Research on the synthesis of new, bio-based adhesion promoters for UV-curable coatings

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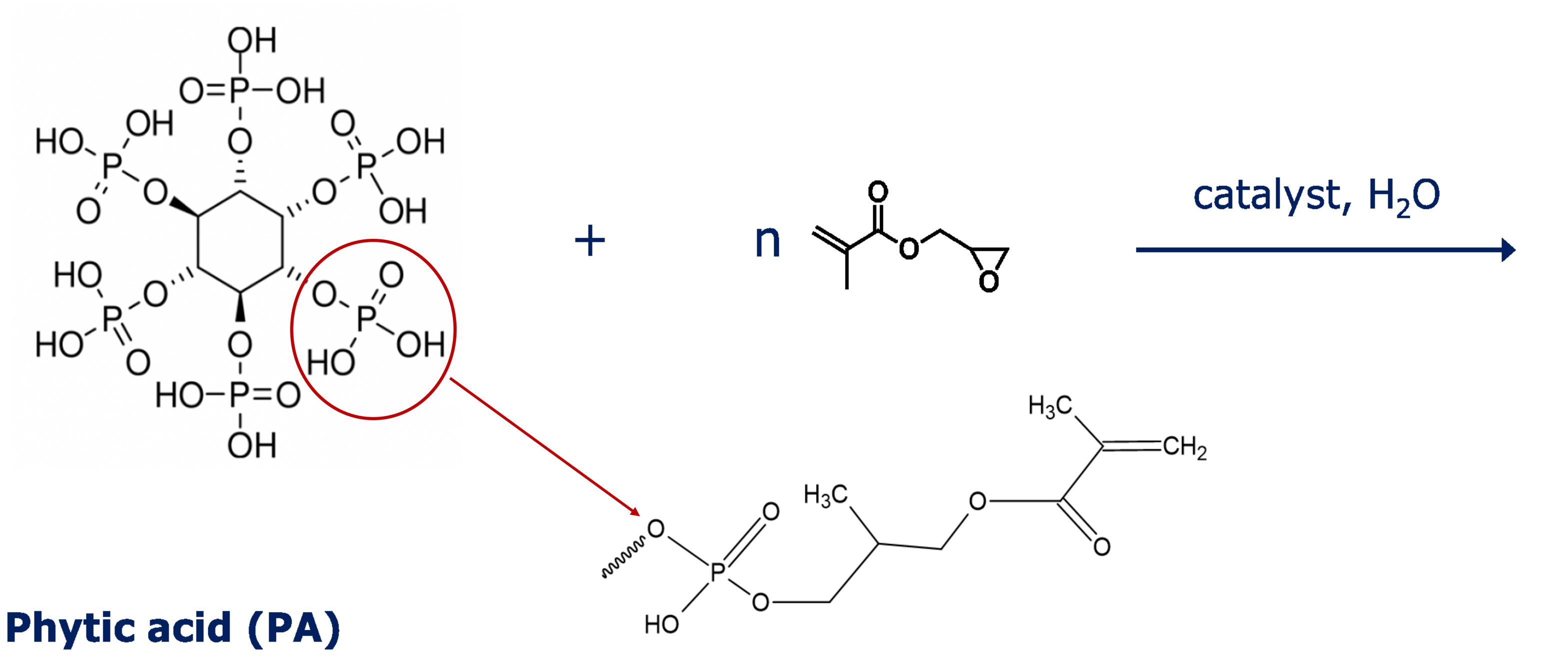
INTRODUCTION

UV curing technology is widely used in the furniture, plastic and printing industries. The growing interest in this curing technique is due to its numerous advantages, including low energy consumption, almost zero volatile organic compounds (VOC), fast production speed, etc. The use of UV-cured products on metal substrates is still very limited, despite many advances made in recent years. The main problems are lack of adhesion to the substrate or limited corrosion resistance.

The aim of the project is to develop new adhesion promoters based on green raw materials such as phytic acid and glycidyl methacrylate. Nuclear magnetic resonance (NMR) was used to characterize the chemical structure of the obtained products. Starter formulas for UV-cured coatings were also developed, which will be improved by the addition of adhesion promoters and then tested for their usability. The compositions will also be enriched with special surface modified pigments, in order to improve corrosion resistance. Thanks to increased adhesion and improved corrosion profile, it will be possible to expand the application area of UV-cured paints on metal. After the project is completed, the knowledge gained will be used for the needs of the industry.

SYNTHESIS



Phytic acid (PA)

- 6 phosphate ester groups
- 12 hydroxyl groups

→

- **easy to react**
- **good for anticorrosive products**

- bio-based raw material

→

- **ecological product**

Glycidyl methacrylate (GMA)

- presence of a glycidyl group and an unsaturated bond

→

- **possibility of reaction with PA and components of UV-cured products**
- **regulation of hydrophilic-hydrophobic properties of PA**

Other components: catalysts, hydroquinone, solvents (water and organic solvents)

CHARACTERISATION OF PRODUCTS

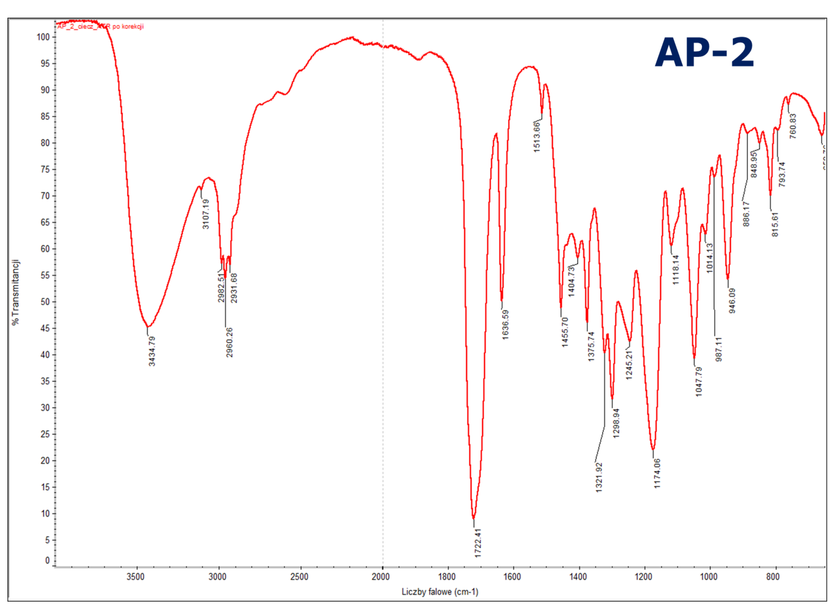


Fig. 1. FTIR spectrum of AP-2

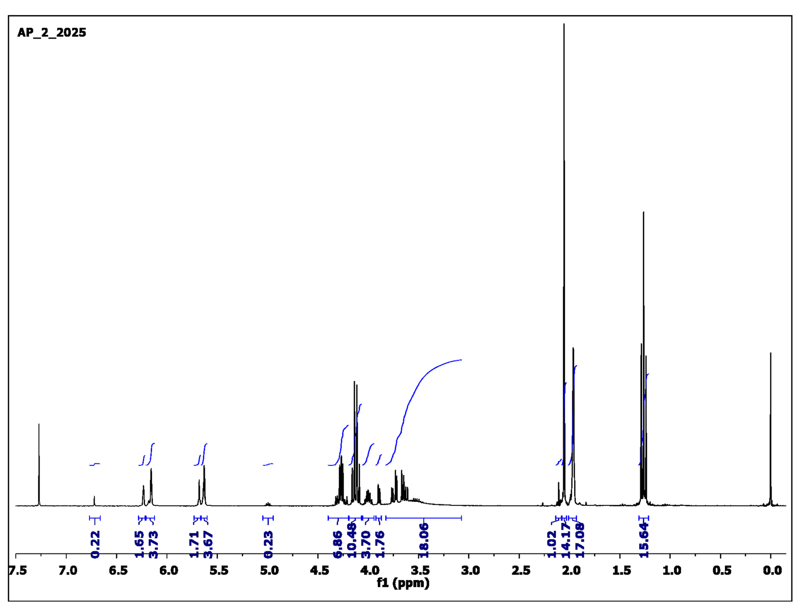


Fig. 2. ^{1}H NMR spectrum of AP-2

Chemical structure of products was confirmed by ^{1}H NMR and FTIR analysis.
In the ^{1}H NMR spectrum, the absorption peaks of acrylate double bond in the range of 5.6 to 6.3 ppm and peaks of methyl group at 1.9 ppm were observed.
In the FTIR spectrum, the bands at 1722 cm^{-1}, 1636 cm^{-1}, 810 cm^{-1} ascribed to the streching vibration peak of carbonyl group, streching vibration peak of saturated C-H and bending vibration peak of C=C were identified.

Table 1. Components used for synthesis of promotors

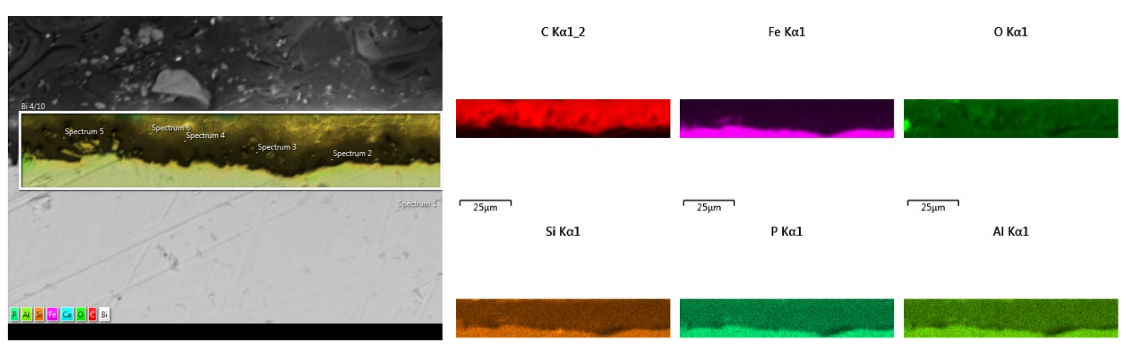
No	$n_{PA} : n_{GMA}$	Phytic acid (PA), mol (g)	Glycidyl methacrylate (GMA), mol (g)	Catalyst, % w/w
AP-1	1 : 9	0.01 (6.6)	0.09 (12.8)	Tetraethylammonium bromide 1.0
AP-2	1 : 9	0.01 (6.6)	0.09 (12.8)	Tetrabutylammonium bromide 1.0
AP-3	1 : 9	0.03 (19.8)	0.27 (38.4)	Tetrabutylammonium bromide 1.0
AP-4	1 : 6	0.01 (6.6)	0.06 (8.5)	Tetrabutylammonium bromide 1.0
AP-5	1 : 3	0.01 (6.6)	0.03 (4.3)	Tetrabutylammonium bromide 1.0
AP-6	1:12	0,06 (37,0)	0,34 (47,9)	Tetrabutylammonium bromide 1.0

The synthesized compounds were used in a model coating composition based on a mixture of a modified oligomer (a derivative of bisphenol A) and an acrylic oligomer based on an amine-modified polyether.
The synthesized compounds were in the form of homogeneous, transparent liquids. They were characterized by very good compatibility with other paint components. They improved the adhesion of coatings to a steel substrate.

Table 2. Properties of coating

Properties	Method of determination	Value
Appearance of the coating	-	homogeneous, transparent
Adhesion to substrate, degree	EN ISO 2409:2021-03	0
Cross-linking of the coating	Confirmed by FTIR and DSC	

The next step was to add 5% by weight (calculated on the basis of varnish) of developed and acidic commercial adhesion promoters to the polymer composition selected in the first stage of the project.
The paints were applied with an applicator to standard steel plates measuring 0.8 x 70 x 150 mm. The average coating thickness according to PN-EN ISO 2808:2020-01 was 50 µm. Samples placed in corrosion chambers – salt and humidity – will be exposed in the chambers until the first changes are noticed (tests are ongoing).Tests of the anti-corrosion properties of the coatings obtained by the EIS method are also being conducted. The tests are performed in a two-electrode system using an IViumStat impedance analyser after 240 hours of immersion in a 5% NaCl solution.
A morphological examination was also performed for each formulation using a scanning electron microscope [SEM] before immersion ageing and after 240 hours of immersion in order to determine potential sub-coating corrosion and material decomposition in the coating.



SEM images show no significant changes in the outer surface coating of the sample exposed to corrosive agents compared to samples of the same type that were not aged. The dispersion of pigments in the binder matrix is regular.

SUMMARY

A method for obtaining new adhesion protomers based on phytic acid was developed. The structure of the obtained products was confirmed and preliminary tests were performed to use them to improve the adhesion of coatings to steel substrates and promissing anticorrosion properies.

ACKNOWLEDGMENTS

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