renewable resources.
At this point in time, however, neither plant-based acrylic acid nor methacrylic acids are commercially available. Hence, other monomers are required. Not all double bonds are reactive in radical polymerisation. Monomers that can be used practically in emulsion polymerisation need to match the general structure shown in *Figure 1*.
In the case of acrylate and methacrylate monomers, for instance, X and Y are oxygen, and R1 is hydrogen or a methyl group. In practice, five different plant-based structures can be envisaged that are both reactive in radical polymerisation and (potentially) commercially available.

PLANT SUBSTITUTION IN (METH)ACRYLATES

The first practical alternative considered is based on using plant-based alcohols (R_2 in *Figure 1*) in (meth)acrylate monomers, which would result in partially plant-based building blocks. From a polymerisation reactivity perspective, this is a very practical approach, since the monomers can be perfect drop-ins for the current monomers.
A second advantage is that the contributions of the monomers to polymer properties are well understood. Unfortunately, not all alcohols that are currently used in (meth)acrylic monomers are currently available from renewable resources. A final consideration of this approach is that, depending on the number of carbon atoms in the alcohol, the contribution to the renewability content can be limited.
Using plant-based alcohols yields acrylic monomers with bio-based concentrations (calculated on carbon atoms) ranging from 25% for methyl to 73% for octyl. For methacrylates these values range from 20% to 67% respectively. Hence, to prepare a coating containing a reasonable concentration of renewable carbon the longer alcohols in particular provide significant opportunities.
Commercially, existing options are acrylic monomers containing ethyl or n-butyl alcohols. In literature, other options have also been described, such as 2-octyl acrylate [7] and isobornyl (meth)acrylates [8]. 2-octyl acrylate in particular seems an interesting monomer, since it

Figure 1: General structure of monomers that can be useful in radical polymerisation.

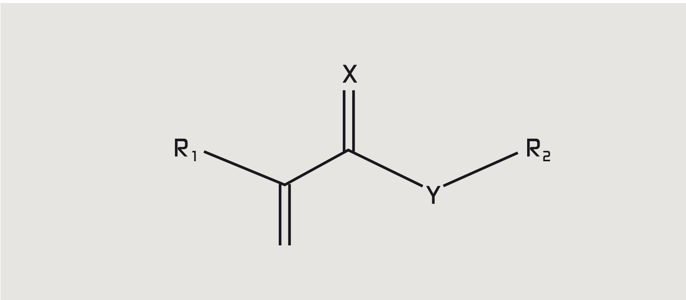
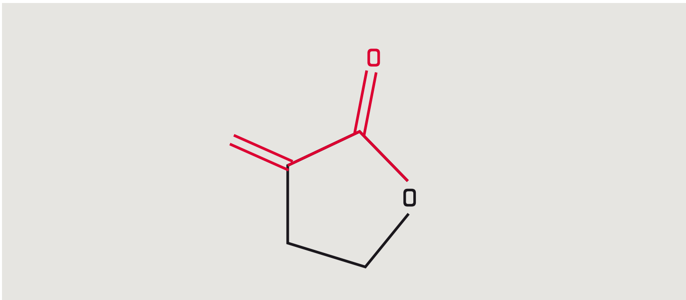


Figure 2: Structure of -methylene butyrolactone.



has a high renewable content and appears an easy replacement for the commonly used 2-ethylhexyl acrylate.

ITACONIC ACID: PROMISING, BUT WITH SOME PROBLEMS

A second plant-based alternative is based on dialkyl esters of itaconic acid (DRI), where R_1 in *Figure 1* is a $CH_2C(O)OR_2$-group, and X and Y are oxygen. Itaconic acid has been produced via fermentation ever since the 1960s [9], and at this moment fermentation of sugars is even the preferred production route [10].

As mentioned in the previous section, plant-based versions of the most common alcohol residues are not generally available at cost-effective prices. Using fossil fuel-based alcohols, however, obviously would go at the expense of the plant-based content of DRI monomers. Moving from methyl to octyl esters, bio-contents of DRI monomers range from 71% down to 24%.

Obviously, DRI monomers containing plant-based alcohols would result in 100% bio-renewable monomers. Commercial sources of some of those 100% plant-based itaconate monomers are available, especially dimethyl itaconate (DMI) and di-n-butyl itaconate (DBI).

Itaconic esters have two advantages for use in binders: both the glass transition contribution (as reported by Cowie et al [11]) and the water solubilities are comparable to those of methacrylic esters containing the same alcohols.

The use of itaconic esters in emulsion polymerisation does, however, also provide challenges. Due to the presence of the very bulky R1-group, reactivity is low. Typically, the propagation rate constant of dialkyl itaconates is in the 5 - 10 l/mole.s range [12].

As a result, it is challenging to produce dialkyl itaconate functional copolymers containing a significant DRI monomers concentration with high monomer conversion and high molecular weight. By controlling polymerisation conditions and optimising the polymerisation procedure, however, these effects can be mitigated [13].

CROTONIC AND MALONIC ACID ESTERS: OPPOSING PROBLEMS

Esters of crotonic acid offer a third plant-based option for bio-based monomers. Crotonic acid can be obtained from plant-based raw materials, for instance, via pyrolysis of 3-hydroxy butyrate [14]. Although their structure closely resembles those of methacrylate esters, they do not copolymerise effectively enough to yield copolymers and can thus be discarded.

A fourth class of plant-based monomers are diesters of methylene malonate, where R1 in *Figure 1* is a $C(O)OR_2$-group. Malonic acid can be obtained from renewable resources, such as 3-hydroxy propionic acid [15]. Synthesis of methylene malonate esters was indeed described early in the 1940s by Bachman et al [16].

Since the double bond of methylene malonates is double activated, these monomers are very reactive, especially in anionic polymerisation. In fact, their reactivity in anionic polymerisation is so high, that when brought into contact with non-acidic water, these monomers will spontaneously polymerise. Hence, methylene malonates are not practical for use in emulsion copolymerisation.

ONE FURTHER POTENTIAL OPTION IS NOT YET AVAILABLE

Finally, the fifth class of potentially plant-based monomers is based on the α-methylene butyrolactone structure as shown in *Figure 2*. The first description of this monomer dates back to 1947 [17]. Radical polymerisation was described in 1979 [18]. In the same year copolymerisation of α-methylene butyrolactone with methyl methacrylate, styrene, acrylamide and acrylonitrile was described [19].

α-methylene butyrolactone polymerises at high rates [20] and the contribution to film properties can also be useful, with for instance a Tg contribution of 195 °C [19]. Unfortunately, this product is not yet commercially available.

In conclusion, itaconate esters and (meth)acrylate esters currently represent the most promising routes for partially plant-based copolymers.

SELF-CROSSLINKING EXTERIOR FINISHES PERFORM WELL

Film properties of partially plant-based polymer binders have been compared to those of compositions based on fossil fuel monomers. Comparisons were made for a 1K self-crosslinking coating for use in exterior, and for a 2K NCO curing coating for interior furniture coating applications.

Table 3: Clear formulation for interior 2K NCO curing coatings. Properties of the crosslinked coatings are presented in *Table 4*.

	Clear formulation
Binder*	100.0
Water	4.4
Butyl diglycol	8.0
"Radiasolve 7529"	2.0
"Tego Airex 902W"	0.6
"Coatex BR100P" (1:1 in water)	1.0
"Bayhydur 2655" (70% in MPA)	18.1
Water	10.0

* Used at a solids content of 40%

Table 4: Film properties of 2K isocyanate crosslinking interior furniture coatings containing binders made from only fossil fuel-based monomers or partially plant-based monomers.

		Fossil fuel based	Plant based
Bio-content of binder (on carbon)		0%	40%
Gloss (20°/60°)		58/80	64/89
Chemical resistances*			
Ethanol	1 hr	5	5
Red wine	6 hrs	4-5	5
Coffee	16 hrs	5	5
Water	16 hrs	5	5
Mustard	6 hrs	3	3
Onion juice	6 hrs	3-4	3-4

* 0 is poor, 5 is excellent

1K self-crosslinking coatings, containing ketone functional binders which react with polyhydrazides upon film formation, have for long been a standard in the market for exterior wood coatings. A representative commercial binder, typically containing a combination of methacrylate and acrylate monomers, was selected and the monomers replaced with both partially plant-based acrylate and itaconate monomers, adding up to a plant based content of 40%.
Clear and pigmented formulations were made according to the recipes shown in *Table 1*. Coating properties are compared in *Table 2*. This shows that there are very minor differences in performance between the reference binder and the new plant-based binder.
The marginal differences observed in clear formulations are considered to fall within experimental error. In the comparison of the pigmented paints practically no differences were observed.
Hence, it seems to be very feasible to formulate coatings based on partially plant-based binder compositions for exterior wood applications with an acceptable property set which is comparable to that of coatings using standard fossil fuel-based binders.

INTERIOR FURNITURE COATINGS ARE ALSO SATISFACTORY

Secondly, a water-based 2K NCO crosslinking system was selected as a typical interior furniture coating, based on a styrene-acrylate water-based binder with a hydroxyl number of 50 mg KOH/g of solid resin.
In this case, the (meth)acrylate monomers were replaced with a combination of partially plant-based methacrylate and itaconate diester monomers. The comparison was made in a clear, high gloss paint cured with "Bayhydur 2655", at an NCO:OH ratio of 1.6. The coating formulation that was used for the comparison is shown in *Table 3*.
Again, performance of the plant-based interior coating is closely comparable to the fossil fuel-based reference. Gloss levels were a little better, but all chemical resistances were similar. Considering the low hydroxyl value of the binder, both coatings yielded excellent resistance towards ethanol, red wine, and coffee (see *Table 4*).
Hence, 2K isocyanate crosslinking interior furniture coatings based on plant-based polymer emulsions can be very useful alternatives for the fossil fuel-based types.

HIGHER BIO-DERIVED CONTENT SHOULD SOON BE POSSIBLE

Using currently available plant-based monomers, it is clearly possible to prepare binders with plant-based contents of around 40% yielding properties that are very similar to those of commercially available reference binders based on fossil fuel-based monomers.
Fully bio-based alternatives to the current (meth)acrylate monomers or, for instance, commercially available butyrolactones (*Figure 2*) are not yet commercially available. It can be expected that within two to five years from now, such monomers will become available, in addition to the current plant-based monomers.
The combination of all these monomers will make it possible, within the same period, to produce (meth)acrylate copolymers with a plant-based content as high as 50 - 70% on carbon. Such binders have already been prepared on a laboratory scale. However, polymerisation process conditions and formulation requirements will need to be optimised before these developments are ready for the market.
At present, partially plant-based industrial wood coatings can be prepared with bio-contents in the binder of 40%, attaining coating properties comparable to those of fossil fuel-based types. Currently this is made feasible using two approaches; (meth)acrylate monomers containing plant-based alcohol residues or diesters of itaconic acid.
Using a combination of these approaches yields plant-based binders with similar performance to standard binders used for commercial industrial wood coatings. In the near future, the plant-based content of copolymeric binders can probably be extended to 50% or higher.

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Table 2: Comparison of properties of exterior wood coatings containing binders made from only fossil fuel-based monomers or from partially plant-based monomers.

	Clear formulation		Pigmented formulation	
	Fossil fuel based	Plant based	Fossil fuel based	Plant based
Bio-content of binder (on carbon)	0%	40%	0%	40%
Early water resistance (4 hrs)*	2/5	3/5		
Early blocking resistance (500 m)*	4	4	3	3
Elongation at break (110 m)	117	122	94	96
Toughness (MPa)	8	12	7.5	7.5
Impact (N) – RT/7 °C	8/6	7/6	8/7	9/7
Outdoor exposure (24 months)			Good	Good
QUV EN 927-6 (2016 hours)			Good	Good
Gardner wheel (357 cycles)			Good	Good

* 0 is poor, 5 is excellent

"This bio-based monomer will be produced from secondary waste streams"

3 questions to Tijs Nabuurs

Dr Tijs Nabuurs
DSM Coating Resins
Tijs.Nabuurs@dsm.com

What are the reasons for stopping at 40% bio-based carbon at the moment? *At this point in time, our "Decovery" binders have proven bio-based contents of between 30 and 50 %, based on carbon atoms. Since performance is key for our coatings, we need to balance bio-based content against performance and costs. At this moment, increasing bio-based content would not deliver the required performance or will be too costly. We however keep looking for ways to increase biobased content while maintaining the required balance of performance and cost.*

Are the bio-based feedstocks you are using in competition with the food supply chain? *We have the unique opportunity that we can combine bio-based binder development with development of fermentation processes. At this point in time, production of all but one of our plantbased monomers do not compete with the food chain. As soon as we can scale up, this bio-based monomer will be produced from secondary waste streams, thus enabling us to completely avoid competition with the food chain.*

Can you explain why do you think that fully bio-based alternatives to meth(acrylates) should become available in the next years? And where would they come from? *We only have one planet. As leading technology partner, we wish to drive the transformation of the paint and coating industry towards a sustainable future, using renewable materials. By developing high performance resins that are plant-based, we aim to positively impact the world; for people today and generations to come.*

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