Consiglio Nazionale delle Ricerche

Influence of processing parameters on cracking behavior: insights from a comparative study based on a full factorial design

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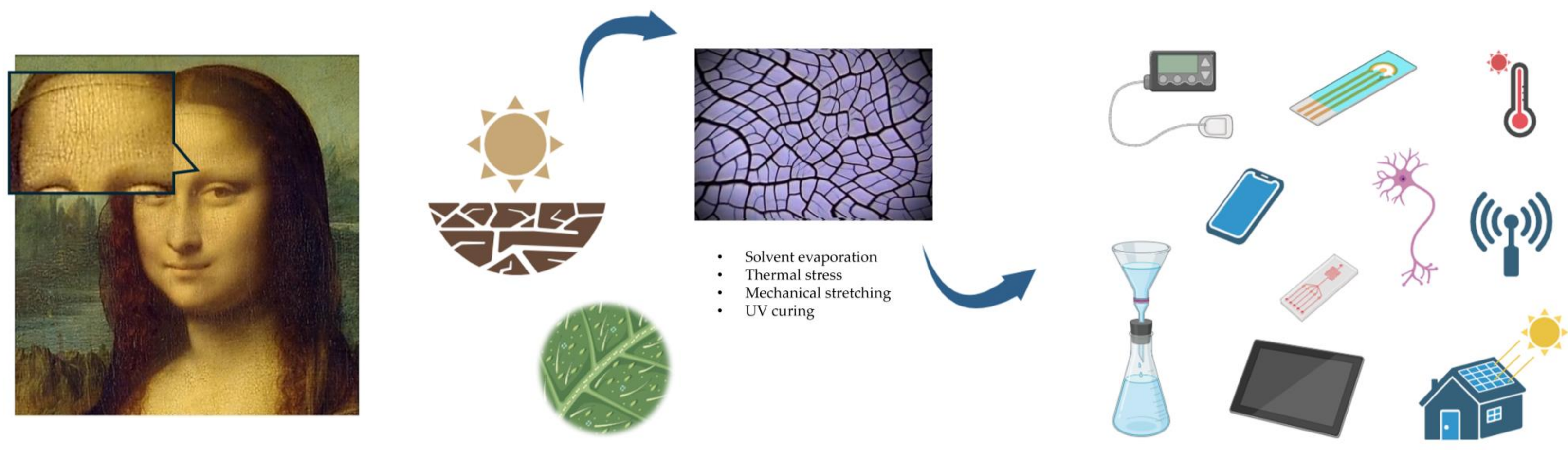
INTRODUCTION & AIM

Cracks are a universal phenomenon: they appear in dried riverbeds, soil, and even in the surface of old paintings. Inspired by these naturally occurring fracture networks, researchers have developed ***crack lithography*** (or ***crack templating***) as a patterning strategy that transforms apparent flaws into functional tools. Exploiting the natural tendency of thin films to fracture during drying or stress release, crack networks can be exploited as a design tool in electronics, optics, and smart materials. However, the cracking behavior of different materials remains insufficiently understood, as multiple processing parameters can influence it in distinct ways, leading to diverse morphologies and outcomes.



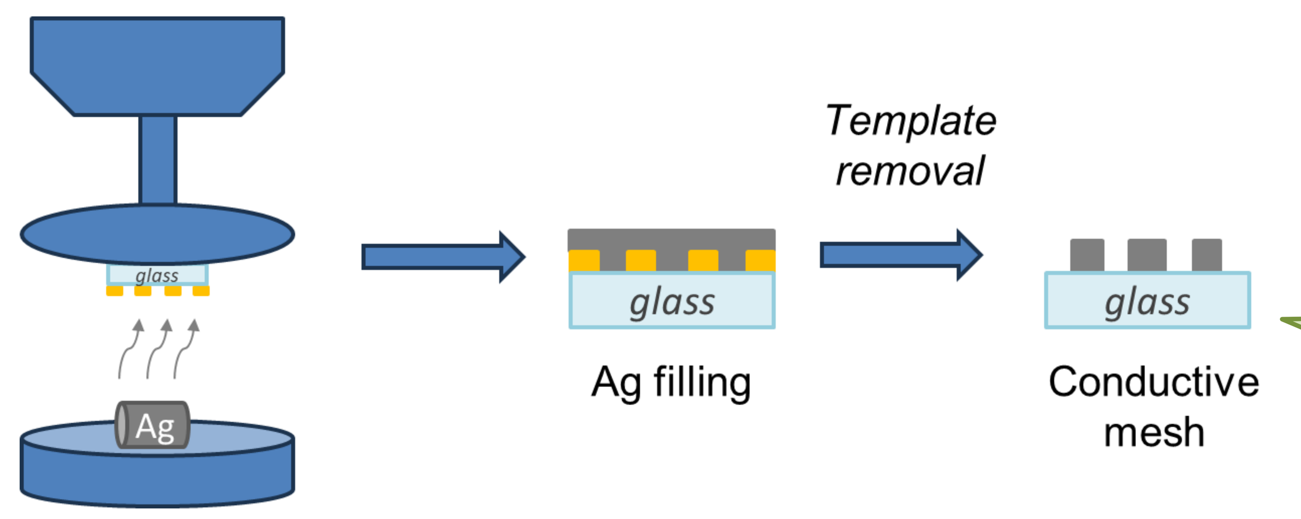
For multiple materials, finding the best combination of processing parameters can be highly challenging, as it would require a prohibitive number of experiments to re-optimize every variable independently. A **Design of Experiments** (DoE) approach addresses this limitation, allowing to systematically study different material classes and identify the optimal conditions governing controlled cracking in each case, reducing the number of required experiments compared to trial-and-error method. The aim of this study is to systematically assess the suitability of organic and inorganic materials for controlled cracking and to elucidate how their distinct physicochemical properties influence crack formation and morphology, with the ultimate goal of generating **crack-derived mesh structures** that can be exploited as **transparent electrodes.**

METHODS

A wide range of **organic and inorganic** materials were tested to evaluate their suitability for controlled cracking, including D-sorbitol, deoxycholic acid (DCA), chitosan, hydroxypropyl methylcellulose (HPMC), methyl cellulose (MC), Carbopol (Ultrez 10 and 30), ascorbic acid, agar-agar, Pluronic F127, titanium dioxide (TiO_2), egg white, and soluble coffee. Solutions or dispersions were prepared at representative concentrations (typically 1-15% w/v) and deposited onto glass substrates via **drop-casting** at either 4°C, room temperature or 50 °C. Among the so obtained cracking patterns, two chemically distinct systems were selected for in-depth analysis based on their contrasting physicochemical properties: **TiO_2**, a well-known inorganic oxide, and **DCA**, a small organic molecule explored here for the first time.

Using a full factorial DoE, we studied the effect of 3 key processing parameters: substrate **temperature** (**X1**), ranging from 4 to 50 °C; deposited **volume** (**X2**) ranging from 15 to 40 µL/cm²; solute (in the case of DCA) or co-solvent (ethyl acetate, in the case of TiO_2) **concentration** (**X3**). The lower and higher levels tested for each parameter were coded with -1 and +1, respectively. The morphological outcomes of film cracking were quantitatively assessed using 2 key responses: average **crack width** (**Y1**), and **fill factor** (**Y2**, interpreted as crack density).

The films were prepared via drop-casting onto glass substrates. Analyses were conducted primarily through optical microscopy, scanning electron microscopy (SEM), profilometry, and image processing performed with Fiji software. The DoE was performed using STATISTICA software.



A 50 nm-thick Ag layer was thermally evaporated onto the fabricated crack templates at a deposition rate of 0.7 Å s^{-1} under a vacuum of 2×10^{-6} mbar. After template removal via sonication, a metallic mesh was formed on the substrate. The optical transmittance of the resulting Ag mesh was characterized using a Lambda 900 UV–Vis spectrophotometer (Perkin Elmer, Germany).

REFERENCES

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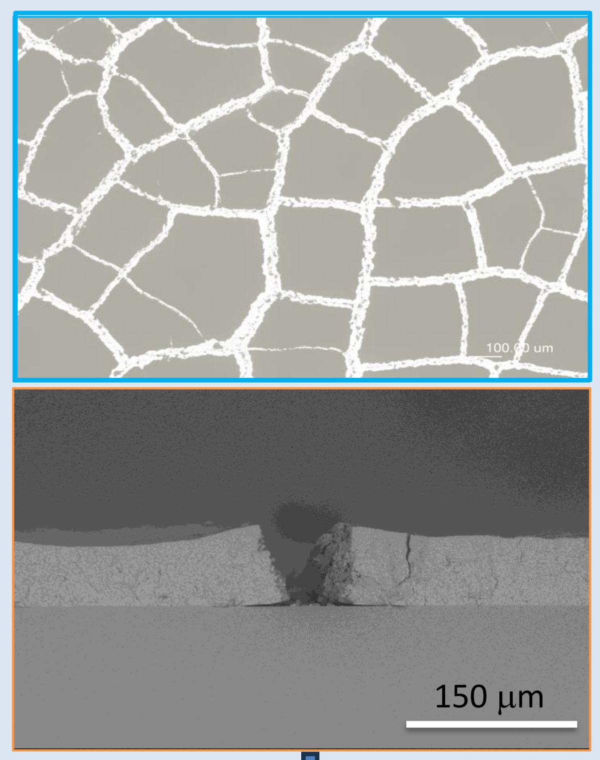
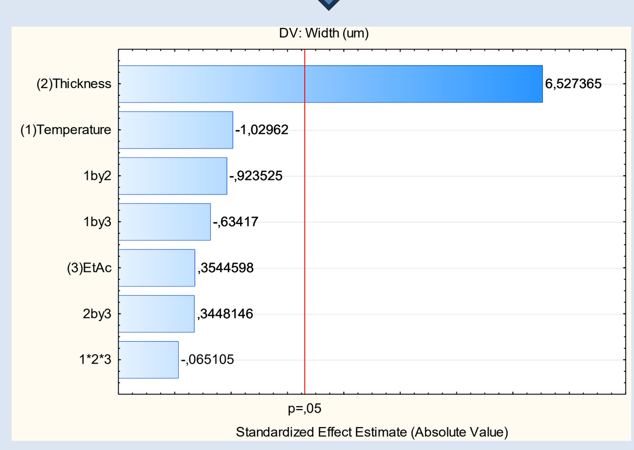
RESULTS & DISCUSSION

TiO_2

a)
b)

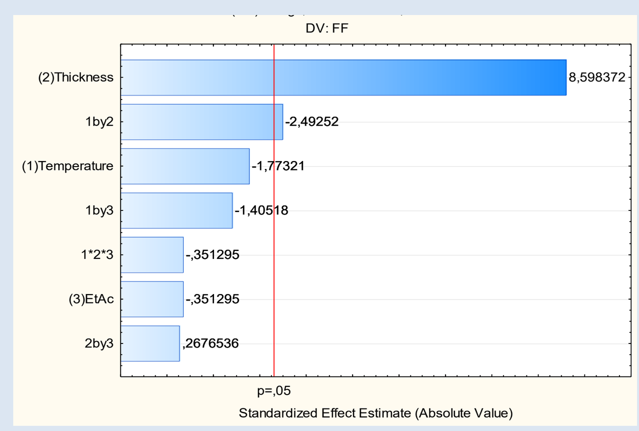


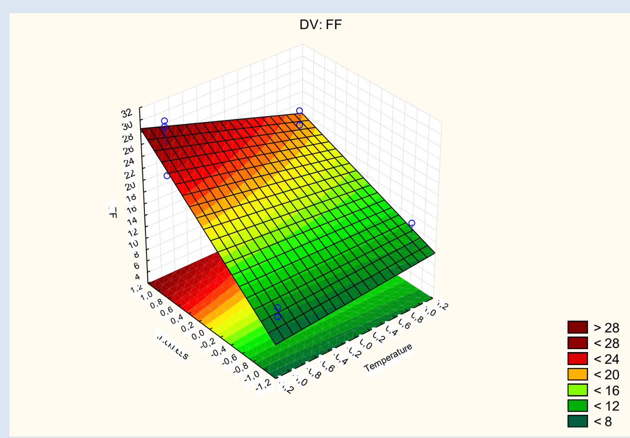
Y1



Film thickness is the dominant factor influencing crack widening in TiO_2 films.

Y2

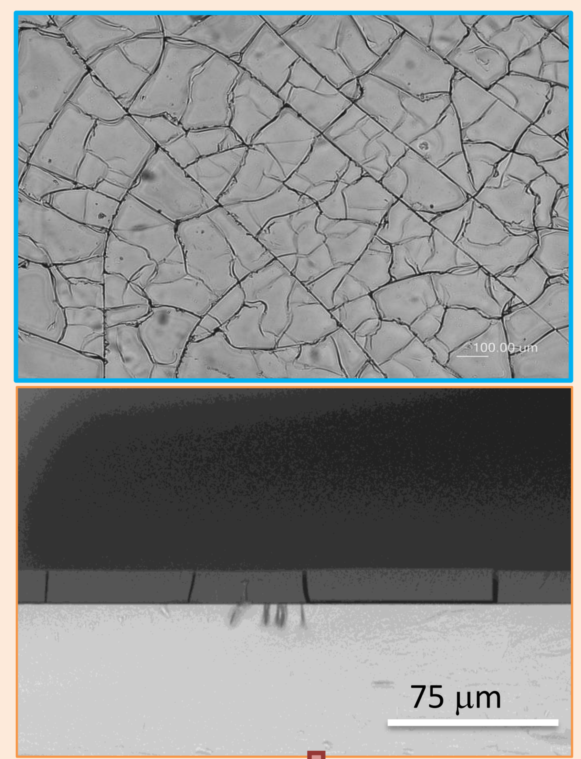




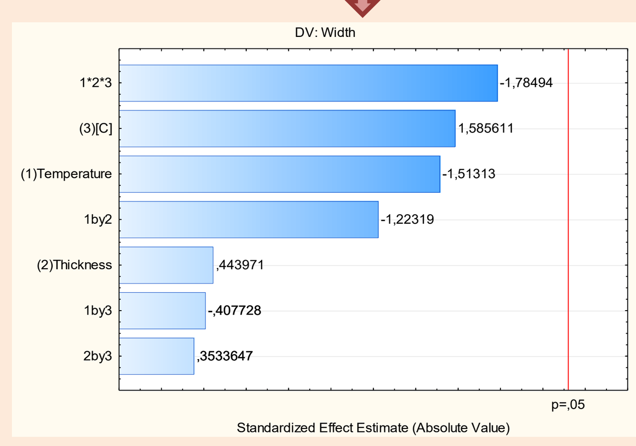
Temperature subtly influences how film thickness affects fill factor, highlighting a significant interaction between the two.

DCA

c)
d)

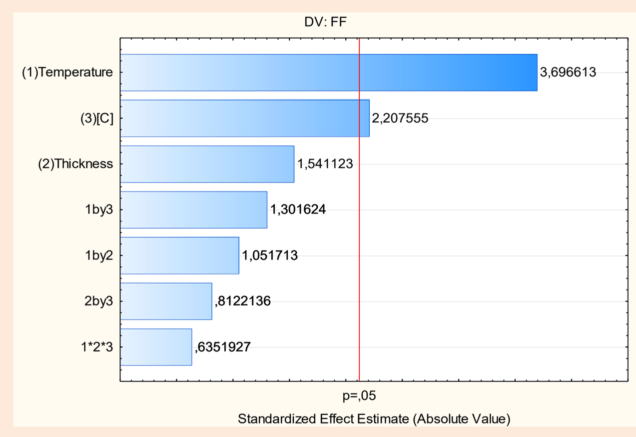


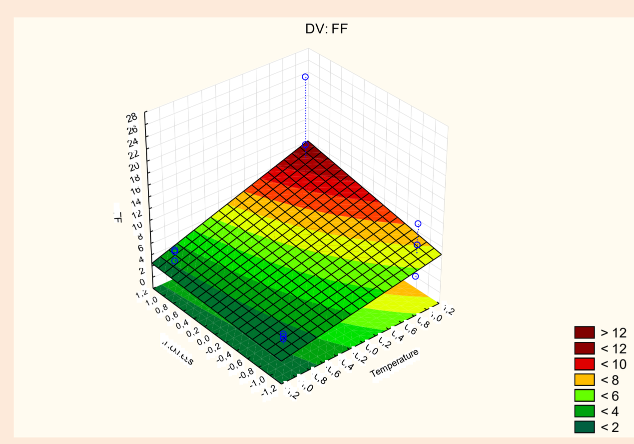
Y1



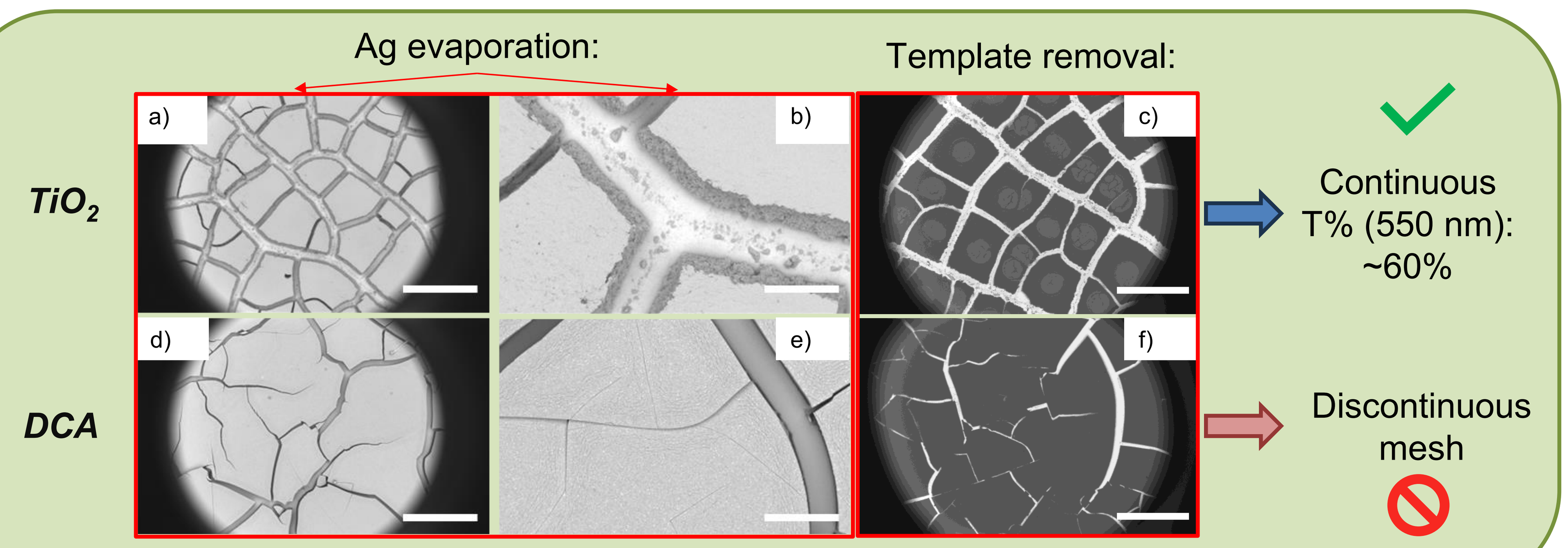
For crack width, no individual factor reached statistical significance.

Y2





Higher temperature and DCA concentration synergistically boost fill factor by improving crack coverage, regardless of film thickness.



SEM images of TiO_2 (a-c) and DCA (d-f) substrates after Ag evaporation. Scale bar = 500 µm for (a, c, d, f), 100 µm for (b, e).

CONCLUSION

- Cracking behaviour is highly **material-specific:** tailoring processing parameters to each material enabled **controlled** crack morphology.
- In **DCA** films, fill factor and spacing were primarily influenced by drying **temperature** and DCA **concentration**.
- In **TiO_2** films, **thickness** was instead the dominant factor affecting all cracking responses.
- TiO_2 templates yielded a **continuous Ag mesh** after evaporation, while DCA produced a discontinuous one (shallow cracks, not suitable for electrode fabrication).