

Document Version

Final published version

Licence

CC BY

Citation (APA)

Darikwa, T. C., Mojon, M. L., Picken, S. J., & Garcia, S. J. (2026). Controlling segregation states and chemical interactions to modulate the water-triggered release of organic corrosion inhibitors from polymer films. *Materials Today Advances*, 31, Article 100948. <https://doi.org/10.1016/j.mtadv.2026.100948>

Important note

To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright

In case the licence states "Dutch Copyright Act (Article 25fa)", this publication was made available Green Open Access via the TU Delft Institutional Repository pursuant to Dutch Copyright Act (Article 25fa, the Taverne amendment). This provision does not affect copyright ownership.
Unless copyright is transferred by contract or statute, it remains with the copyright holder.

Sharing and reuse

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.



Controlling segregation states and chemical interactions to modulate the water-triggered release of organic corrosion inhibitors from polymer films

Tinashe C. Darikwa^a, Marlon L. Mopon Jr.^{a,b}, Stephen J. Picken^c, Santiago J. Garcia^{a,*}

^a Department of Aerospace Structures and Materials, Delft University of Technology, Delft, the Netherlands

^b Department of Chemical Engineering, University of the Philippines, Diliman, Quezon City, Philippines

^c Advanced Soft Matter, Department of Chemical Engineering, Delft University of Technology, Delft, the Netherlands

ARTICLE INFO

Keywords:

Self-stratifying coatings
Controlled release
Organic corrosion inhibitor
Self-healing
Anticorrosion coatings
HSP
Polymer blends

ABSTRACT

This work presents a strategy to control the dispersion and stratification degree of functional organic molecules, such as organic corrosion inhibitors, in polymeric matrices and studies its effect on their water-controlled release. 2,5-Dimercapto-1,3,4-thiadiazole (DMTD) was used as the model inhibitor and p (BMA-co-MMA) as the polymer matrix. By systematically varying solvent-inhibitor compatibility and inhibitor loading, films with distinct and previously unreported self-stratified architectures were obtained, exhibiting different degrees of inhibitor dispersion and aggregation. Poor DMTD solubility, as in toluene, produced stratified films, whereas better solvents such as tetrahydrofuran, methyl ethyl ketone, and methyl isobutyl ketone yielded dispersions governed by solubility and evaporation rate. Uniform dispersion, typically accompanied by larger T_g depression, generally correlated with faster initial release in salty water, though this effect could be offset by stronger inhibitor-matrix interactions. Aggregate- or layer-rich structures supported extended inhibitor release through gradual inhibitor dissolution in the DMTD-rich domains in the hydrophobic polymer matrix. Preliminary immersion tests on AA2024 demonstrate that DMTD released from the coatings remains corrosion-active, effectively suppressing localized corrosion following coating damage. Overall, the ability to tailor film structure through solvent selection and inhibitor concentration represents a powerful tool for embedding reactive molecules in polymer matrices for use in engineering coatings.

1. Introduction

Organic coatings with certain degree of hydrophobicity provide an effective means of protecting metallic substrates against corrosive environments. However, the protection that the organic polymer matrix provides is largely passive and inevitably lost over time through natural water diffusion accelerated by ageing or mechanical damage, unless so-called intrinsic healing polymer coatings are used [1,2]. To overcome this limitation, coating systems incorporate functional additives such as corrosion inhibitors. When the coating is damaged, these inhibitors leach out from the coating, at the damage site, to interact with the exposed metallic substrate and suppress corrosion reactions [3,4]. This inhibition mechanism mitigates the effect of the coating damage and effectively extends the service life of metallic structures broadly used across construction, transportation, chemical processing, marine, and other industrial sectors, ultimately supporting safer operation, higher reliability, and reduced maintenance costs.

Implementing such active protection strategies ultimately depends on the use of effective corrosion inhibitors. For decades, hexavalent chromium compounds were regarded as the benchmark for achieving such functionality. However, their well-known carcinogenicity pushed the search for safer alternatives [5]. Among the most extensively studied replacements are phosphates [6,7], rare-earth salts [8–10], lithium compounds [11,12], and a diverse range of organic compounds [13–20]. The recent designation of rare-earth elements and lithium as critical raw materials [21] has nonetheless reinforced the focus on organic corrosion inhibitors, which not only offer a more sustainable supply but are also considered generally safer than their inorganic counterparts [22].

While organic corrosion inhibitors show great potential for providing active protection, their direct incorporation into organic coatings often presents practical challenges. Issues such as poor compatibility with the polymer matrix, uncontrolled leaching, and loss of inhibitor functionality during film formation due to unwanted side reactions with the binder can significantly limit coating performance [16]. To address

* Corresponding author.

E-mail address: S.J.GarciaEspallargas@tudelft.nl (S.J. Garcia).

<https://doi.org/10.1016/j.mtadv.2026.100948>

Received 14 April 2026; Received in revised form 25 August 2026; Accepted 25 August 2026

Available online 3 September 2026

2590-0498/© 2026 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

these issues, recent approaches rely on the use of inhibitor carriers such as nanocontainers [3,23–25], layered double hydroxides [26,27], polymer microcapsules [28,29], and even naturally-occurring microparticles [30,31] that act as reservoirs capable of controlled inhibitor release and reducing matrix-inhibitor interactions. Nevertheless, carrier-based systems add formulation complexity and may still compromise coating uniformity, adhesion, or mechanical integrity over time [32].

An alternative incorporation approach is to apply the concept of self-stratification, in which coating components spontaneously segregate into distinct regions during curing or solvent evaporation. Notably, while this approach eliminates the need for discrete carrier structures, it still faces similar challenges related to inhibitor incorporation in the organic coating matrix. To the best of our knowledge, there are no published reports describing the application of self-stratifying coating concepts for the direct incorporation of organic corrosion inhibitors. Most reported self-stratifying coating studies focus on achieving multifunctional properties, such as combining corrosion resistance with fouling release or decorative effects, by integrating multiple resins into a single coating rather than using multicoat systems [33,34]. The self-stratifying behavior in these coatings generally arises from deliberate incompatibility between components [35,36]. Meanwhile, current studies on direct inhibitor incorporation into polymer matrices largely concern inorganic inhibitors (e.g., Li [11,37] and Ce [38] salts), with only a few exceptions such as the work of Galliano et al. [39] on the inclusion of an organic inhibitor in a waterborne coating. These studies indicate that, while self-stratification in multi-resin systems is relatively well understood, much less is known about how corrosion inhibitors phase-separate from the polymer matrices that contain them. Here, we address this gap by demonstrating, for the first time, that the self-stratification concept can be applied to incorporate a leachable organic inhibitor directly into a single-resin coating formulation. Beyond establishing feasibility for corrosion protection, this approach also highlights a broader materials-design pathway that may be adapted for systems that also involve the release of an active component from a polymer matrix, such as in drug-delivery [40], agricultural [41], antimicrobial, and antifouling systems [42].

In this work, we introduce the use of the self-stratification concept as a strategy for the direct incorporation of an organic corrosion inhibitor into a polymer matrix and study the so-far unexplored effect on the corrosion inhibitor release properties. DMTD was selected as the model inhibitor because of its well-established corrosion-inhibiting performance, particularly for aerospace aluminium alloys such as AA2024 [16, 19,43]. A butyl methyl methacrylate copolymer, further denoted as p (BMA-co-MMA), was used as the model matrix due to the relevance of methacrylate coatings, which are valued for their hydrophobicity, inherent stability, and versatility when combined with other coating chemistries [44–47]. In this system, the chemical identities of both the polymer and inhibitor were fixed. Hence, formulation control was achieved primarily through adjustments in inhibitor loading and solvent selection. By systematically varying solvent–inhibitor compatibility as well as the inhibitor loading, we investigated how these parameters influence the resulting self-stratifying architecture and corresponding inhibitor release behavior of free-standing polymer films in salty water. These free-standing film experiments were designed to provide fundamental mechanistic insight into the influence of solvent-controlled morphology on inhibitor release. To provide an initial proof-of-concept of the functionality of the developed films, preliminary corrosion inhibition results are also presented for the case of aluminium alloy AA2024-T3. The results demonstrate that the released inhibitor at damaged locations retains its expected protective effect, while a comprehensive evaluation of coating performance on metallic substrates is reserved for a follow-up study.

2. Experimental

2.1. Materials

Poly (butyl methacrylate-co-methyl methacrylate), (p (BMA-co-MMA), >99%, Sigma-Aldrich) was used as resin for the films. 2,5-dimercapto-1,3,4-thiadiazole (DMTD, >99%, Sigma-Aldrich) was used as corrosion inhibitor. Methyl ethyl ketone (MEK, >99%), methyl isobutyl ketone (MIBK, >99%), tetrahydrofuran (THF, >99%), and toluene (>99%) from Sigma-Aldrich were used as solvents. All chemicals were used as received.

2.2. Solubility evaluation

Interactions between film components (DMTD, p (BMA-co-MMA)) and the four solvents (MEK, MIBK, THF, toluene) were first investigated to assess viability of the solvents for film fabrication. Each DMTD solution was prepared by dissolving 75 mg of DMTD in 10 mL of the respective solvent. Meanwhile, p (BMA-co-MMA) solutions were prepared by dissolving 150 mg of the polymer in 10 mL of the solvent. The interactions were evaluated by visually observing DMTD solubility and by acquiring the Raman spectra of the solutions with a Renishaw inVia with 32 mW laser source at 532 nm operated at 5% maximum power.

2.3. Film fabrication

Eight film formulations with varying solvents and DMTD amounts were prepared. The DMTD amount was either at 5 or 20 wt% of the total solids (i.e., resin + DMTD). The 5 wt% loading was selected as a representative formulation with relatively low inhibitor content, whereas the 20 wt% loading was intentionally included to accentuate the influence of solvent-controlled dispersion on film morphology and inhibitor release at maximum inhibitor concentrations used in other protective primers such as CrVI-rich epoxy primers. Film batches were prepared by dissolving 4 g of the solids, with appropriate resin-DMTD ratio, in 40 mL of the target solvent (MEK, MIBK, THF, or toluene). It is noted that, at 5 wt% loading, the DMTD-to-solvent ratio (5 mg mL⁻¹) is comparable to that used in the solubility evaluation, whereas at 20 wt % loading it is substantially higher (20 mg mL⁻¹). The mixtures were agitated for 15 h with a shaker plate rotating at 200 rpm. Afterwards, the dispersions were sonicated in an ultrasonic bath for 20 min before casting into a 60 mm (diameter) x 20 mm (depth) borosilicate petri dish (Duroplan). The casted solutions were dried at room temperature for 24 h to facilitate film formation. The films were then removed and vacuum-dried at room temperature for 24 h, yielding dry free-standing films used for subsequent tests. Table 1 summarizes the film labels and their corresponding components.

2.4. Film characterization

To analyse the cross-section of the fabricated films, fragments were embedded in cold-curing epoxy (Epofix) and cured for 15 h. The

Table 1

Composition of free-standing film batches. Each batch contained 4 g of polymer–DMTD mixture (at the specified ratio) dissolved in 40 mL of the designated solvent.

Film Label	p (BMA-co-MMA) wt%	DMTD wt%	Solvent
MEK-05	95	5	MEK
MIBK-05			MIBK
THF-05			THF
TOL-05			toluene
MEK-20	80	20	MEK
MIBK-20			MIBK
THF-20			THF
TOL-20			toluene

embedded films were dry-polished (i.e., no solvent used) with SiC paper up to a grain of 5 μm . The morphology of the embed cross-sections was analysed with a confocal laser scanning microscope (Keyence VK-X1000). Chemical information corresponding to the film cross-sections was obtained through confocal Raman microscopy (Renishaw inVia; pixel resolution: $2.5 \times 2.5 \mu\text{m}$; 32 mW laser source at 532 nm). Raman maps were acquired at 5% of the maximum power and a Stream HTR scan mode (0.5 s exposure time; single accumulation). The spectral range measured was from 175.36 to 1925.1 (centre 1100) cm^{-1} .

The effect of the formulation variations on the thermal properties of films was studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA experiments were performed with a Perkin Elmer TGA 4000 at a temperature range of 30 to 700 $^{\circ}\text{C}$ and a heating rate of 5 $^{\circ}\text{C min}^{-1}$ under N_2 flow. DSC experiments were performed in a TA Instruments Discovery DSC 250 with a temperature range of -20 to 100 $^{\circ}\text{C}$ at a heating and cooling rate of 10 $^{\circ}\text{C min}^{-1}$. Each DSC test involved 2 heat-cool cycles with a 5-min isothermal time after each heating or cooling step.

2.5. Inhibitor release tests

Immersion tests in 0.05M NaCl water solutions, following previously established release protocols [9,30,31], were performed to quantify the effect of the polymer-organic inhibitor architecture on inhibitor release. To this aim, ~ 50 mg of films were immersed in 200 mL of 0.05 M NaCl (Millipore Elix 3 UV treated) for 3 h. At set time intervals, 3.5 mL aliquots of the immersion solution were withdrawn and analysed using a Perkin Elmer Lambda 35 UV-Vis spectrometer. After measurement, each aliquot was returned to the container to keep the bath volume constant. The absorbance values were compared against a DMTD calibration curve to quantify the inhibitor released by the films over time. The calibration data is provided in [Supporting Information 1](#).

2.6. Preliminary assessment of corrosion inhibition

The corrosion protection provided by the polymer-organic inhibitor architectures was preliminarily evaluated using coated AA2024-T3 substrates. Prior to coating application, AA2024-T3 panels were sequentially ground using 180 and 320 grit SiC abrasive papers, followed by surface conditioning with Scotch-Brite™ 3M Clean-N-Finish AVFN under running water. The specimens were subsequently rinsed with ethanol and distilled water, with drying by compressed air after each rinsing step. Prior to coating application, the substrates were immersed in 2 M NaOH solution for 10 s to generate a pseudoboehmite surface layer for higher adhesion, rinsed thoroughly with distilled water, dried with compressed air, and allowed to stabilize for 30 min before coating application.

Given the limited adhesion of the p (BMA-co-MMA) coatings to the metallic substrates, an approximately 6 μm thick epoxy primer layer was first applied by spin coating. To this aim, a solution consisting of Epikote 2500 epoxy resin and Ancamine curing agent (mixing ratio 1:0.58) dissolved in xylene was used. Spin coating was performed at 2000 rpm for 60 s, followed by curing at 60 $^{\circ}\text{C}$ for 24 h.

The p (BMA-co-MMA)-inhibitor formulations were prepared by speed mixing at 2500 rpm for 10 min to obtain solutions containing 20 wt% total solids (polymer and HDMTD) and 80 wt% solvent. Three coating formulations containing 0, 5, and 20 wt% HDMTD relative to the dry polymer mass were prepared using p (BMA-co-MMA) as the polymer matrix. The formulations were applied by pouring onto the epoxy-primed metals, producing coating morphologies representative of those obtained in the free-standing film study. The coatings were air dried at room temperature ($\sim 20^{\circ}\text{C}$) for 24 h, followed by post-curing at 85 $^{\circ}\text{C}$ for 15 h. The resulting dry coating thickness was approximately 180 μm , depending on formulation, to closely match the thickness of the free-standing films used in the inhibitor release experiments and decrease the effect of film thickness on polymer morphology.

The coated specimens were subsequently subjected to a preliminary corrosion screening. Prior to exposure, a circular scribe approximately 1 mm in diameter was introduced through the coating to expose the underlying AA2024 substrate. The specimens were then immersed in 0.05 M NaCl solution for 15 h. A longer immersion time than that used for the inhibitor release experiments was selected to allow sufficient time for electrolyte ingress, initiation of localized corrosion at the exposed substrate, and development of a measurable number of corrosion pits for comparison among the different coating formulations. Following exposure, the scribed region was examined using optical microscopy in a first preliminary analysis of the corrosion protection effect and the relation to the coating-inhibitor architecture.

3. Results and discussion

3.1. DMTD-solvent interactions

Fig. 1 shows solutions of DMTD and p (BMA-co-MMA) in the target solvents: toluene, THF, MEK, and MIBK. The DMTD solutions (**Fig. 1a**) show visible differences in turbidity, with the toluene system appearing completely cloudy and the THF, MEK, and MIBK systems appearing clear. The cloudiness of the toluene system indicates that, at a concentration of 7.5 mg mL^{-1} , DMTD is only partially soluble in the solvent. Meanwhile, the p (BMA-co-MMA) solutions (**Fig. 1b**) in the four solvents were all clear indicating that the solvents were all compatible and capable of completely dissolving the resin at a concentration of 15 mg mL^{-1} . Since the films are formed from mixed solutions of DMTD and p (BMA-co-MMA), the different solubility behaviors of DMTD are expected to influence how it distributes within the polymer matrix during film formation. The effects should already be evident in the 5 wt % systems, which have a comparable DMTD-to-solvent ratio, and are expected to be further amplified in the 20 wt% systems, where the initial DMTD-to-solvent ratio is 2.6 times higher than that used in the solubility tests.

a) DMTD



b) p(BMA-co-MMA)



Fig. 1. Solutions of (a) DMTD in the target solvents show variations in turbidity indicative of differences in solubility behavior. Corresponding solutions of (b) p (BMA-co-MMA) in the same set of solvents show comparable clarity indicative of good solubility.

The partial solubility of DMTD in toluene is further confirmed by Raman analysis of the solutions (Fig. 2a–d). Because hydrogen bonding of the solvents with the thiol groups of DMTD can affect electron distribution throughout the molecule, it can reduce the electron density of the ring C-S bond. The resulting shift of the ring C-S vibration mode (originally at 658 cm^{-1}) to 650 cm^{-1} was analysed to semi-quantitatively evaluate inhibitor solubility (Fig. 2e). It was found that the shift is minimal for the toluene system (Fig. 2a) but is more pronounced for the THF, MEK, and MIBK ones (Fig. 2b–d, red lines showing 658 peak shift to lower wavenumber). The partial solubility of DMTD in toluene, compared to its high solubility in THF, MIBK, and MEK, can be explained by differences in solvent polarity. This is supported by the Hansen solubility parameters (HSPs) of the solvents and DMTD, summarized in Table 2. The HSP values for DMTD were estimated using the method of Stefanis and Panayiotou [48] and the calculations are provided in Supporting Information 2. A key observation is that the polar component (δ_p) of toluene is much lower than both the corresponding values of the other solvents and that of DMTD itself. This difference in polarity reflects a solvent–inhibitor interaction that governs how DMTD is accommodated within the otherwise soluble p (BMA-co-MMA) matrix, and can be purposefully leveraged to tune solubility and thereby control the resulting film morphology. Notably, Hansen distance (R_a) calculated for DMTD and the solvents indicate the following solubility order:

Table 2

Hansen solubility parameters of DMTD and the selected solvents [48,49]. The R_a reported for the solvents is with respect to DMTD.

	δ_D (MPa ^{0.5})	δ_P (MPa ^{0.5})	δ_H (MPa ^{0.5})	R_a
DMTD	25.2	18.9	17.2	-
Toluene	18.0	1.4	2.0	27.29
THF	16.8	5.7	8.0	23.26
MIBK	15.3	6.1	4.1	26.97
MEK	16.0	9.0	5.1	24.14

toluene < MIBK < MEK < THF.

3.2. Free-standing film cross-sectional morphology and DMTD distribution

Fig. 3 presents the resulting cross-sectional film morphology when DMTD is incorporated into the p (BMA-co-MMA) matrix using the target solvents. The A and S labels on the left side of each image indicate which surface of the film was exposed to air (A) and which surface was in contact with the borosilicate substrate (S). Overall comparison of the images show visible differences in the morphology both as a function of DMTD loading and of the solvent used.

The TOL-05 film was characterized by a thin, translucent yellowish

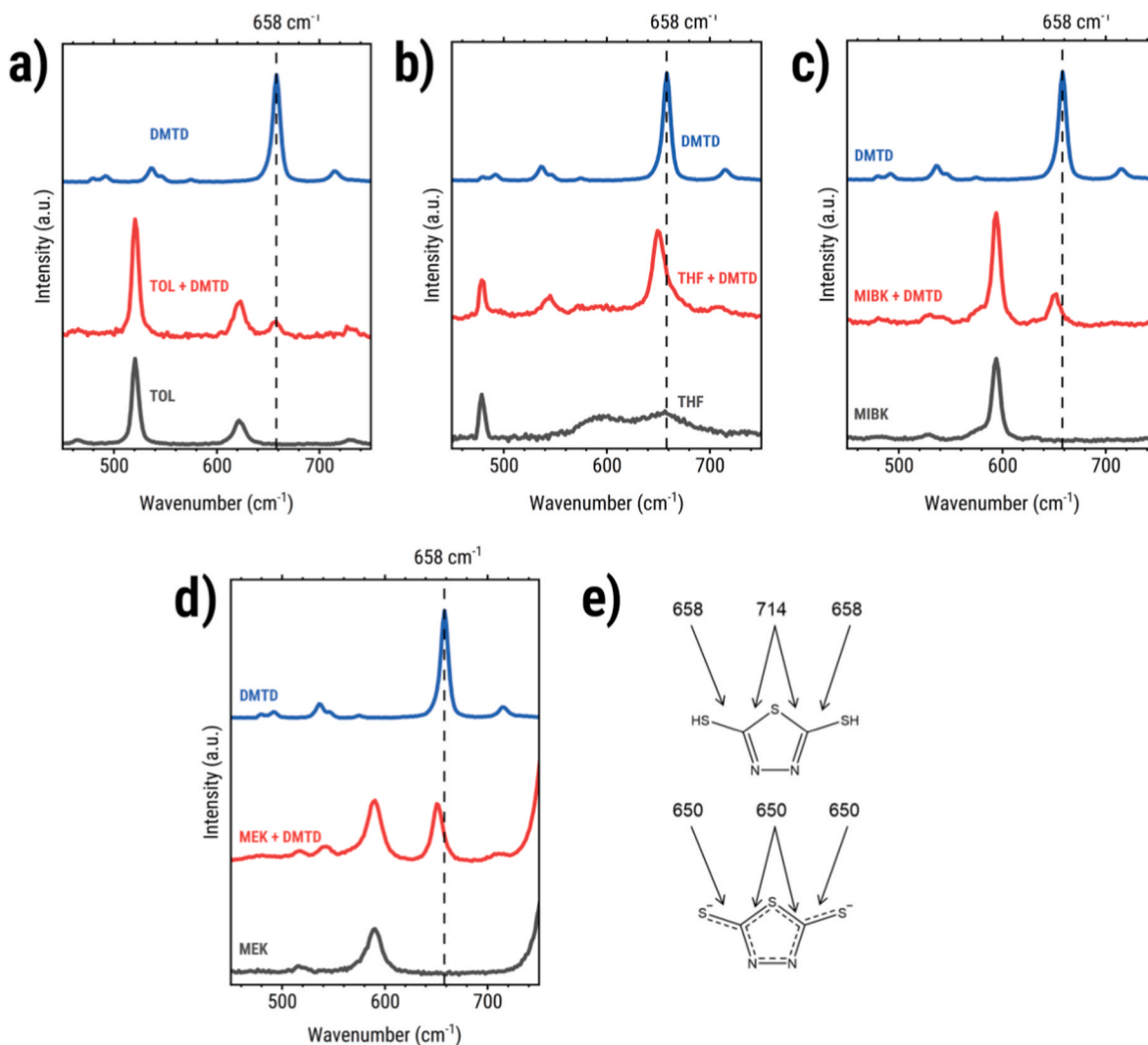


Fig. 2. Raman spectra of the solution of DMTD in the selected solvents: (a) toluene, (b) THF, (c) MIBK, and (d) MEK. The spectra shown are those of the solvent (black curve), crystalline DMTD (blue curve), and the solution of the two components (red curve) with the dashed line denoting the C-S bond stretch characteristic to DMTD. The changes in the molecular bonds associated with the peak shifts are presented in (e).

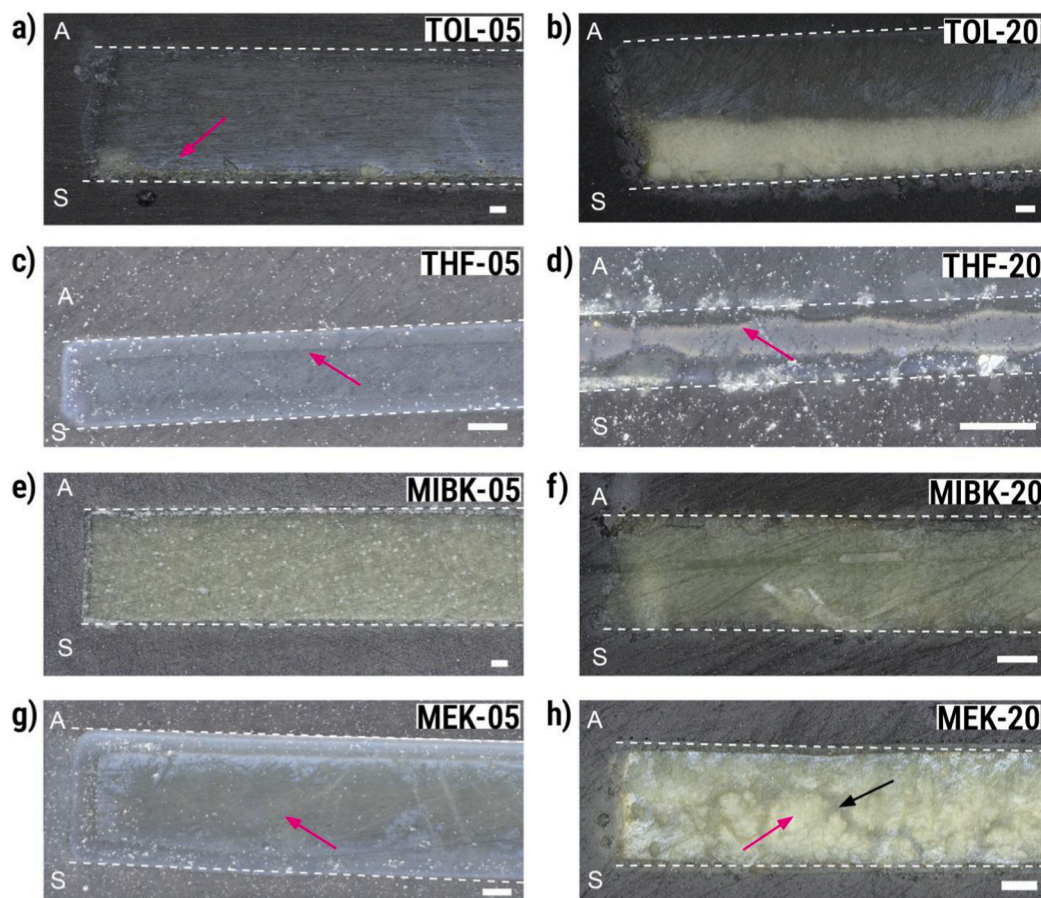


Fig. 3. Microscopy images of the embedded films, showing the cross-sectional morphology of film formulations: (a) TOL-05, (b) TOL-20, (c) THF-05, (d) THF-20, (e) MIBK-05, (f) MIBK-20, (g) MEK-05, and (h) MEK-20. A and S respectively denote the air and substrate interface of the films during film formation. Scale bar is 100 μm .

layer close to the S side of the film (see magenta arrow in Fig. 3a). The coloration of the layer is attributed to the presence of DMTD. Meanwhile, the rest of the film remains essentially colourless, consistent with the appearance of the base polymer. In contrast, the TOL-20 film (Fig. 3b) exhibited a thicker and more defined translucent yellowish layer near the S side.

Both the THF-05 (Fig. 3c) and the THF-20 (Fig. 3d) films exhibit some form of core-shell separation (light color surrounding darker color in the film). The core-shell boundaries (see magenta arrows in Fig. 3c and d) are attributed to potential interactions of the film with the epoxy system used for embedding, as confirmed with Raman analysis in Fig. 4. Thus, only the core parts are considered relevant to the morphology analysis in this case. The THF-05 showed a more homogeneous cross-section than the TOL films. It is also slightly more translucent than the clear section of the TOL films, but DMTD-rich sites were difficult to ascertain visually. The THF-20 core was also found to be homogeneous, but visibly more translucent and with a more yellowish tint than that of the THF-05. This suggests good dispersion of DMTD across the film, which is consistent with the low R_a value calculated for THF (Table 2).

The MIBK-05 film (Fig. 3e) exhibited a more yellowish cross-section than all of the other 5 wt% systems. Notably, the yellow coloration is not evenly distributed leading to a mottled appearance. The yellowish tint is even more apparent for the MIBK-20 film (Fig. 3f). Similar to its low wt% counterpart, the yellowing is also uneven. As with the earlier films, the yellow coloration throughout the film is associated with the presence of DMTD in a dispersed state which is related to the use of a solvent with a relatively low R_a value.

Both the MEK-05 and MEK-20 films (Fig. 3g and h) showed core-shell morphologies similar to the THF films. Unlike the THF films though, the

shells found in the MEK films were relatively thinner which suggests less extensive interaction with the epoxy system used for embedding. The MEK-05 core was also homogeneous with a yellowish tint (see magenta arrow in Fig. 3g). The addition of more DMTD in MEK-20 resulted in a cloudy yellow cross-section characterized by high-opacity regions (see magenta arrow in Fig. 3h) traversed by thin translucent paths (see black arrow in Fig. 3h).

Complementary Raman mapping (Fig. 4) shed more light on the DMTD distribution initially seen in the cross-section microscopy images (Fig. 3). Each set of maps in Fig. 4 is composed of an optical microscopy (OM) image of the embedded film cross-section accompanied by the Raman maps corresponding to the C-S stretching mode of DMTD at 534 cm^{-1} [50], the phenyl ring stretching mode of the epoxy embedding resin at 1609 cm^{-1} [51], and the carbonyl stretching mode of p (BMA-co-MMA) at 1730 cm^{-1} [52]. The C-S stretching mode of DMTD was selected for visualizing DMTD distribution since the location of the peak corresponding to this stretching mode is not expected to be significantly affected by interactions with the polymer matrix, unlike the 650 cm^{-1} vibration mode presented in Fig. 2. Meanwhile, the 1609 and 1730 cm^{-1} maps were used to establish the boundaries between the films and the epoxy matrix used for embedding.

Raman maps confirm that the TOL-05 films have a p (BMA-co-MMA) matrix largely devoid of DMTD (Fig. 4a). A few yellow spots appear in the midsection of the 534 cm^{-1} map, likely due to DMTD particles redistributed during polishing. A distinct DMTD aggregate was observed near the bottom of the film (see white arrow in 534 cm^{-1} map of Fig. 4a), compatible with the thin yellow layer seen in Fig. 3a. In contrast, the THF-05 Raman maps (Fig. 4b) reveal a uniform DMTD distribution throughout the film core, despite the minimal yellowing observed in

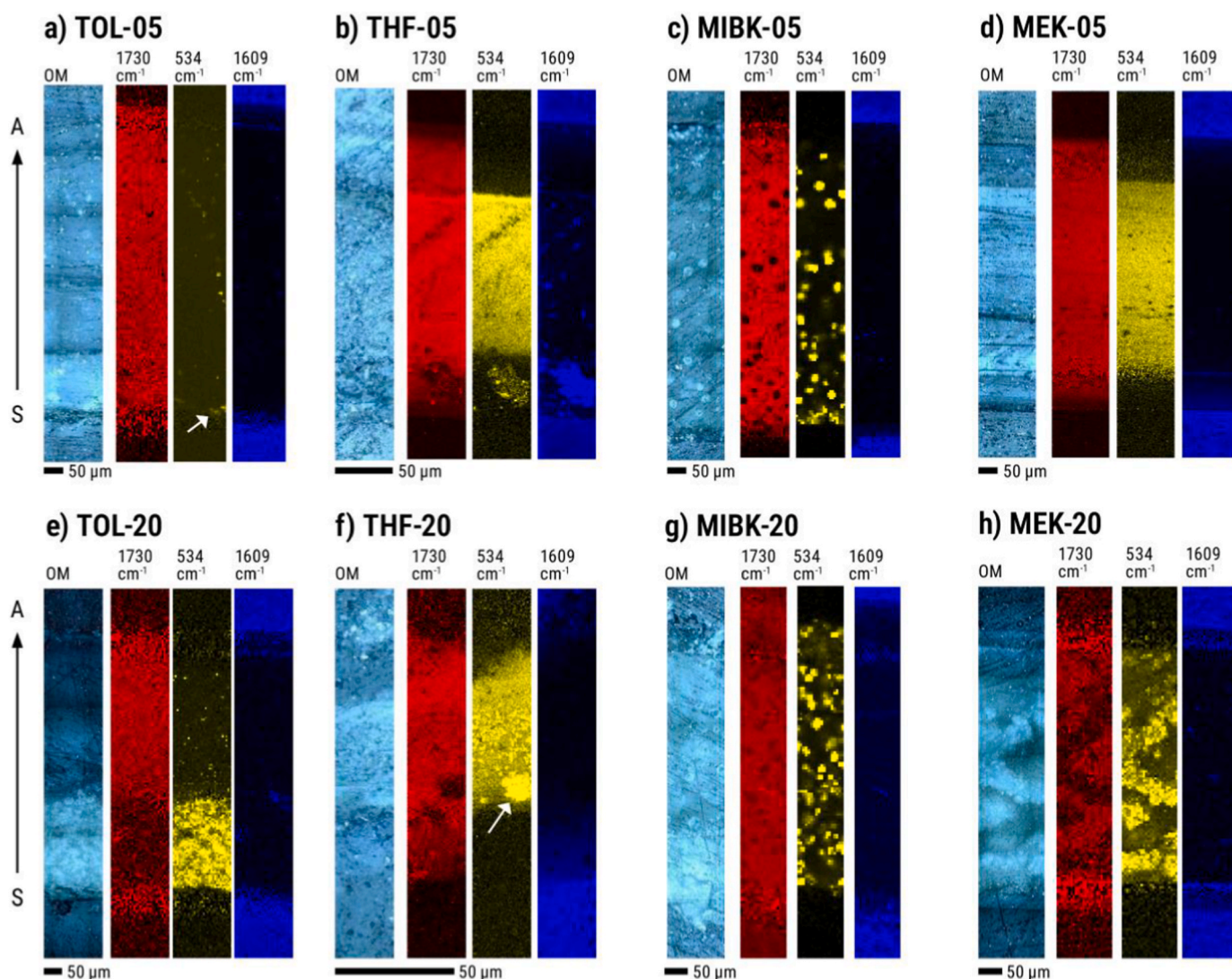


Fig. 4. Optical microscopy (OM) and Raman microscopy maps of cross-sectioned embedded films, showing the spatial distribution of components in film formulations: (a) TOL-05, (b) THF-05, (c) MIBK-05, (d) MEK-05, (e) TOL-20, (f) THF-20, (g) MIBK-20, and (h) MEK-20. Raman maps are color-coded by characteristic frequency shifts: 1730 cm^{-1} (red) for p (BMA-co-MMA), 534 cm^{-1} (yellow) for DMTD, and 1609 cm^{-1} (blue) for the Epofix embedding resin. The symbols A and S indicate the air and substrate interfaces, respectively, during film formation.

Fig. 3c. It is noted that the 1730 cm^{-1} map did not show any signs of reduced intensity in the region containing DMTD which suggests that the inhibitor is well incorporated into the polymer matrix. The mottled appearance of MIBK-05 (Fig. 3e) can be attributed to DMTD aggregates identified in the corresponding Raman maps (Fig. 4c). These aggregates were present throughout the entire film thickness, with a slightly higher density near the bottom. The corresponding 1730 cm^{-1} map showed diminished intensity, seen as black spots, wherever the DMTD aggregates are located. This indicates that there is minimal polymer presence at these aggregate locations, which points at a film morphology consisting of discrete DMTD particles in a p (BMA-co-MMA) matrix. Similar to THF-05, the MEK-05 Raman maps (Fig. 4d) also indicate a uniform DMTD distribution, even though its optical image (Fig. 3g) showed only limited yellowing. Uniform intensity of the 1730 cm^{-1} map is also consistent with good degree of mixing of p (BMA-co-MMA) with DMTD.

In contrast to the 5 wt% formulations, the Raman maps of the films with 20 wt% DMTD showed distributions that more closely aligned with the yellowing observed in the optical images. TOL-20 Raman maps (Fig. 4e) showed that the majority of the DMTD present in the film was located at the bottom layer. There is reduced 1730 cm^{-1} intensity in this layer which suggests that it has a similar nature to the aggregates seen in

MIBK-05. As with the THF-05, the THF-20 maps (Fig. 4f) also showed a uniform DMTD distribution throughout the film thickness although a large DMTD aggregate were also observed (see white arrow in 534 cm^{-1} map of Fig. 4f). A higher density of DMTD aggregates was observed in MIBK-20 maps (Fig. 4g) combined with a more detectable DMTD presence in the matrix. The MEK-20 maps also showed DMTD distribution throughout the film but with the presence of interconnected DMTD aggregates. Overall, the optical and Raman analyses confirm the different aggregation and dispersion states including complex morphological distributions as a function of the DMTD content and solvent type.

Quantitative comparison of the DMTD distribution in the 534 cm^{-1} maps from Fig. 4 was based on two metrics: the variation within pixel rows (VWR) and the variation across pixel rows (VAR). VWR is calculated as the average of the row-standard deviation of pixel intensities, whereas VAR is calculated as the standard deviation of the row-average of pixel intensities. Fig. 5a shows the scheme for calculating these parameters. High VWR values indicate stronger intensity differences between pixels in the same row, consistent with DMTD aggregation, where aggregated domains appear with high intensity and the surrounding polymer matrix with low intensity. Conversely, high VAR values mean that some rows contain more DMTD than others, which is consistent

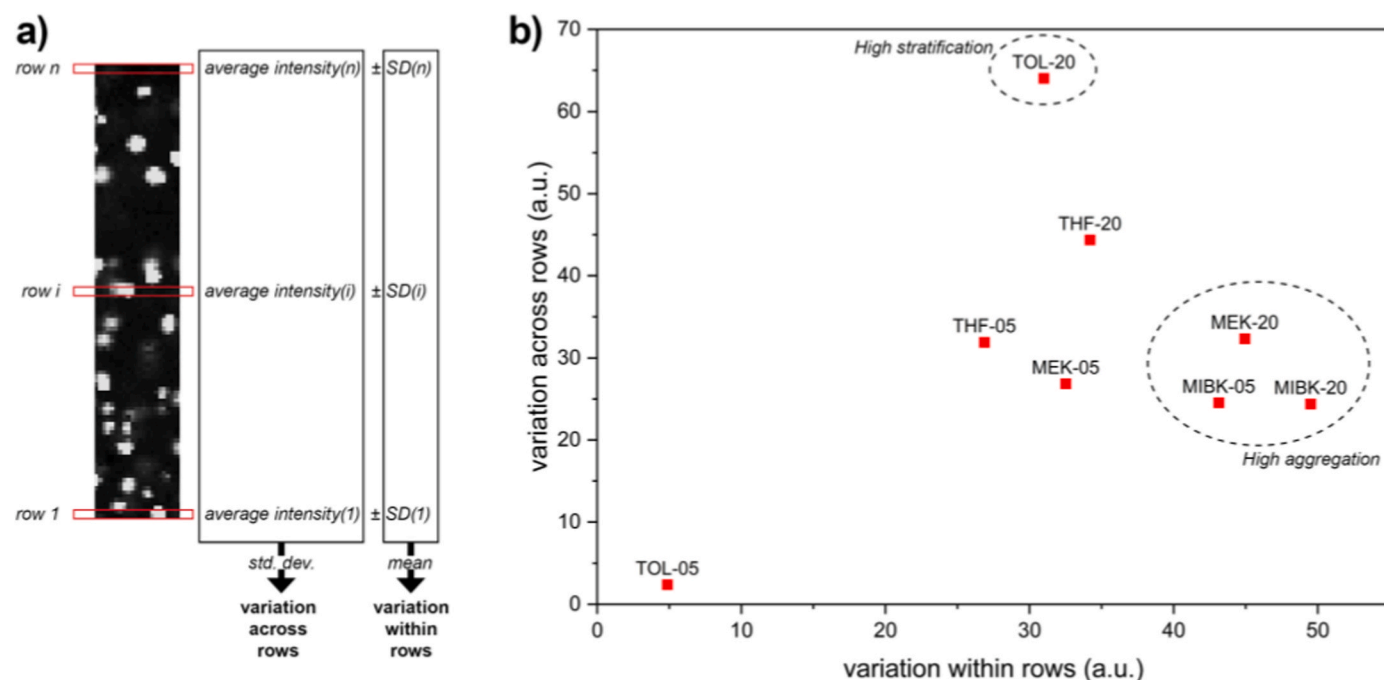


Fig. 5. (a) Schematic representation of the calculation of variation across rows of pixels (VAR) and variation within rows of pixels (VWR). VAR is an indicator of the degree of stratification. VWR is an indicator of the degree of DMTD aggregation. (b) Comparison of the DMTD distribution morphologies resulting from the solvent used based on the variation across and within pixel rows of the 534 cm^{-1} activity maps in Fig. 4.

with stratification. [Supporting Information 3](#) provides additional details of the calculation process for VWR and VAR.

VAR results (Fig. 5b) show the order of film stratification (i.e., across film thickness) as: TOL-05 < MIBK-05, MIBK-20 < MEK-05 < THF-05 < MEK-20 < THF-20 < TOL-20. Both toluene formulations occupy the extremes due to low DMTD solubility in the solvent which led to the formation of an inhibitor layer at the bottom of the film. At 5 wt% DMTD loading (TOL-05), this layer was thin and relatively heterogeneous, as seen in the distribution of yellow aggregates along the film length in Fig. 4a, leading to most pixel rows having comparable average intensity and low VAR. At 20 wt% DMTD loading (TOL-20), the layer was thicker and more uniform across the length of the film, producing more pronounced intensity differences between bottom and top rows. THF, MIBK, and MEK films occupied the middle range consistent with their greater ability to dissolve DMTD and incorporate it into the polymer matrix. Interestingly, the VAR values of the MIBK films were relatively insensitive to DMTD content, whereas THF and MEK films showed stronger apparent stratification at higher loadings. This is attributed to the tendency of the two to form bigger aggregates at higher DMTD loadings.

VWR analysis (Fig. 5b) ranked aggregation as follows: TOL-05 < THF-05 < TOL-20 < MEK-05 < THF-20 < MIBK-05 < MEK-20 < MIBK-20. Both toluene formulations are at the lower end of the hierarchy because their layers were generally uniform despite their stratification. Similar behavior was evident for the THF films and MEK-05. In contrast, MIBK films and MEK-20 displayed a higher degree of aggregation, consistent with their aggregates being visible in the Raman maps.

Correlation of the VWR and VAR values with DMTD solubility in the solvents (based on the R_a values in Table 2) shows that, for equally soluble polymer matrices, the solubility of the organic salt in the solvent is a key factor controlling film morphology. Poor solubility, as in toluene, favored film stratification. Among the better solvents, differences in relative solubility appear to correlate with the extent of aggregation. Solvents with lower R_a values formed fewer aggregates, whereas those with higher R_a values showed more pronounced aggregation. Nonetheless, the solubility differences alone cannot account for the emergence of the discrete aggregates (i.e., MIBK films). In most self-

stratifying coating studies, component incompatibility typically results in either uniform dispersion or preferential migration of a component toward the substrate side or air interface [36]. The formation of uniformly distributed, discrete DMTD-rich domains (i.e., aggregates) within the polymer matrix is therefore a previously unreported outcome.

The aggregate-rich morphology is hypothesized to arise from the interplay between good DMTD solubility and differences in solvent evaporation rates. The corresponding solvent evaporation parameters are summarized in Table 3. THF and MEK, with their low boiling points and high evaporation rates, promote rapid solvent loss and limited phase development, whereas MIBK and toluene evaporate more slowly, allowing extended molecular mobility and segregation. In toluene, the combination of poor DMTD solubility and slow evaporation promotes stratification, as DMTD separates early from the toluene-p (BMA-co-MMA) system. In contrast, the high dissolving power of MIBK maintains DMTD dispersion throughout most of the drying period. Only at later stages, as solvent content decreases and polymer-inhibitor incompatibility becomes more dominant, does phase segregation occur, giving rise to the discrete DMTD-rich aggregates observed. Increasing the DMTD loading from 5 to 20 wt% enhances the polymer-inhibitor incompatibility across all solvent systems resulting in more prominent aggregation. Overall, these results demonstrate that organic inhibitor solubility and inhibitor concentration, together with solvent evaporation kinetics, jointly determine the extent and morphology of DMTD aggregation within the p (BMA-co-MMA) films.

Table 3
Parameters describing evaporation behavior of pure solvents [53].

Solvent	Boiling point (°C)	Evaporation Rate (vs. BuAc)
Toluene	110.6	2
THF	66	6.3
MIBK	116	1.4
MEK	80	4.6

3.3. Chemical state of DMTD incorporated in *p* (BMA-co-MMA)

The Raman maps in Fig. 4 highlight the spatial distribution of DMTD in the polymer films. However, another aspect to consider when incorporating organic inhibitors or other reactive molecules in polymeric matrices is the possibility of chemical interactions between the inhibitor and the polymer matrix. Such interactions may alter the molecular state of the incorporated inhibitor, potentially influencing inhibitor–polymer interactions, molecular release behavior in the presence of water, and other polymer properties. To examine the presence and relative extent of these interactions between the incorporated DMTD and the *p* (BMA-co-MMA) matrix, Raman spectra were collected at different locations across the film cross-sections and examined alongside the thermal behavior obtained from TGA and DSC.

Fig. 6 shows the Raman spectra (450–850 cm^{-1}) from points in the film cross-sections compared with the Raman signals of the solvents, pure *p* (BMA-co-MMA), and solute powder. To this end, locations in the films with a clear DMTD signal but with high or low peak intensity, as seen in the 534 cm^{-1} map in Fig. 4, were selected. As discussed in Section 3.2, high-intensity points generally correspond to DMTD-rich

domains (e.g., DMTD layer at the bottom of TOL-20, DMTD aggregates in MIBK-20). For the systems with less substantial phase separation (i.e., THF-05, MEK-05, THF-20), the high- and low-intensity locations, seen as red and blue curves in Fig. 6 respectively, were randomly selected points from the cross-section. Fig. 6a–d shows that, with the exception of TOL-05, films with 5 wt% DMTD exhibited a redshift of the 658 cm^{-1} band. As with the DMTD in solution (Fig. 2), the shift is here attributed to the coordination of the inhibitor with the *p* (BMA-co-MMA) matrix. This shift is accompanied by a marked increase in the intensity of the bands between ~ 460 cm^{-1} and ~ 540 cm^{-1} (yellow region in the figure). The increase was low for TOL-05 but considerably higher for THF-05, MIBK-05, and MEK-05, to the point that they have comparable or even higher intensity than that seen for 658 cm^{-1} , which is the dominant signal in the DMTD powder (black curves). The observed change could be attributed to an increase in the number of bonds involving the thiolate S, such as the formation of disulfide bonds [19,54,55]. Apart from the formation of disulfide bonds, changes in the 1000 to 1100 cm^{-1} region of the THF-05, MIBK-05, and MEK-05 spectra also point to a possible tautomeric shift away from the dithiol form. More specifically, Fig. 7b–d (yellow regions) show an intensity increase of the 1025 cm^{-1} mode

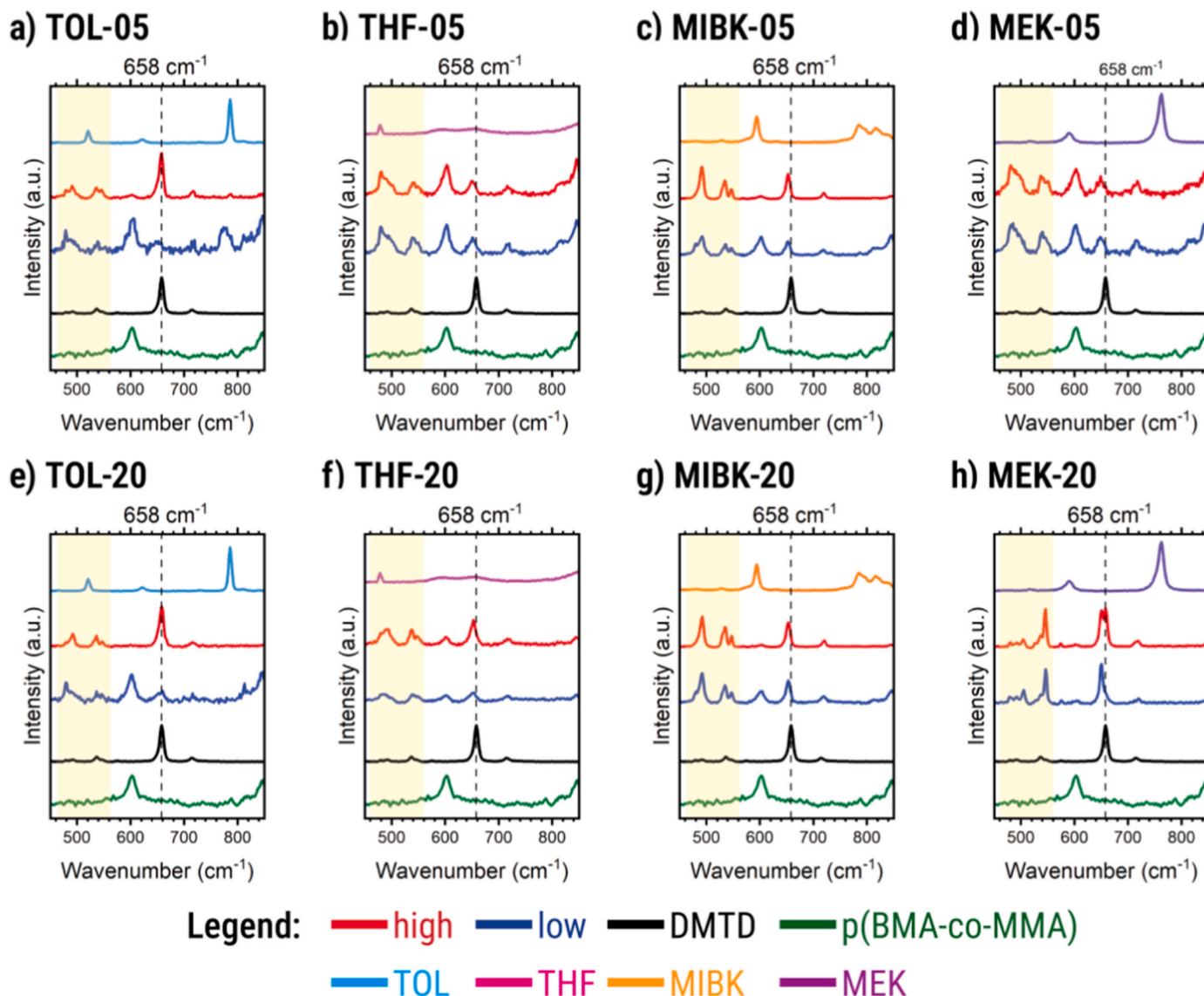


Fig. 6. Raman spectra from 450 cm^{-1} to 850 cm^{-1} collected from regions of high (red curve) and low (blue curve) DMTD signal intensity in the following formulations: (a) TOL-05, (b) THF-05, (c) MIBK-05, (d) MEK-05, (e) TOL-20, (f) THF-20, (g) MIBK-20, and (h) MEK-20. For THF-05, MEK-05, and THF-20, no distinct phase separation was observed; in these cases, the red and blue spectra correspond to two randomly selected points across the film cross-section.

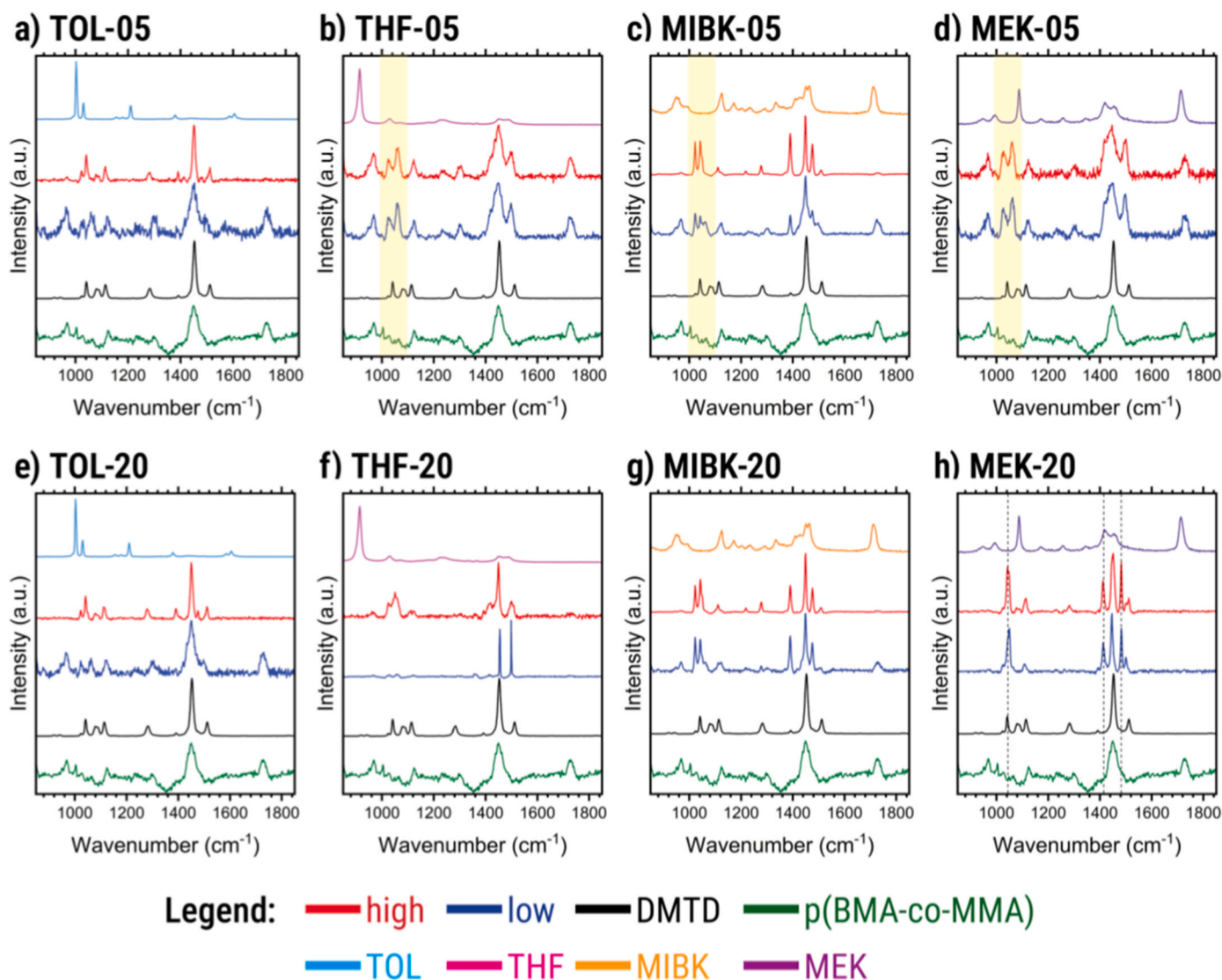


Fig. 7. Raman spectra from 850 cm^{-1} to 1850 cm^{-1} collected from regions of high (red curve) and low (blue curve) DMTD signal intensity in the following formulations: (a) TOL-05, (b) THF-05, (c) MIBK-05, (d) MEK-05, (e) TOL-20, (f) THF-20, (g) MIBK-20, and (h) MEK-20. The spectra are extensions of the ones shown in Fig. 6.

(coupled C–S stretch and N–H bend in dithione [15]) and the potential coalescence of the 1040 cm^{-1} (N–N stretch [15]) and 1080 cm^{-1} (coupled N–N stretch and CSH bend [15]) modes resulting in a high intensity mode at 1060 cm^{-1} . The blueshift of the N–N stretching mode is associated with the protonation of a ring N. Meanwhile, the redshift of the coupled N–N stretch and CSH bend suggests potential weakening of the coupling, which could be due to the conversion of CSH to C=S or formation of disulfide bonds. The observed changes in the Raman spectra of the DMTD locations when incorporated at 5 wt% in the polymer matrix suggest some degree of deprotonation of the thiol groups into a higher content of disulfide and C=S bonds. Qualitative comparison of the spectra indicates that the apparent degree of conversion follows the order TOL-05 < MIBK-05 < MEK-05, THF-05, in good agreement with trends in inhibitor-solvent compatibility.

The high and low spectra of TOL-20, THF-20, and MIBK-20 (Fig. 6e–g, Fig. 7e–g) closely resemble those in the corresponding 5 wt % DMTD films. Additionally, the curves corresponding to the locations with high amounts of DMTD show a $\sim 603 \text{ cm}^{-1}$ mode (Fig. 6e–g) less prominent than those seen in the curves with low amounts of DMTD, consistent with a lower local polymer fraction. This is in agreement with the intensity distribution seen in the 1730 cm^{-1} maps (Fig. 4) since both

modes reflect the relative amounts of the polymer. As with the films with 5 wt% DMTD loading, the changes in the spectra of TOL-20, THF-20, and MIBK-20 are here attributed to a combination of disulfide bond formation and tautomeric shift. Nonetheless, the changes in the intensity of bands are less pronounced for the 20 wt% films, unlike their 5 wt% counterparts. These are particularly seen with the 658 cm^{-1} band which is more pronounced for all 20 wt% films (Fig. 6e–g) as well as the bands from 1400 cm^{-1} to 1500 cm^{-1} (Fig. 7e–g) which appear sharper than in the 5 wt% films. These changes are likely due to increased aggregation which essentially led to higher amounts of DMTD aggregates with chemical states similar to powder DMTD. Interestingly, while the MEK-20 film exhibited this increased aggregation, it also showed a more intense 546 cm^{-1} mode (NH out-of-plane bend [15]) compared to the other 20 wt% film formulations. The higher intensity of this mode is potentially due to a more substantial tautomeric shift in MEK-20 to the thiol-thione or dithione forms. Higher intensities of the 1043 cm^{-1} (C=S stretch [50]), 1412 cm^{-1} (coupled C=N stretch, N–N stretch, and NH bend [15]), and 1482 cm^{-1} (N–H in-plane bend [50]) modes shown in Fig. 7h (see dashed lines) further support this tautomeric shift away from the dithiol form of DMTD. Altogether, the 20 wt% films are increasingly dominated by aggregation-related spectral features, which

attenuate but do not eliminate solvent-dependent effects. Qualitative comparison of the spectra suggests that the degree of conversion follows the order TOL-20 < MIBK-20, THF-20 < MEK-20, broadly mirroring the trend observed at 5 wt% DMTD loadings.

The TGA data was used to determine how the molecular changes of DMTD, observed through Raman spectroscopy, affect the thermal stability of the different film formulations. This serves as an indicator of differences in interaction strength between DMTD and the polymer matrix. Fig. 8a shows the temperature-dependent weight changes of the 5 wt% DMTD films. The thermal degradation curves of powder DMTD and p (BMA-co-MMA) are also provided for reference. These reference curves show that DMTD is expected to begin degradation at around 193 °C while p (BMA-co-MMA) at around 278 °C. Nonetheless, the films exhibited degradation curves that are quite similar to each other and closer to that of pure p (BMA-co-MMA). The delayed DMTD degradation suggests strong interaction between the inhibitor and the polymer matrix and is likely a consequence of the molecular changes previously observed via Raman spectroscopy. Despite their similarities, comparison of the temperatures at which the 5 wt% DMTD films exhibited 5% loss (Fig. 8c) showed that MIBK-05 degraded much earlier than the others. A closer look at the initial stages of degradation (Fig. 8a inset) also shows that MIBK-05 exhibited faster degradation after 193 °C, with TOL-05 closely following. Faster degradation of TOL-05 relative to THF-05 and MEK-05 is expected as its Raman spectrum (Figs. 6a and 7a) showed minimal deviations relative to powder DMTD. Meanwhile, although the Raman spectra of MIBK-05 (Figs. 6c and 7c) exhibited visible changes, the changes are still arguably less extensive than those

of THF-05 and MEK-05 especially if the bands from 1400 cm^{-1} to 1500 cm^{-1} are considered (Fig. 7). The thermal degradation of the 5 wt % films shows that the order of DMTD-p (BMA-co-MMA) interaction is TOL-05, MIBK-05 < THF-05, MEK-05.

Fig. 8b shows that increasing the DMTD loading makes the thermal degradation curves of the films move closer to that of powder DMTD. Among the 20 wt% DMTD films, MIBK-20 again exhibited the lowest temperature at 5% loss, with TOL-20 and THF-20 following closely (Fig. 8a inset, Fig. 8c). The faster degradation of these three films is potentially due to the increase in their degree of aggregation which led to incorporated DMTD with a chemical state much closer to powder DMTD, as seen in the Raman spectra of the films (Figs. 6 and 7). Interestingly, MEK-20 appeared to be more thermally stable than the other films despite its own increase in aggregation. This stability may result either from stronger chemical interactions between DMTD and the polymer matrix or increased thermal stability of DMTD itself, potentially due to its tautomeric shift observed in Figs. 6h and 7h. Thiols have been reported to be highly active and easily oxidizable [56]. Thus, a shift from the thiol to the thione or thione-thiol tautomers can potentially improve the thermal stability of DMTD and, consequently, of the film. Altogether, the thermal degradation of the 20 wt% films shows that the order of DMTD-p (BMA-co-MMA) interaction is MIBK-20, TOL-20, THF-20 < MEK-20.

While the TGA data reflect the strength of DMTD interaction with the polymer matrix, the DSC thermograms probe how the polymer matrix is affected by the presence of DMTD, specifically in terms of changes in the midpoint glass transition temperature (T_g). Fig. 9a shows that all of the

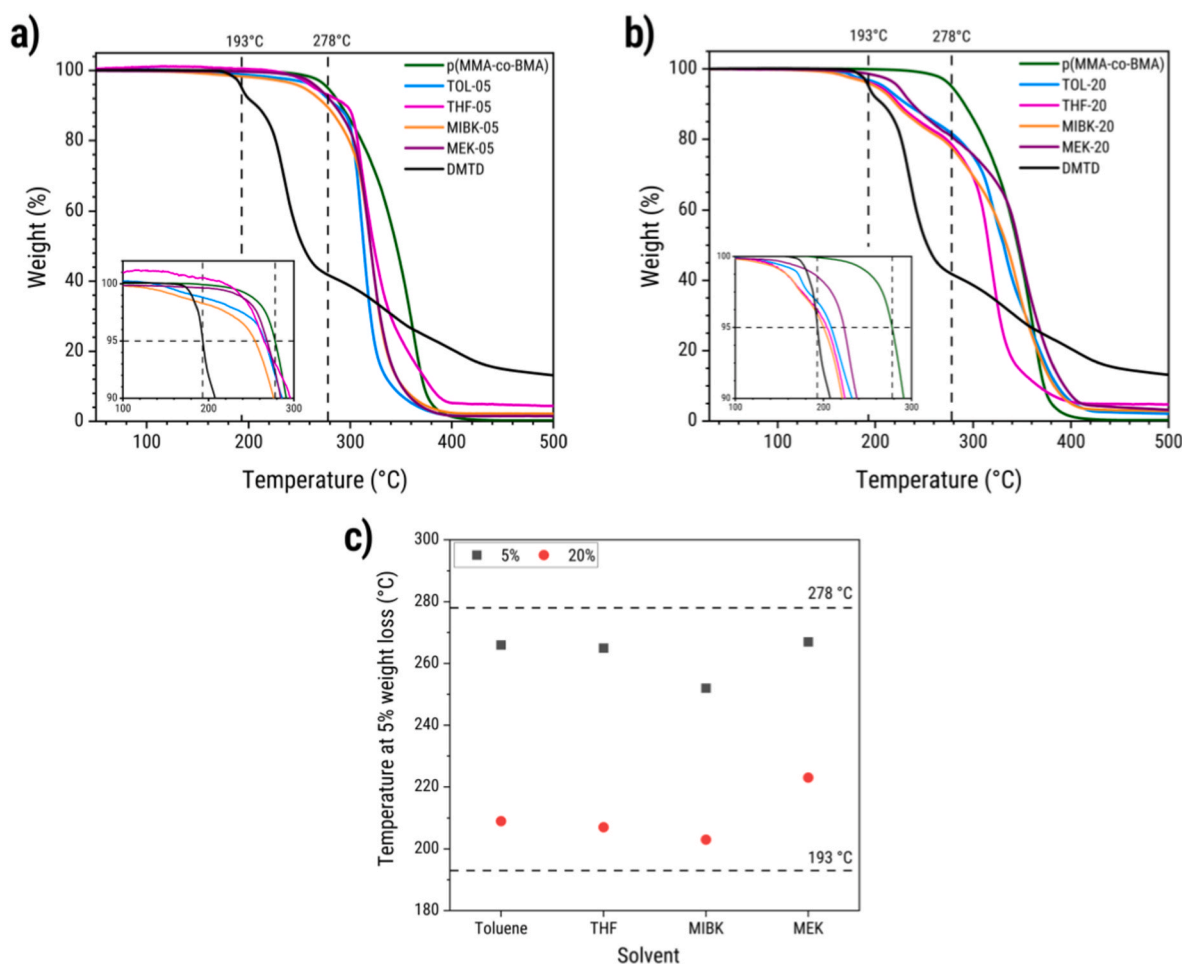


Fig. 8. Temperature-dependent degradation of the p (BMA-co-MMA)-DMTD films with (a) 5 wt% and (b) 20 wt% inhibitor loading. The insets show zoomed in views of the initial weight changes. Temperatures at which 5% weight loss is observed for each of the film compositions are reported in (c).

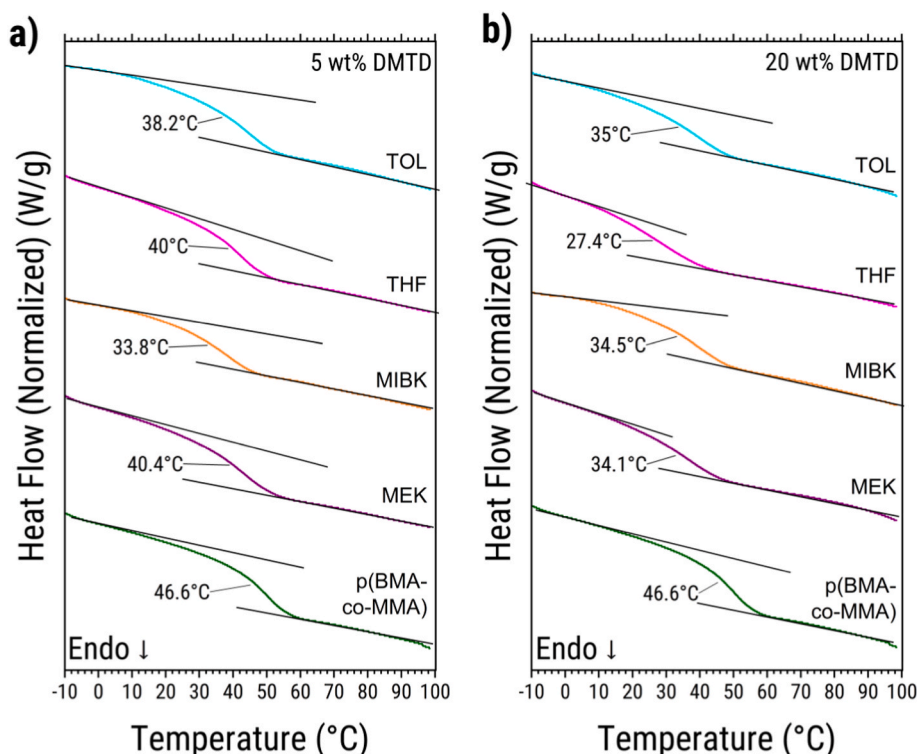


Fig. 9. DSC thermograms of the p (BMA-co-MMA) films loaded with (a) 5 wt% and (b) 20 wt% DMTD. The glass transition temperature indicated in the thermograms were calculated from the second heating cycle and is based on the midpoint of the onset temperatures. [Supporting Information 3](#) provides additional details of the fitting process.

5 wt% DMTD films exhibited a clear drop in T_g relative to pure p (BMA-co-MMA). This behavior is attributed to a plasticization effect associated with the incorporated DMTD, consistent with T_g depression reported in polymer systems containing fillers or plasticizers [57,58]. Notably, similar to the trend observed in the TGA data, MIBK-05 also exhibited the largest T_g depression (around 13 °C). This enhanced T_g reduction is likely due to the dual role of DMTD in this system. In addition to acting as plasticizing species when molecularly dispersed, the inhibitor is also present as aggregated, filler-like domains, which can introduce additional interfacial voids within the polymer matrix that further reduce T_g beyond that expected from plasticization alone [59]. A similar, albeit less pronounced, effect may account for the slightly lower T_g of TOL-05 compared to THF-05 and MEK-05. TOL-05 also has DMTD-rich domains close to the bottom of the film which may have introduced additional interfacial voids.

[Fig. 9b](#) shows that increasing the DMTD content from 5 wt% to 20 wt % resulted in solvent-dependent changes in T_g . Among the systems, THF-20 exhibited the largest additional T_g reduction (around 13 °C), relative to its 5 wt% counterpart, followed by MEK-20 (around 6 °C). In contrast, TOL-20 showed only a modest additional decrease (around 6 °C), while MIBK-20 exhibited little to no additional change in T_g . The muted response of MIBK-20 is likely due to the higher DMTD loading promoting increased aggregation rather than increased dispersion within the polymer matrix. As a result, the additional T_g depression arising from interfacial voids associated with larger or more numerous aggregates appears less significant than the plasticization effect driven by molecular DMTD dispersion within the p (BMA-co-MMA) chains, which dominates in the less aggregated systems (e.g., THF-20 and MEK-20). A similar mechanism may account for the limited additional T_g reduction observed for TOL-20. As with MIBK-20, the increased DMTD content in TOL-20 does not appear to enhance dispersion, but instead leads primarily to the growth of DMTD aggregates, as evidenced by the thickening of the DMTD-rich bottom layer.

3.4. Inhibitor release upon exposure to salty water

[Fig. 10](#) shows the DMTD fractional release curves of the 5 wt% DMTD films immersed in 0.05 M NaCl, a common test solution in corrosion studies. Fractional release was calculated by dividing the amount of inhibitor present in the solution, measured using UV-vis spectroscopy, by the amount of DMTD initially present in the sample (see [Supporting Information 1](#) for calculation procedure). Comparison of the curves shows that TOL-05 had the fastest initial release as well as the highest fraction released after extended immersion (3 h). This is largely attributed to the cross-section morphology of TOL-05. [Figs. 3a and 4a](#) show that the DMTD-rich domains of TOL-05 are concentrated close to the bottom of the free-standing film. As a result, water only needs to diffuse a short distance to reach these hydrophilic regions, and the dissolved inhibitor similarly has a short path to the film-solution interface, making it readily available for release. Furthermore, the Raman spectra showed that the DMTD-rich domains are in a chemical state similar to powder DMTD, this suggests a low degree of chemical interactions with the polymeric network that can potentially impede its dissolution and release. During extended immersion, dissolution of its DMTD-rich domains can potentially lead to the formation of pores that further improve water uptake and leaching of DMTD.

In contrast, the other 5 wt% films show DMTD distributed deeper within the film, such that water must penetrate further into the film before the inhibitor can dissolve and diffuse out, resulting in longer effective diffusion paths relative to TOL-05. Furthermore, the dissolution and release of DMTD is considered to be also affected by their degree of interaction with the polymer matrix. As such, even if there is DMTD available close to the film-solution interface, the over release is sluggish relative to TOL-05. This interplay of contributing factors is reflected in the hierarchy of fractional release of the films which follows the order MEK-05 < THF-05 < MIBK-05. The order is consistent with the hierarchy of temperature corresponding to 5% loss measured with TGA (i.e., TOL-05 < MIBK-05 < THF-05, MEK-05; [Fig. 8c](#)) which is used as an

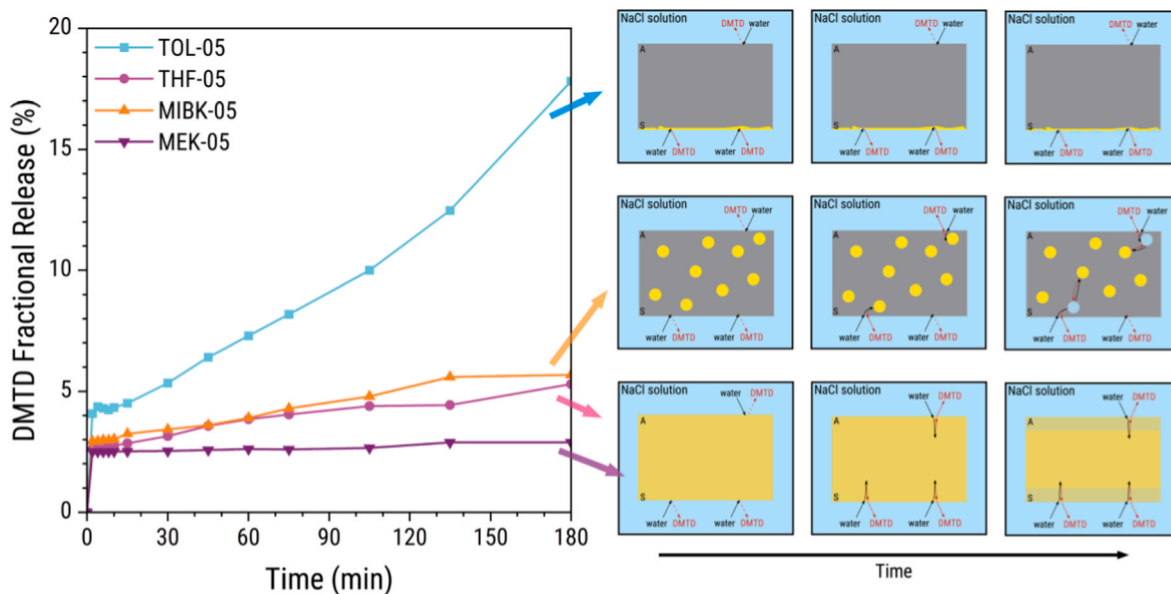


Fig. 10. Release profile of the 5 wt% films with THF, MEK, MIBK and toluene in 200 mL of 0.05 M NaCl. The fractional release pertains to mass of DMTD released divided by the mass of DMTD present in the film. The schematic diagrams on the right show the proposed leaching mechanisms for the films during immersion in the NaCl solution.

indicator of the strength of the inhibitor-polymer interaction. The films with weaker interactions are more capable of releasing the inhibitor more easily. To a certain degree, the fractional release order is also consistent with the extent of T_g depression in the 5 wt% films (i.e. MEK-05, THF-05 < MIBK-05; Fig. 9a). Apart from the degree of plasticization, T_g depression is also linked to free volume, which in turn relates to water uptake [60,61]. As such, films with faster water uptake allow for higher DMTD dissolution and release at a given period of time compared to the films with slower uptake. Moreover, the aggregate-rich morphology of MIBK-05 likely contributed to faster release kinetics than those observed for MEK-05 and THF-05. Once diffusion paths are established between

the solution and the aggregates, dissolving aggregates with weak interactions with the matrix can generate local sites of high DMTD concentration, increasing the driving force for diffusion. Their dissolution can also leave behind voids, which further enable water ingress and DMTD leaching.

Fig. 11 shows the fractional release profile of the 20 wt% DMTD films in the same 0.05 M NaCl electrolyte. The early-stage fractional release (i.e., first 20 min) follows the order TOL-20 < MEK-20 < MIBK-20 < THF-20. The fast initial release of THF-20 is potentially due to the weaker interactions of some of the inhibitor with the polymer matrix (Fig. 8c), unlike its 5 wt% counterpart, as well as the faster water uptake based on

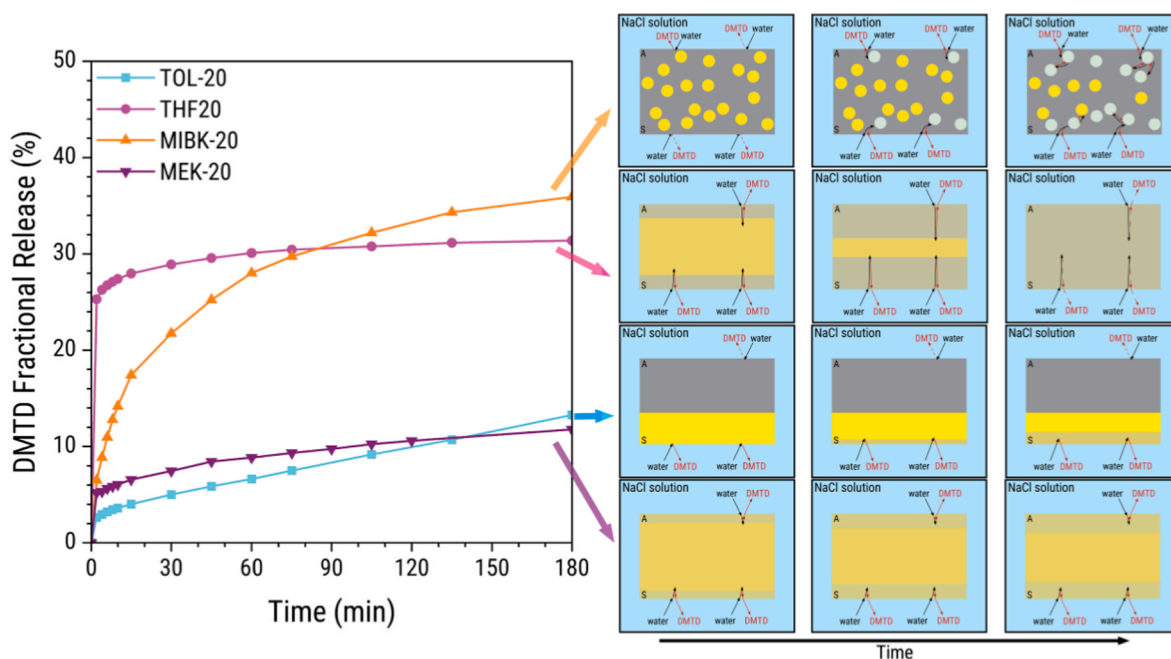


Fig. 11. Release profile of the 20 wt% films with THF, MEK, MIBK and toluene in 200 mL of 0.05 M NaCl. The fractional release pertains to mass of DMTD released divided by the mass of DMTD present in the film. The schematic diagrams on the right show the proposed leaching mechanisms for the films during immersion in the NaCl solution.

its low T_g (Fig. 9b). The amount released plateaus after some time likely because the weakly incorporated DMTD already dissolved and diffused out. Meanwhile, although initial diffusion through the MIBK-20 polymer matrix is relatively slow, the higher aggregate loading compared to MIBK-05 causes the release process to become increasingly dominated by aggregate-derived pathways once dissolution begins. The larger number and greater connectivity of these pathways in MIBK-20 progressively increases water ingress and inhibitor release. Moreover, the DMTD in MIBK has weaker interactions with the matrix (Fig. 8c). As a result, MIBK-20 eventually overtakes THF-20 at longer immersion times, whereas THF-20 remains largely governed by the diffusion of the remaining strongly-incorporated DMTD. Notably, TOL-20 and MEK-20 show the lowest release attributed to different phenomena. MEK-20 has a slow initial release likely because of the increased interaction between DMTD and the polymer matrix (Fig. 8c). Increased water uptake with time does lead to increased dissolution of the strongly-incorporated DMTD resulting in the overall sluggish inhibitor release from MEK-20. TOL-20 had the slowest initial release likely because of its morphology (Fig. 3b). Its stratification meant that it effectively had its mass transfer area halved since the polymer-rich side is less penetrable to water. Unlike its 5 wt% DMTD counterpart, the DMTD layer of TOL-20 is substantially thicker which requires water ingress deeper into the film for substantial inhibitor dissolution and release. It is important to note that while the fractional release during the first 20 min is comparable for TOL-05 and TOL-20, the corresponding absolute amount of inhibitor released is higher for TOL-20, indicating a faster initial dissolution of the outermost DMTD-rich layer in the 20 wt% film. Similar to

MIBK-20, the dissolution of the layer leads to the generation of voids and channels which increase the amount of DMTD released with time. This leads to the continuously increasing fractional release of TOL-20 which eventually overtakes MEK-20 after the 140 min mark.

3.5. Corrosion inhibition performance of formulations applied to AA2024

Fig. 12 shows optical microscopy images of the scribed regions of AA2024 samples after exposure to NaCl solution, illustrating the extent of localized corrosion/inhibition for coatings prepared using different solvents and DMTD loadings. In AA2024, localized corrosion is characterized by dealloying and trenching at and around intermetallic particles, which appear optically as dark spots distributed across the exposed metal surface. Qualitative comparison of the images indicates that samples coated with films containing 5 wt% DMTD (Fig. 12e–f) and 20 wt% DMTD (Fig. 12i–l) generally exhibited fewer dark spots and less extensive darkening than the corresponding samples without DMTD (Fig. 12a–d). This is indicative of reduced local corrosion. The only apparent exception was MIBK-20 (Fig. 12k), which exhibited an extent of surface darkening comparable to its uninhibited counterpart. However, this darkening is likely associated with deposits of released DMTD remaining on the exposed surface rather than extensive localized corrosion. This interpretation is supported by the side-by-side comparison in Fig. 12m, where area 1 (MIBK-00) exhibits extensive darkening of the intermetallic particle surfaces and pronounced trenching of the surrounding matrix, characteristic of active localized corrosion. In contrast, area 2 (MIBK-20) shows only limited darkening of the

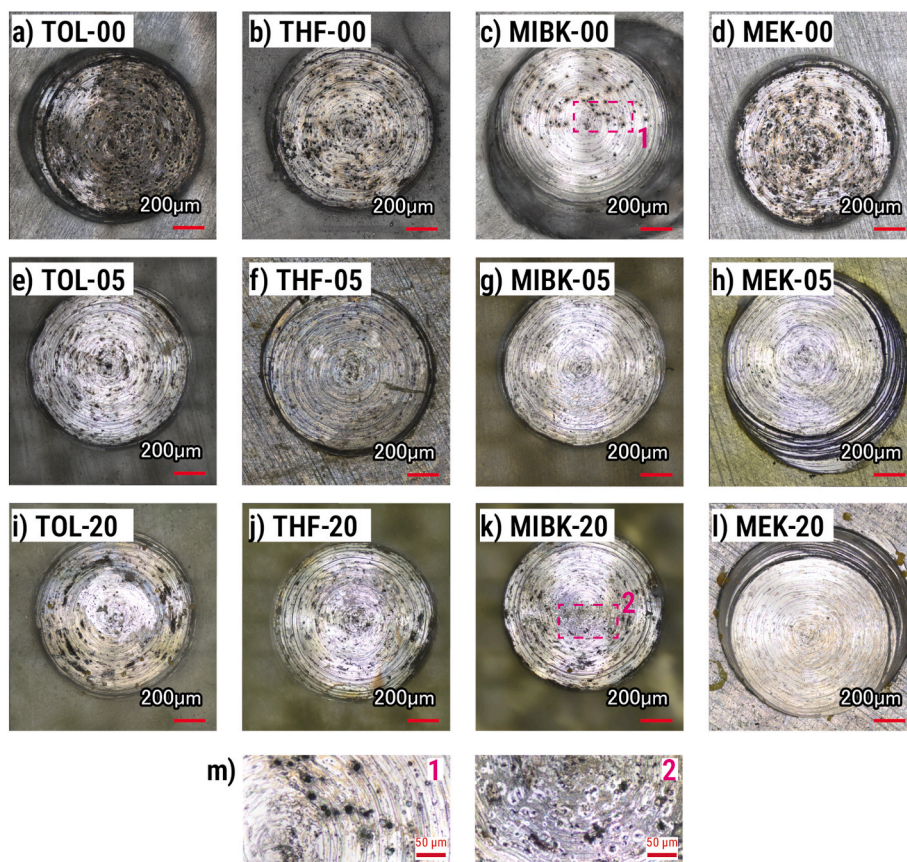


Fig. 12. Micrographs of the scribed regions on film-coated AA2024 substrates after 15 h immersion in 0.05 M NaCl for different film formulations. Exposed metal at scribe in the samples coated with inhibitor-free coatings (a–d) exhibit visible (local) darkening related to local and extended corrosion. Exposed metal at scribe in samples coated with 5 wt% DMTD-rich coatings (e–h) and 20 wt% DMTD (i–l) show none-to-very little darkening sites compatible with high levels of corrosion inhibition, especially at 5 wt% DMTD and MEK. Magnified regions 1 and 2 of MIBK-00 and MIBK-20 (m) show different local features compatible with a change in local attack in presence of large inhibitor amounts and suggest a trend change with inhibitor content using MIBK from inhibition at 5 wt% to inefficient inhibition at 20 wt% likely due to excessive inhibitor release (c–g–k/m-2).

intermetallic particles with minimal trenching of the adjacent matrix, features that are more consistent with inhibited corrosion [62], even though a negative effect of inhibitor excess or inhibitor chemical state cannot be discarded at this point. Overall, these observations are consistent with the inhibitor release behavior discussed in the preceding sections and provide direct evidence that DMTD released from the polymer coatings remained active, suppressing localized corrosion following coating damage.

Although all DMTD-containing coatings exhibited improved corrosion resistance relative to their uninhibited counterparts, noticeable differences in the extent of localized corrosion were observed among formulations prepared with different solvents at both the 5 wt% and 20 wt% DMTD loadings. These variations suggest that solvent-induced differences in coating architecture, which influence inhibitor release behavior, may also affect the resulting corrosion inhibition performance. However, establishing a direct quantitative relationship between coating morphology, inhibitor release kinetics, and corrosion protection requires a more comprehensive investigation. A detailed analysis of these relationships will therefore be the focus of a follow-up study.

3.6. Controlling inhibitor release behavior through solvent selection

The DMTD release curves (Figs. 10 and 11) highlight how the leaching of DMTD from the films is the result of the combined effect of morphology, water uptake behavior (reflected by the T_g depression), and chemical interactions between the inhibitor and the polymer matrix (reflected by the temperature at 5% loss). The results also show that the release behavior can be divided into early-stage and extended release behaviors. For consistency in this discussion, early-stage pertains to the first 20 min of immersion while extended immersion pertains to at least 3 h of immersion. In practice, early-stage behavior is relevant to rapid inhibition of local corrosion [9,10] while extended immersion behavior is relevant for achieving inhibition stability.

The hierarchy of released fractions during early-stage release for both low and high loadings indicate that the temperature at 5 wt% loss and the T_g depression are useful predictors of the initial inhibitor release rate. Films with stronger inhibitor-polymer interactions show 5 wt% loss at higher temperatures, which, generally, translate to slower inhibitor release. The inhibitor-polymer interaction can be, to a certain extent, counteracted by the plasticization effect reflected in the T_g depression. Films with larger T_g depression have faster initial water uptake which increases the initial amount of inhibitor leached out.

From the film formulations tested in this work, it was observed that the temperature at 5% loss is strongly dependent on the loading. Lower loading leads to stronger inhibitor-polymer interaction. The dominance of this process minimizes any potential release rate increase from other processes, even from T_g depression. Meanwhile, at higher loading, coupling of the inhibitor-polymer interaction strength and T_g depression becomes more substantial. Weaker interaction combined with high T_g depression leads to very rapid release (e.g., THF-20) while stronger interaction still leads to slow release, regardless of the T_g depression (e.g., MEK-20).

Meanwhile, the hierarchy of released fractions during extended release suggests that morphology is the stronger controlling factor for this regime. Morphologies dominated by DMTD-rich domains (e.g., aggregates, layers) appear to promote higher fractional release rates in the long run as dissolution of these domains potentially leads to the formation of diffusion pathways which support faster transport as well as the extended availability of weakly-incorporated DMTD. As with early-stage release, the effect of morphology in extended inhibitor release can also be enhanced by T_g depression and counteracted by inhibitor-matrix interactions. Although these factors result in differences in the extended release behavior among the formulations, all coatings sustained DMTD release over the immersion period, thereby contributing to effective corrosion inhibition as demonstrated by the reduced localized corrosion observed after immersion.

Inhibitor-polymer interaction strength, T_g depression, and film cross-sectional morphology can be controlled through the solvent used for film casting. Solvents that can effectively dissolve DMTD (e.g., THF, MIBK, MEK) lead to more uniform films while poor solvents for DMTD (e.g., TOL) lead to more stratified films. Uniform dispersion appears to lead to both a potential for stronger inhibitor-polymer interaction and a more substantial T_g drop. Notably, specific solvent chemistries also lead to further changes in the interaction as observed with MEK-20 which warrant further investigation. The degree of aggregation can also be controlled by selecting effective solvents with less affinity for the inhibitor (e.g., MIBK) and a faster evaporation rate as well as by adjusting the inhibitor loading. Fig. 13 provides a generalized schematic on how inhibitor-solvent compatibility can be used to tailor the inhibitor release rate at different stages, focusing on the 20 wt% formulation. While some differences in release behavior were observed for the 5 wt% films, these variations were comparatively limited and accompanied by relatively low overall inhibitor release. The schematic shows that, in the absence of dominant inhibitor-matrix interactions, the solvent power together with solvent evaporation rates can be tuned to achieve different release profiles which can be used to enhance both the effectiveness and stability of corrosion inhibition.

4. Conclusion

A formulation strategy based on solvent-controlled inhibitor dispersion is demonstrated in this work. Using solvents with varying dissolving power toward DMTD enabled the formation of films with distinct architectures and dispersion states. The results show that solvent-inhibitor compatibility, solvent evaporation kinetics, and inhibitor loading collectively control the resulting film morphology. Poor DMTD solubility, as in toluene, led to stratified films, whereas better solvents such as THF, MIBK, and MEK produced relatively more uniform structures with aggregation levels dependent on solubility and evaporation rate. MIBK, combining strong dissolving power with slow evaporation, yielded uniformly distributed DMTD-rich domains, whereas MEK and THF, which have strong dissolving power and fast evaporation, resulted in uniformly dispersed DMTD. On top of the solvent-inhibitor compatibility, higher inhibitor loading also intensified phase segregation and aggregate formation in all systems. These morphological variations directly influenced inhibitor release behavior. Films exhibiting weaker inhibitor-polymer interaction and larger T_g depression showed faster initial release due to enhanced water uptake. Furthermore, morphologies characterized by DMTD-rich aggregates or layers promoted extended inhibitor release through gradual but sustained domain dissolution. Preliminary corrosion tests at damaged locations of the films applied onto AA2024-T3 substrates show a clear effect of the DMTD dispersion on the anticorrosive behavior of the coatings, with uniform and/or segregated dispersion apparently leading to higher inhibition levels at 15 h immersion and lower DMTD contents leading to very effective corrosion inhibition. Overall, this work highlights how controlling solvent compatibility and inhibitor concentration provides a simple yet effective route to tailor both film structure and release kinetics. Such potential enables the design of active corrosion protection coatings with optimized release behavior which is essential in achieving more effective and stable corrosion inhibition.

CRedit authorship contribution statement

Tinashe C. Darikwa: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Marlon L. Mopon:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Formal analysis, Data curation. **Stephen J. Picken:** Writing – review & editing, Supervision, Methodology, Formal analysis, Conceptualization. **Santiago J. Garcia:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Methodology, Funding acquisition, Formal analysis, Conceptualization.

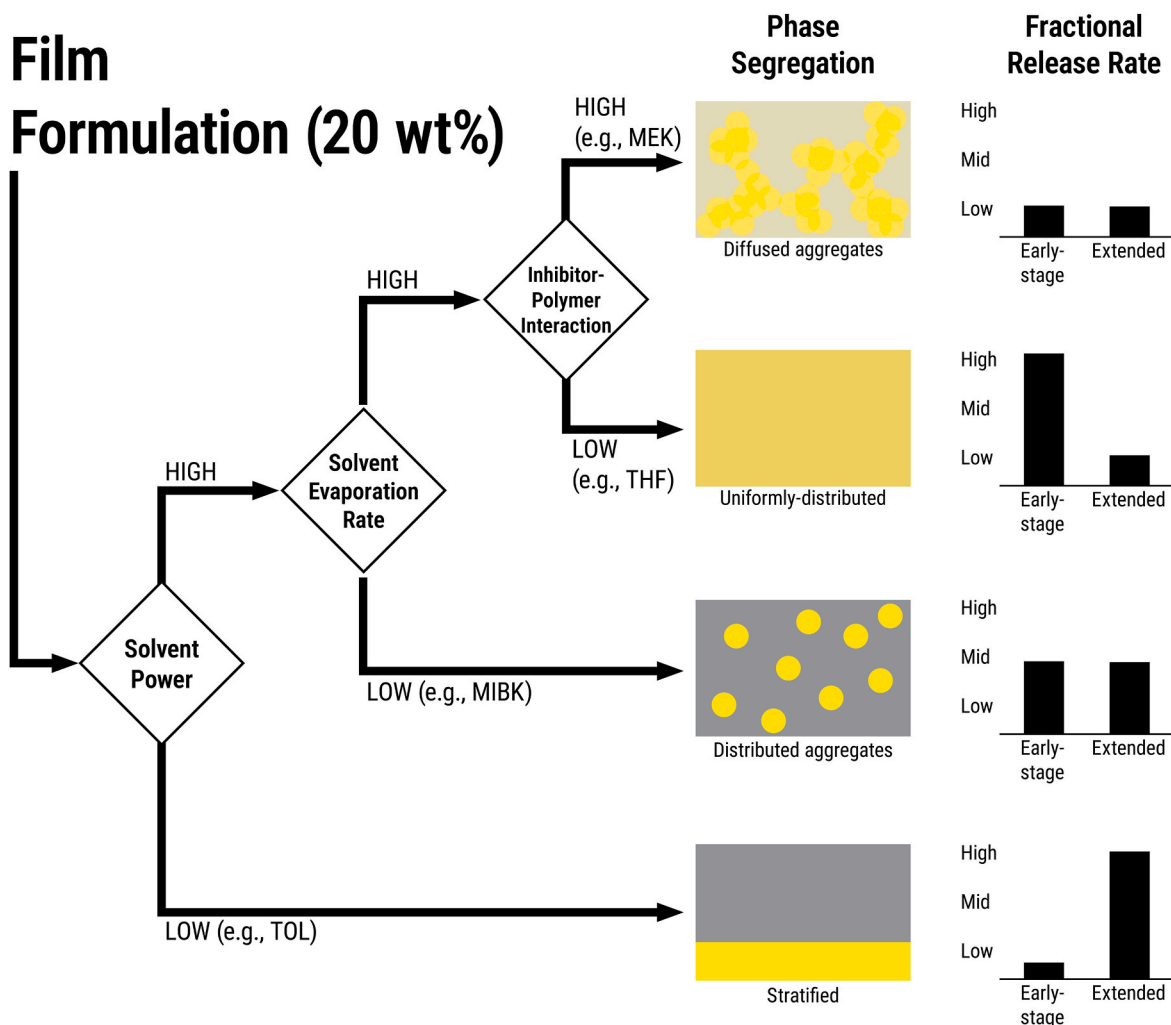


Fig. 13. Impact of solvent power, solvent evaporation rate, and inhibitor-polymer interaction on film morphology and fractional release rates for high inhibitor loading rates (20 wt%).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The author acknowledges the financial support by Airbus Operations GmbH and Holland High Tech Program. The authors acknowledge Dr. Markus Jordan from Airbus Operations GmbH for his continued support and constructive discussions.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mtaadv.2026.100948>.

Data availability

Research Link Provided.

References

- [1] M. Abdollah Zadeh, S. van der Zwaag, S.J. Garcia, Adhesion and long-term barrier restoration of intrinsic self-healing hybrid sol-gel coatings, *ACS Appl. Mater. Interfaces* 8 (2016) 4126–4136, <https://doi.org/10.1021/acsami.5b11867>.
- [2] V. Montano, W. Vogel, A. Smits, S. van der Zwaag, S.J. Garcia, From scratch closure to electrolyte barrier restoration in self-healing polyurethane coatings, *ACS Appl. Polym. Mater.* 3 (2021) 2802–2812, <https://doi.org/10.1021/acspm.1c00323>.
- [3] M.L. Zheludkevich, J. Tedim, M.G.S. Ferreira, “Smart” coatings for active corrosion protection based on multi-functional micro and nanocontainers, *Electrochim. Acta* 82 (2012) 314–323, <https://doi.org/10.1016/j.electacta.2012.04.095>.
- [4] F. Peltier, D. Thierry, Review of Cr-Free coatings for the corrosion protection of aluminum aerospace alloys, *Coatings* 12 (2022) 518, <https://doi.org/10.3390/coatings12040518>.
- [5] R.L. Twite, G.P. Bierwagen, Review of alternatives to chromate for corrosion protection of aluminum aerospace alloys, *Prog. Org. Coating* 33 (1998) 91–100, [https://doi.org/10.1016/S0300-9440\(98\)00015-0](https://doi.org/10.1016/S0300-9440(98)00015-0).
- [6] Y. Hao, F. Liu, E.-H. Han, S. Anjum, G. Xu, The mechanism of inhibition by zinc phosphate in an epoxy coating, *Corros. Sci.* 69 (2013) 77–86, <https://doi.org/10.1016/j.corsci.2012.11.025>.
- [7] L. Yohai, M. Vázquez, M.B. Valcarce, Phosphate ions as corrosion inhibitors for reinforcement steel in chloride-rich environments, *Electrochim. Acta* 102 (2013) 88–96, <https://doi.org/10.1016/j.electacta.2013.03.180>.
- [8] A. Kosari, M. Ahmadi, F. Tichelaar, P. Visser, Y. Gonzalez-Garcia, H. Zandbergen, H. Terry, J.M.C. Mol, Editors’ Choice—dealloying-driven cerium precipitation on intermetallic particles in aerospace aluminium alloys, *J. Electrochem. Soc.* 168 (2021) 041505, <https://doi.org/10.1149/1945-7111/abf50d>.
- [9] M. Mopon, A. Mol, S.J. Garcia, Effect of delayed inhibitor supply on AA2024-T3 intermetallic activity: a local in situ analysis with reflected microscopy, *Corros. Sci.* 230 (2024) 111910, <https://doi.org/10.1016/j.corsci.2024.111910>.
- [10] P.J. Denissen, A.M. Homborg, S.J. Garcia, Requirements for corrosion inhibitor release from damaged primers for stable protection: a simulation and experimental

- approach using cerium loaded carriers, *Surf. Coat. Technol.* 430 (2022) 127966, <https://doi.org/10.1016/j.surfcoat.2021.127966>.
- [11] P. Visser, Y. Liu, H. Terryn, J.M.C. Mol, Lithium salts as leachable corrosion inhibitors and potential replacement for hexavalent chromium in organic coatings for the protection of aluminum alloys, *J. Coating Technol. Res.* 13 (2016) 557–566, <https://doi.org/10.1007/s11998-016-9784-6>.
 - [12] Z. Bergseth, X. Qi, V. Upadhyay, D. Battocchi, Lithium salts as active corrosion inhibitors for aluminum substrates, *Appl. Surf. Sci. Adv.* 16 (2023) 100432, <https://doi.org/10.1016/j.apsadv.2023.100432>.
 - [13] T.G. Harvey, S.G. Hardin, A.E. Hughes, T.H. Muster, P.A. White, T.A. Markley, P. A. Corrigan, J. Mardel, S.J. Garcia, J.M.C. Mol, A.M. Glenn, The effect of inhibitor structure on the corrosion of AA2024 and AA7075, *Corros. Sci.* 53 (2011) 2184–2190, <https://doi.org/10.1016/j.corsci.2011.02.040>.
 - [14] C. Özkan, P.R. Anusuyadevi, P. Visser, P. Taheri, A. Mol, Factors to consider in the quest for organic alternatives to hexavalent chromium based corrosion inhibitors, *Corros. Sci.* 256 (2025) 113183, <https://doi.org/10.1016/j.corsci.2025.113183>.
 - [15] N. Maiti, R. Chadha, A. Das, S. Kapoor, Surface selective binding of 2,5-dimercapto-1,3,4-thiadiazole (DMTD) on silver and gold nanoparticles: a raman and DFT study, *RSC Adv.* 6 (2016) 62529–62539, <https://doi.org/10.1039/C6RA10404E>.
 - [16] P.J. Denissen, V. Shkirskiy, P. Volovitch, S.J. Garcia, Corrosion inhibition at scribed locations in coated AA2024-T3 by Cerium- and DMTD-loaded natural silica microparticles under continuous immersion and wet/dry cyclic exposure, *ACS Appl. Mater. Interfaces* 12 (2020) 23417–23431, <https://doi.org/10.1021/acsami.0c03368>.
 - [17] V. Garg, M. Magnan, S. Zanna, A. Seyeux, F. Wiame, V. Maurice, P. Marcus, Corrosion inhibition mechanisms of 2-mercaptobenzothiazole on AA2024 T3 aluminium alloy, *npj Mater. Degrad.* 9 (1) (2025) 1–19, <https://doi.org/10.1038/s41529-025-00653-z>, 2025.
 - [18] A.C. Balaskas, M. Curioni, G.E. Thompson, Effectiveness of 2-mercaptobenzothiazole, 8-hydroxyquinoline and benzotriazole as corrosion inhibitors on AA 2024-T3 assessed by electrochemical methods, *Surf. Interface Anal.* 47 (2015) 1029–1039, <https://doi.org/10.1002/sia.5810>.
 - [19] J. Zhao, A. Santoso, S.J. Garcia, Small concentrations of NaCl help building stable inhibiting layers from 2,5-dimercapto-1,3,4-thiadiazole (DMTD) on AA2024-T3, *Corros. Sci.* 225 (2023) 111562, <https://doi.org/10.1016/j.corsci.2023.111562>.
 - [20] S.V. Lamaka, M.L. Zheludkevich, K.A. Yasakau, M.F. Montemor, M.G.S. Ferreira, High effective organic corrosion inhibitors for 2024 aluminium alloy, *Electrochim. Acta* 52 (2007) 7231–7247, <https://doi.org/10.1016/j.electacta.2007.05.058>.
 - [21] W.L. Filho, R. Kotter, P.G. Özüyar, I.R. Abubakar, J.H.P.P. Eustachio, N. R. Matandirotya, Understanding rare Earth elements as critical raw materials, *Sustainability* 15 (2023) 15, <https://doi.org/10.3390/SU15031919>, 2023.
 - [22] M.A. Ahmed, S. Amin, A.A. Mohamed, Current and emerging trends of inorganic, organic and eco-friendly corrosion inhibitors, *RSC Adv.* 14 (2024) 31877–31920, <https://doi.org/10.1039/D4RA05662K>.
 - [23] F. Maia, J. Tedim, A.D. Lisenkov, A.N. Salak, M.L. Zheludkevich, M.G.S. Ferreira, Silica nanocontainers for active corrosion protection, *Nanoscale* 4 (2012) 1287–1298, <https://doi.org/10.1039/C2NR11536K>.
 - [24] D. Yu, J. Wang, W. Hu, R. Guo, Preparation and controlled release behavior of halloysite/2-mercaptobenzothiazole nanocomposite with calcined halloysite as nanocontainer, *Mater. Des.* (2017), <https://doi.org/10.1016/j.matdes.2017.05.033>.
 - [25] M. Abdolazadeh, J. Tedim, M. Zheludkevich, S. van der Zwaag, S.J. Garcia, Synergetic active corrosion protection of AA2024-T3 by 2D- anionic and 3D-cationic nanocontainers loaded with Ce and mercaptobenzothiazole, *Corros. Sci.* 135 (2018) 35–45, <https://doi.org/10.1016/j.corsci.2018.02.018>.
 - [26] J. Tedim, M.L. Zheludkevich, A.N. Salak, A. Lisenkov, M.G.S. Ferreira, Nanostructured LDH-container layer with active protection functionality, *J. Mater. Chem.* 21 (2011) 15464, <https://doi.org/10.1039/c1jm12463c>.
 - [27] T.T.X. Hang, T.A. Truc, N.T. Duong, N. Pèbère, M.-G. Olivier, Layered double hydroxides as containers of inhibitors in organic coatings for corrosion protection of carbon steel, *Prog. Org. Coating* 74 (2012) 343–348, <https://doi.org/10.1016/j.porgcoat.2011.10.020>.
 - [28] V.V. Gite, P.D. Tatiya, R.J. Marathe, P.P. Mahulikar, D.G. Hundiwale, Microencapsulation of quinoline as a corrosion inhibitor in polyurea microcapsules for application in anticorrosive PU coatings, *Prog. Org. Coating* 83 (2015) 11–18, <https://doi.org/10.1016/j.porgcoat.2015.01.021>.
 - [29] T. Matsuda, N. Jadhav, K.B. Kashi, M. Jensen, V.J. Gelling, Release behavior of pH sensitive microcapsules containing corrosion inhibitor, *Prog. Org. Coating* 132 (2019) 9–14, <https://doi.org/10.1016/j.porgcoat.2019.03.032>.
 - [30] P.J. Denissen, S.J. Garcia, Cerium-loaded algae exoskeletons for active corrosion protection of coated AA2024-T3, *Corros. Sci.* 128 (2017) 164–175, <https://doi.org/10.1016/j.corsci.2017.09.019>.
 - [31] J. Zhao, D.H. Na, S.J. Garcia, Surface modification of natural porous silica microparticles to control the loading and release of organic corrosion inhibitors in coatings, *NPG Asia Mater.* 17 (1) (2025) 1–18, <https://doi.org/10.1038/s41427-025-00608-5>, 2025.
 - [32] D. Snihirova, S.V. Lamaka, P. Taheri, J.M.C. Mol, M.F. Montemor, Comparison of the synergistic effects of inhibitor mixtures tailored for enhanced corrosion protection of bare and coated AA2024-T3, *Surf. Coat. Technol.* 303 (2016) 342–351, <https://doi.org/10.1016/j.surfcoat.2015.10.075>.
 - [33] S.S. Pawar, R.B. Naik, S.K. Rath, B. Kandasubramanian, Pigmented silicone/epoxy novel blends for preparation of stratified nontoxic foul release coatings, *J. Coating Technol. Res.* 19 (4) (2022) 1269–1285, <https://doi.org/10.1007/S11998-022-00610-4>, 2022.
 - [34] E. Langer, H. Kuczyńska, E. Kamińska-Tarnawska, J. Łukaszczuk, Self-stratifying coatings containing barrier and active anticorrosive pigments, *Prog. Org. Coating* 71 (2011) 162–166, <https://doi.org/10.1016/j.porgcoat.2011.01.016>.
 - [35] P. Vink, T.L. Bots, Formulation parameters influencing self-stratification of coatings, *Prog. Org. Coating* 28 (1996) 173–181, [https://doi.org/10.1016/0300-9440\(95\)00595-1](https://doi.org/10.1016/0300-9440(95)00595-1).
 - [36] J. Baghdachi, H. Perez, P. Talapatcharoenkit, B. Wang, Design and development of self-stratifying systems as sustainable coatings, *Prog. Org. Coating* 78 (2015) 464–473, <https://doi.org/10.1016/j.porgcoat.2014.06.017>.
 - [37] A. Hughes, J. Laird, C. Ryan, P. Visser, H. Terryn, A. Mol, Particle characterisation and depletion of Li₂CO₃ inhibitor in a polyurethane coating, *Coatings* 7 (2017) 106, <https://doi.org/10.3390/coatings707106>.
 - [38] X. Chen, J. Tang, H. Wei, H. Zhang, Y. Tang, X. Zhao, Y. Zuo, Effect of cerium tartrate on the corrosion resistance of epoxy coating on aluminum alloy and its mechanism, *Coatings* 12 (2022) 785, <https://doi.org/10.3390/coatings12060785>.
 - [39] F. Galliano, D. Landolt, Evaluation of corrosion protection properties of additives for waterborne epoxy coatings on steel, *Prog. Org. Coating* 44 (2002) 217–225, [https://doi.org/10.1016/S0300-9440\(02\)00016-4](https://doi.org/10.1016/S0300-9440(02)00016-4).
 - [40] N. Kamaly, B. Yameen, J. Wu, O.C. Farokhzad, Degradable controlled-release polymers and polymeric nanoparticles: mechanisms of controlling drug release, *Chem. Rev.* 116 (2016) 2602–2663, <https://doi.org/10.1021/acs.chemrev.5b00346>.
 - [41] K. Lewicka, I. Szymanek, D. Rogacz, M. Wrzaliak, J. Łagiewka, A. Nowik-Zajac, I. Zawierucha, S. Coseri, I. Puiu, H. Falfushynska, P. Rychter, K. Lewicka, I. Szymanek, D. Rogacz, M. Wrzaliak, J. Łagiewka, A. Nowik-Zajac, I. Zawierucha, S. Coseri, I. Puiu, H. Falfushynska, P. Rychter, Current trends of polymer materials' application in agriculture, *Sustainability* 16 (2024) 16, <https://doi.org/10.3390/SU16198439>, 2024.
 - [42] G. Dai, Q. Xie, C. Ma, G. Zhang, Biodegradable Poly(ester-co-acrylate) with antifoulant pendant groups for marine anti-biofouling, *ACS Appl. Mater. Interfaces* 11 (2019) 11947–11953, <https://doi.org/10.1021/acsami.9b01247>.
 - [43] G. Williams, A.J. Coleman, H.N. McMurray, Inhibition of aluminium alloy AA2024-T3 pitting corrosion by copper complexing compounds, *Electrochim. Acta* 55 (2010) 5947–5958, <https://doi.org/10.1016/j.electacta.2010.05.049>.
 - [44] Y. Liu, G. Jin, H. Miao, S. Xu, Preparation and characterization of polydopamine and n-butyl methacrylate copolymer coatings on titanium-nickel alloy stents, *RSC Adv.* 14 (2024) 15240–15248, <https://doi.org/10.1039/D4RA01491J>.
 - [45] A.A. Nazeer, E. Al-Hetlani, M.O. Amin, T. Quiones-Ruiz, I.K. Lednev, A poly(butyl methacrylate)/graphene oxide/TiO₂ nanocomposite coating with superior corrosion protection for AZ31 alloy in chloride solution, *Chem. Eng. J.* 361 (2019) 485–498, <https://doi.org/10.1016/J.CEJ.2018.12.077>.
 - [46] P. Hammer, F.C. Dos Santos, B.M. Cerrutti, S.H. Pulcinelli, C.V. Santilli, Highly corrosion resistant siloxane-polymethyl methacrylate hybrid coatings, *J. Sol. Gel Sci. Technol.* 63 (2) (2012) 266–274, <https://doi.org/10.1007/S10971-011-2672-8>, 2012.
 - [47] M.C. Uvida, A. Trentin, S.V. Harb, S.H. Pulcinelli, C.V. Santilli, P. Hammer, Nanostructured poly(methyl Methacrylate)-Silica coatings for corrosion protection of reinforcing steel, *ACS Appl. Nano Mater.* 5 (2022) 2603–2615, <https://doi.org/10.1021/acsnm.1c04281>.
 - [48] E. Stefanis, C. Panayiotou, Prediction of hansen solubility parameters with a new group-contribution method, *Int. J. Thermophys.* 29 (2008) 568–585, <https://doi.org/10.1007/s10765-008-0415-z>.
 - [49] C.M. Hansen, Hansen Solubility Parameters, CRC Press, 2007, <https://doi.org/10.1201/9781420006834>.
 - [50] M.H. Esmaili, H.A. Basuony, M.K. Al-Nawasany, M.M. Shulkamy, I.A. Shaaban, A. M. Abuelela, W.M. Zoghail, T.A. Mohamed, Thiadiazole-2-Thiol-5-Thione and 2,5-Dimercapto-1,3,4-Thiadiazol tautomerism, conformational stability, vibrational assignments, inhibitor efficiency and quantum chemical calculations, *Z. Phys. Chem.* 234 (2020) 415–440, <https://doi.org/10.1515/zpch-2018-1346>.
 - [51] R. Hardis, J.L.P. Jessop, F.E. Peters, M.R. Kessler, Cure kinetics characterization and monitoring of an epoxy resin using DSC, raman spectroscopy, and DEA, *Composites Part A Appl. Sci. Manuf.* 49 (2013) 100–108, <https://doi.org/10.1016/j.compositesa.2013.01.021>.
 - [52] H.A. Willis, V.J.I. Zichy, P.J. Hendra, The laser-Raman and infra-red spectra of poly (methyl methacrylate), *Polymer (Guildf.)* 10 (1969) 737–746, [https://doi.org/10.1016/0032-3861\(69\)90101-3](https://doi.org/10.1016/0032-3861(69)90101-3).
 - [53] I.McN. Smallwood, Handbook of Organic Solvent Properties, Elsevier, London, 1996, <https://doi.org/10.1016/C2009-0-23646-4>.
 - [54] C. Krafft, E. Pigorsch, B. Weber, F. Ott, S. Brennecke, G.E. Krammer, R. Salzer, Determination of configurational isomers in cyclic polysulfides by raman spectroscopy, *Vib. Spectrosc.* 43 (2007) 49–52, <https://doi.org/10.1016/j.vibspec.2006.06.009>.
 - [55] P. Bazylewski, R. Divigalpitiya, G. Fanchini, In situ raman spectroscopy distinguishes between reversible and irreversible thiol modifications in l-cysteine, *RSC Adv.* 7 (2017) 2964–2970, <https://doi.org/10.1039/C6RA25879D>.
 - [56] S. Stoyanov, I. Petkov, L. Antonov, T. Stoyanova, P. Karagiannidis, P. Aslanidis, Thione-thiol tautomerism and stability of 2- and 4-mercaptopyridines and 2-mercaptopyrimidines, *Can. J. Chem.* 68 (1990) 1482–1489, <https://doi.org/10.1139/v90-227>.
 - [57] S. Barrau, P. Demont, C. Maraval, A. Bernes, C. Lacabanne, Glass transition temperature depression at the percolation threshold in carbon nanotube-epoxy resin and polypyrrole-epoxy resin composites, *Macromol. Rapid Commun.* 26 (2005) 390–394, <https://doi.org/10.1002/marc.200400515>.
 - [58] E.A. Dimarzio, J.H. Gibbs, Molecular interpretation of glass temperature depression by plasticizers, *J. Polym. Sci. A* 1 (1963) 1417–1428, <https://doi.org/10.1002/pol.1963.100010428>.

- [59] Y. Song, J. Bu, M. Zuo, Y. Gao, W. Zhang, Q. Zheng, Glass transition of poly (methyl methacrylate) filled with nanosilica and core-shell structured silica, *Polymer (Guildf.)* 127 (2017) 141–149, <https://doi.org/10.1016/j.polymer.2017.08.038>.
- [60] R.C. Macqueen, R.D. Granata, Positron annihilation spectroscopy study of moisture absorption in protective epoxy coatings, *J. Polym. Sci. B Polym. Phys.* 31 (1993) 971–982, <https://doi.org/10.1002/polb.1993.090310807>.
- [61] G. Dlubek, R. Buchhold, C. Hübner, A. Nakladal, Water in local free volumes of polyimides: a positron lifetime study, *Macromolecules* 32 (1999) 2348–2355, <https://doi.org/10.1021/MA981381S>.
- [62] M. Mopon, A. Mol, S.J. Garcia, Local re-immersion behaviour of Ce-based inhibiting layers on AA2024-T3 intermetallics: enhanced stability through partial dealloying and prolonged exposure, *Corros. Sci.* 255 (2025) 113146, <https://doi.org/10.1016/j.corsci.2025.113146>.