Synthesis of acrylated tannic acid as bio-based adhesion promoter in EB-curable coating

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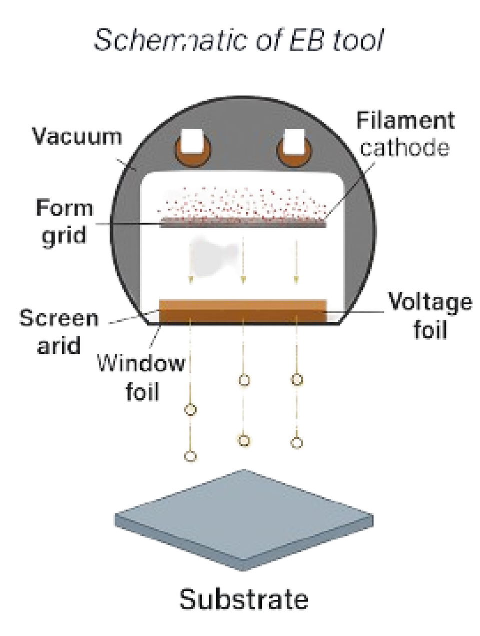
Introduction

Electron beam (EB)-curable coatings are valued for their rapid curing, low energy use, and VOC-free operation. However, their industrial use is limited by poor adhesion to metal substrates. Conventional adhesion promoters are effective but petroleum-based, raising environmental concerns.
This work explores tannic acid (TA), a natural polyphenol, as a sustainable adhesion promoter. While TA can interact with metal surfaces via coordination bonds, its high hydrophilicity reduces compatibility with organic resins. To address this, TA was chemically modified with glycidyl methacrylate (GMA) to produce acrylated derivatives (TA-GMA) with polymerizable double bonds.
Modification of this molecule improved its miscibility in EB-crosslinkable acrylic formulations, allowing them to be applied to metal substrates. Upon EB irradiation, crosslinking, and adhesion were improved. TA-GMA, especially at optimized acrylation levels, enhanced coating performance without compromising cure quality. This study demonstrates a bio-based strategy to improve EB coating adhesion while advancing the sustainability of coating technologies.

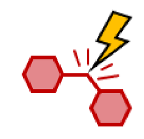
Electron Beam Curing

Schematic of EB tool

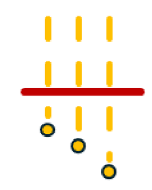


Key parameters affecting EB curing

- **Tension** [kV] Greater acceleration voltage: deeper material penetration
- **EB Dose** [kGy] Total absorbed energy, controlling extent of curing
- **EB Dose Rate** [kGy · s⁻¹] Delivery speed of the dose

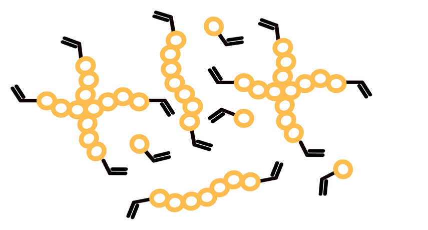


No photoinitiator needed
Electrons are energetic enough to directly radicalize most organic molecules.



Increased penetration
Possibility to obtain complete curing for very thick, colored or reflective coating layers.

Formulations



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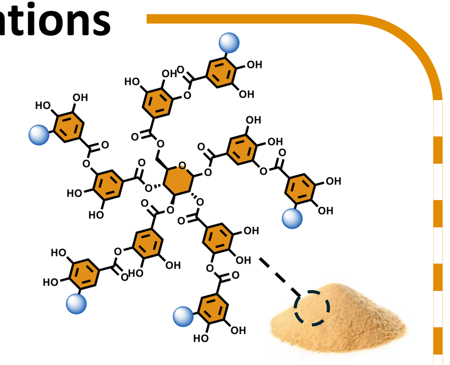
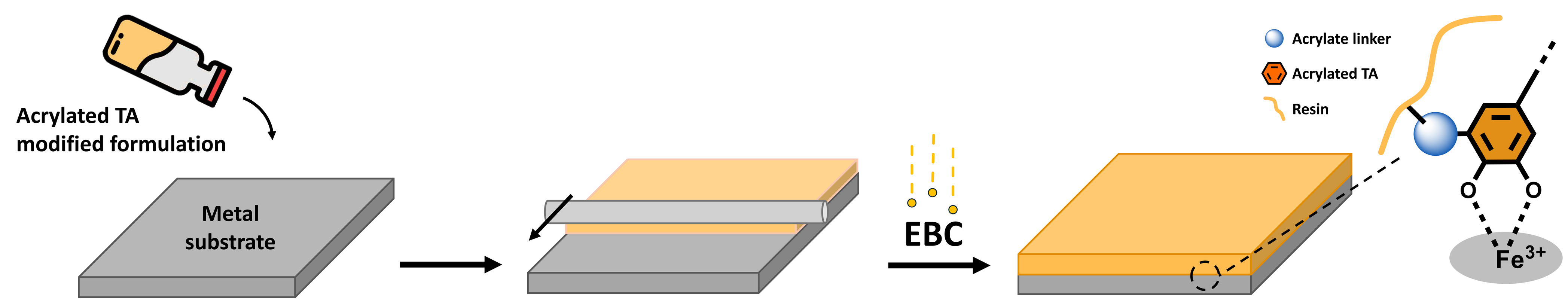


- 3 Diluting acrylates monomers
- Polyester acrylate
- Polyurethane acrylate
- Crosslinker
- Leveling agents

Bio-based Acrylated Tannic Acid

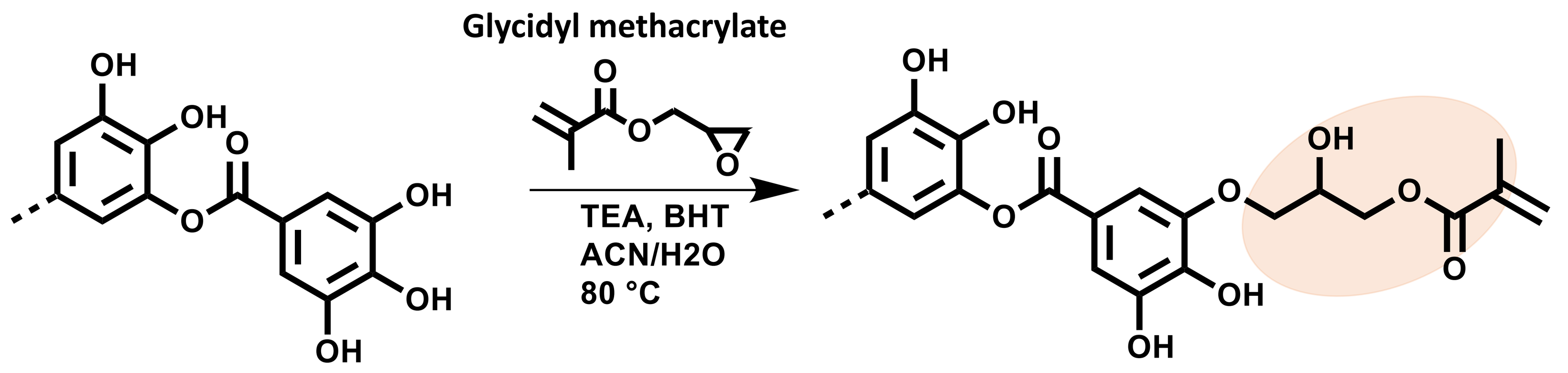
1-3% in weight

From Plant to Performance: Enhancing coating adhesion



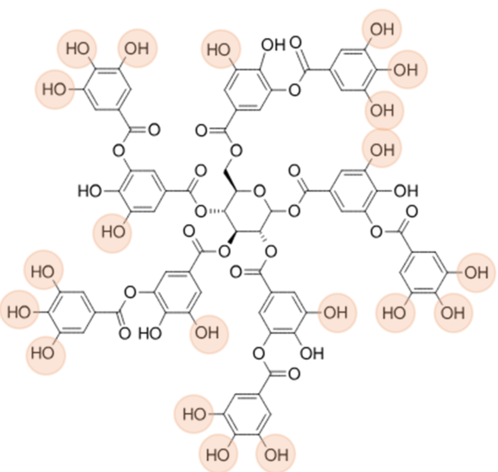
- **Enhanced adhesion** to substrate
- **Catechol** moieties in tannic acid form strong bidentate **coordination bonds with metal** ions (Fe^{3+}, Al^{3+})

Chemical Functionalization of Tannic Acid



Tannic acid was acrylated via a ring-opening reaction with glycidyl methacrylate (GMA), using TEA as catalyst and BHT as inhibitor in a water–acetonitrile medium. By adjusting the TA:GMA ratio (1:5, 1:15, 1:20), three derivatives (TA-GM5, -GM15, -GM20) with increasing acrylation degrees were obtained.

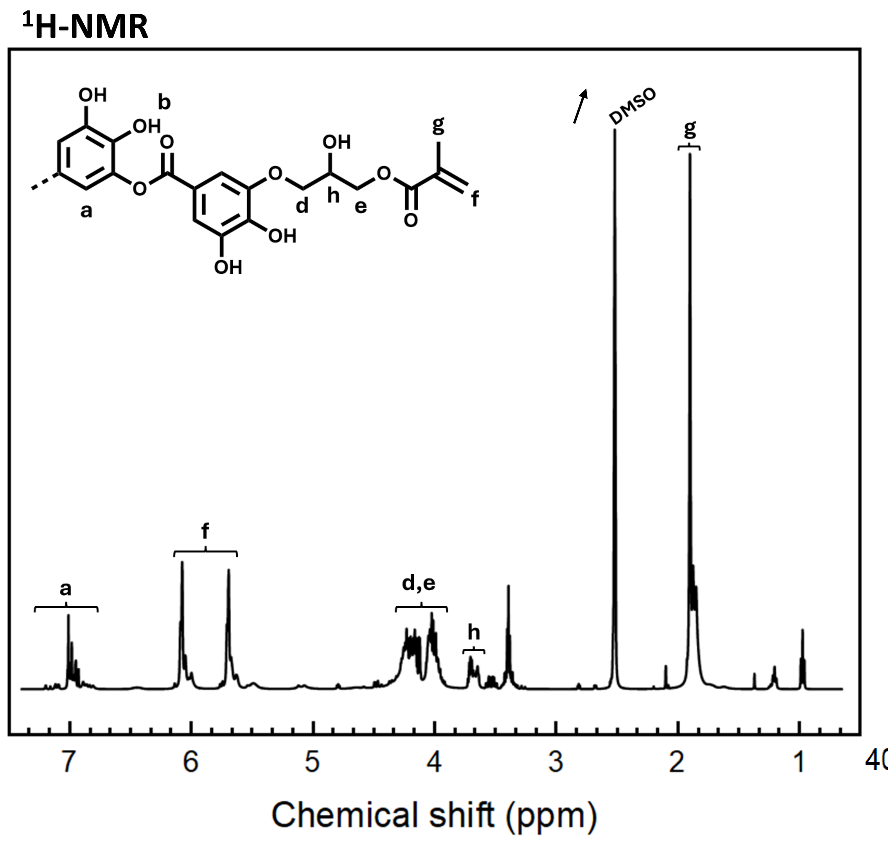
- **TA-GM5**
  TA:GMA (mol) 1:5
- **TA-GM15**
  TA:GMA (mol) 1:15
- **TA-GM20**
  TA:GMA (mol) 1:20



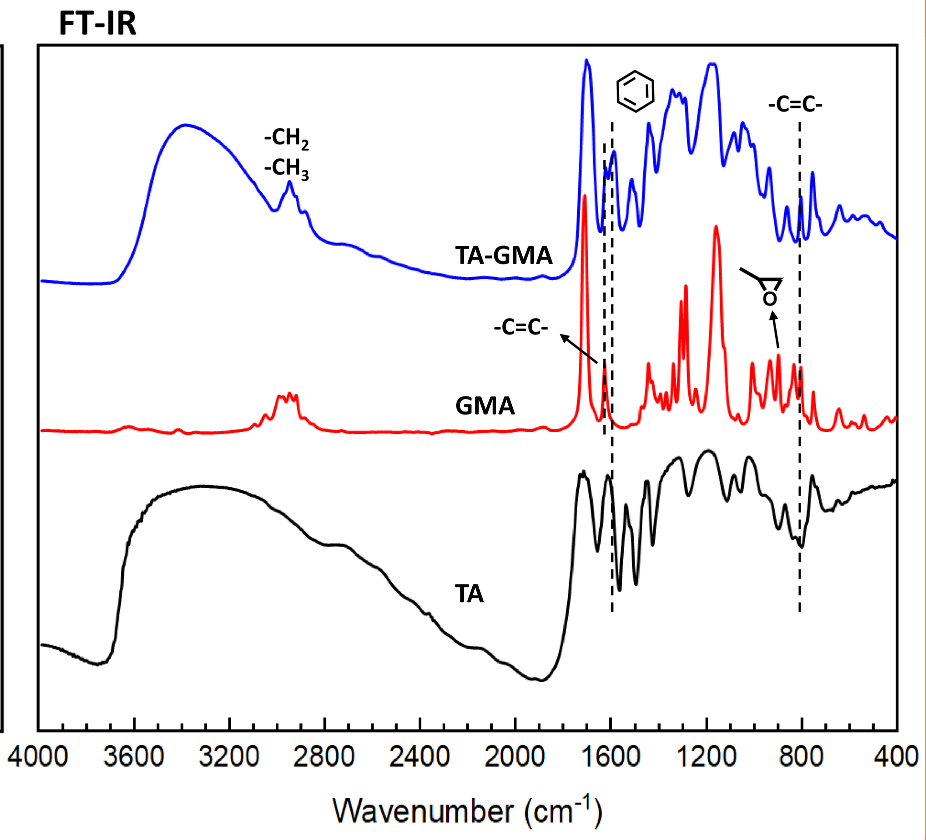
Derivative	TA:GMA Ratio	Acrylation Degree	Miscibility	Tg	Adhesion
TA-GM5	1:5	Low (~16%)	✗ Turbid	↓	✗ Poor
TA-GM15	1:15	Medium (~44%)	✓ Clear	↑	✓ Best
TA-GM20	1:20	High (~67%)	✓ Clear	↑↑	~ Variable

^{1}H NMR and FTIR spectroscopy were used to confirm the successful acrylation of tannic acid. NMR verified the disappearance of epoxy signals from GMA and the appearance of vinyl and methyl protons, indicating ring-opening and grafting. FTIR analysis supported these findings by revealing characteristic C=C vibrations, confirming the formation of acrylated tannic acid.

^{1}H-NMR



FT-IR



- **Epoxy ring opening confirmed**
  → peaks at 3.5-4.5 ppm
- **Methacrylic double bond retained**
  → Peaks at 6.1 and 5.6 ppm
- **Presence of aromatic TA rings**
  → Peaks at 6.8/7.5 ppm

- **Presence of TA catechols –OH groups**
  → peaks at 1200, 1720 and 3400 cm^{-1}
- **New –CH_2 and –CH_3 peaks appeared**
  → peaks at 2960, 2880 cm^{-1}
- **Methacrylic double bond retained**
  → peaks at 1631 and 810 cm^{-1}

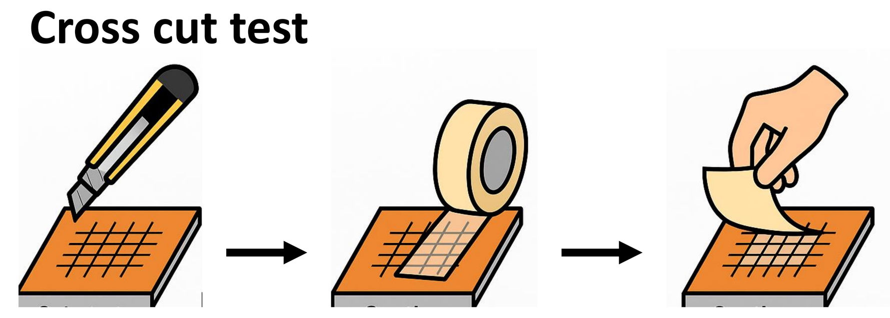
References

[1] Rossella Sesia, Silvia Spriano, Marco Sangermano, *Progress in Organic Coatings* 2024, Volume 189.
[2] Hailong Fan, Qiuya Zhang, and Zhaoxia Jin, *ACS Omega* 2017 *2* (10), 6668-6676.
[3] Gao, Qingtao and Cao, Xiaodong, *Biomater. Sci* 2020, Vol. 8, 2694-2701.

Adhesion tests

To evaluate the interfacial performance of EB-cured coatings, two complementary adhesion tests were performed: a cross-cut tape test and a corrosion simulation using copper sulfate. These tests assess both mechanical anchoring and chemical durability of the coatings on metal substrates.

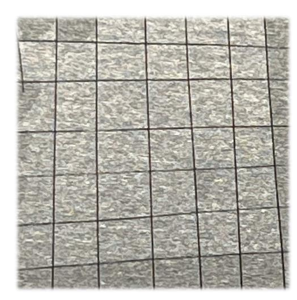
Cross cut test



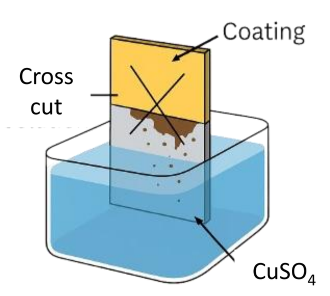
Monomer	No additive	1 wt% additive	3 wt% additive
IBOA	0	4.5	3.5
CTFA	0.5	5	3
THFA	0	4.5	3.5

5 The edges of the cut are completely smooth, **None of the square** of the lattice **is detached**

0 The **coating** has **fully detached** from the substrate and/or a cross-cut area >80% is affected



Corrosion test: EB vs solvent-based coating



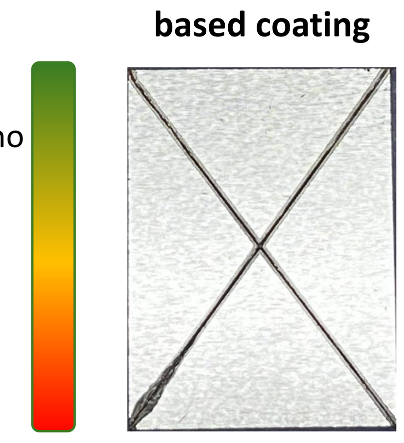
Coated metal panels immersed for 4 hours to simulate accelerated corrosion conditions.

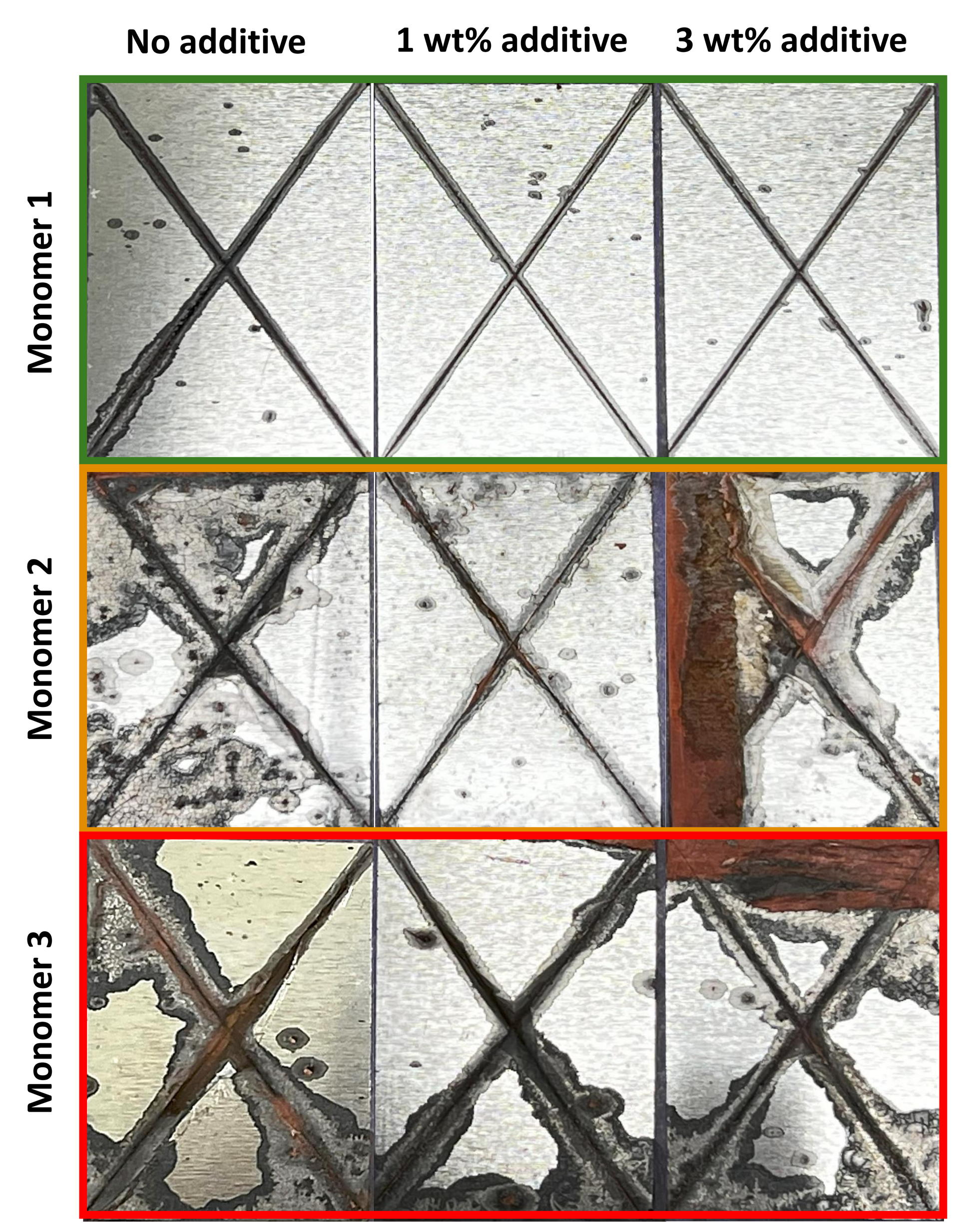
Monomer	No additive	1 wt% additive	3 wt% additive
Reference	4.75	-	-
Monomer 1	3.75	4.5	4
Monomer 2	2.25	3.5	3
Monomer 3	2	2.25	1.75

Traditional solvent based coating

5 **No corrosion**
Surface intact, no delamination

0 **Complete failure**
Full delamination





Conclusions

- Acrylated tannic acid (TA-GMA) was successfully synthetized and characterized as a bio-based adhesion promoters for EB-curable coatings
- NMR and FTIR confirmed the disappearance of the epoxy group and the formation of polymerizable acrylate functionalities
- Among the synthesized derivatives, TA-GM15 offered the best balance between compatibility, crosslink efficiency and adhesion
- Adhesion and corrosion tests demonstrated significantly improved interfacial performance in formulations containing TA-GMA, especially 1 wt% loading
- Performance varied depending on the monomer matrix, underlining the importance of additive–monomer interactions.