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DIRECT EVIDENCE FOR UV SHIELDING AND PHOTOCATALYSIS IN PMMA COMPOSITES CONTAINING TITANIUM DIOXIDE AND ZINC OXIDE

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ABSTRACT

Poly(methyl methacrylate) (PMMA) is a transparent and processable support for titanium dioxide and zinc oxide, but evidence of UV shielding, aqueous photocatalysis and self-cleaning is required individually. The literature cutoff date for this structured critical review was 25 August, 2026. This structured critical review presents 50 identified reports of directly tested PMMA-containing specimens. Studies are classified by architecture, and evaluated for illumination, controls, endpoint validity, normalisation, uncertainty, material integrity, etc. High visible transmission and UV attenuation can still be achieved with low loadings of nanocomposites and thin coatings. Porous, fibrous and surface-exposed formats favour reactant access and recoverable water treatment instead often at the expense of optical clarity. The published disappearance constants do not allow a general ranking of TiO2 versus ZnO due to variations in reactor geometry, concentration, catalyst basis and illumination. The performance of hybrid composites depends on the formulation. The activity of ZnO/PMMA is improved with intermediate Ag deposition but decreases with higher deposition. The reduced apparent optical edge and filler co-presence are not enough evidence of visible-light activity or interfacial charge transfer. Similarly, dye decolorization and contact angle change are not representative of mineralisation and deposited soil removal respectively. The main requirement remaining is to simultaneously validate optical function, contaminant removal and polymer preservation on a single specimen. An integrated compact reporting framework includes total and direct transmission, haze, controlled photocatalysis, repeated cleaning, adhesion, release and weathering. Transparent UV shields and recoverable photocatalytic supports are directly evidenced; durable photocatalytic self-cleaning is not yet sufficiently demonstrated in the identified corpus.

Keywords: PMMA; Titanium Dioxide; Zinc Oxide; UV Shielding; Photocatalysis; Durability

1 INTRODUCTION

Transparent polymer covers and coatings may be needed to shield from UV while still permitting light transmission and resisting contamination. PMMA is attractive because it can be cast, spun, moulded or coated at a relatively low temperature. TiO 2 and ZnO offer useful optical and surface functions. However, a thin oxide coating, a particle-filled

film and a porous fibre are not equivalent materials. Their behaviour is influenced by optical path, aggregation, surface accessibility and adhesion [1–13].

The question raised in this review is what has been demonstrated on the specimen itself containing PMMA. The powder activity cannot be transferred directly to an immobilised architecture and an aqueous dye test cannot establish cleaning of a contaminated optical surface. A directly located PMMA–WO3 report is kept as a photochromic scope boundary only [14]; noble metals are considered where a PMMA-based hybrid was made and tested, especially Ag/ZnO/PMMA [15].

Previous reviews include TiO2 supported on polymers, TiO2 specifically supported in PMMA and polymer/ZnO UV shielding [16–18]. The present contribution is a comparative claim based analysis across TiO2, ZnO and PMMA tested hybrids. It relates architecture to transparency, catalytic access and durability and separates the measurable responses from mechanisms and application claims that still require validation.

2 REVIEW DESIGN AND EVIDENCE BOUNDARIES

This is a structured critical review and not a registered systematic review or meta-analysis . The search cut-off reported is 25 August 2026 with no lower year limit and no language restriction at record level. The core concept string was (PMMA OR “poly (methyl methacrylate)” OR “poly methyl methacrylate” OR polymethylmethacrylate) AND (TiO 2 OR TiO2 OR “titanium dioxide” OR titania OR ZnO OR “zinc oxide”). Additional discoveries were supported by architecture and outcome terms like film, coating, fiber/fibre, membrane, porous, shell, graft, photocatalysis, UV shielding, haze, ageing, adhesion and release, although these terms were not mandatory eligibility terms.

Crossref records supported bibliographic discovery and DOI checking PubMed/PMC Title/Abstract searches supported indexed discovery and accessible primary-text checking. Publisher pages were used to verify candidate metadata and text, and citation tracing forward and backwards extended retrieval. Deduplication was performed based on DOI, then on normalised title, first author and year. Prospective counting of screening flow was not collected and no retrospective hit totals or flow counts from PRISMA are reconstructed.

PMMA had to be a functional phase of the specimen tested in combination with TiO_2 or ZnO and at least one of the following endpoints: optical, UV-shielding, photocatalytic, wettability, soil removal, re-use, weathering, adhesion, release, or polymer integrity to be eligible. We excluded the oxide-only tests, sacrificial PMMA templates, and non-PMMA matrices from the performance synthesis. Antibacterial activity alone was not sufficient, but could be accompanied by an eligible optical or photocatalytic effect. Table 1 shows the distribution of all 50 eligible reports by architecture and evidence role. Note that these are reports, not necessarily 50 independent experimental datasets.

The appraisal considered specimen definition, illumination, matched controls, endpoint validity, normalisation, replication or uncertainty, durability and internal consistency. They are illustrative source-linked observations selected to explain an engineering tradeoff, not a separate ranked or statistical subset. Units and denominators are original; “not reported” denotes the lack of available extracted data, not the lack of measurement. Linked evidence is deemed to include overlapping companion reports. Pooled effects and a material-wide TiO_2-versus-ZnO ranking are precluded by incompatible illumination, catalyst basis, concentration, and reactor conditions.

Table 1: Architecture inventory of the 50 eligible reports and limits of interpretation

Reports	Direct evidence and interpretation
Transparent TiO_2 or hybrid films [1–3,19–20]	Thin coatings, low-loading cast films and PMMA-shell particles support UV/visible optical claims. Short exposure or Fourier-transform infrared (FTIR) retention does not establish outdoor service life; PMMA shells in another adhesive are distinct from bulk PMMA.
ZnO optical architectures [10,21–24]	Quantum dots, multilayers and flexible sheets support UV attenuation and transparency. The multilayer value at 351 nm is near-UV transmission; the ZnO study in [23] adds 200 h optical/mechanical aging.
Porous TiO_2 supports [4,7,11–12]	Fibers, porous films and floating spheres support reactor-specific target disappearance. Geometry, adsorption and catalyst basis differ. Release and long exposure are addressed in selected reports, not uniformly.
Other TiO_2 films and fibers [5–6,8,25–35]	Direct dye or non-dye responses span nanotubes, atomic layer deposition (ALD) structures, grafted layers, sputtered coatings and spun fibers. Reports [5,25] are linked; tetrakis(4-carboxyphenyl)porphyrin (TCPP) sensitization is required for the visible response in [25]. Coating delamination in [8] limits durability claims.

ZnO catalytic films and fibers [9,36–41]	Aqueous dye removal, selected phenol testing and reuse support recoverable photocatalysis. High loading can suppress blue transmission; white films are not transparent covers. Large neat-PMMA control loss in [41] weakens causal attribution.
Direct multicomponent systems [15,42–49]	Ag, SiO_2, SnO_2, MoS_2, magnetic, carbon-nanotube and sensitized formulations broaden functionality. Composition does not prove electronic coupling. Contact angle in [42] is a proxy; [44] reports a negative visible-only test.
PMMA-containing blend membranes [50–52]	Pharmaceutical or dye removal is reported for PMMA/poly(pentafluorophenyl acrylate) (pPFPA), polyvinylidene fluoride (PVDF)/PMMA and xylan-g-PMMA architectures. Separate retention, adsorption and photocatalysis; blend-specific effects cannot be assigned to PMMA alone.
Additional direct formats [13,53–54]	Freestanding comparative films, ALD-coated microcapsules and N–TiO_2 on PMMA extend optical or photocatalytic evidence. Antibacterial outcomes are co-outcomes and are not substitutes for mineralization or soil removal.

3 ARCHITECTURE DETERMINES THE USEFUL OPERATING REGIME

PMMA is an optical support and an organic phase that can be oxidised. UV-induced chain scission and photo-oxidation are known problems and contact with an illuminated photocatalyst can accelerate acrylic-polymer degradation [55–56]. Low loading and small aggregates improve clarity, but once particles are buried they have limited access to water, oxygen and pollutants. Porosity increases access but also scattering and mechanical weakness. Surface coatings expose more oxide but transfer the durability problem to adhesion and substrate protection. These conflicting design requirements are summarised in Fig. 1.

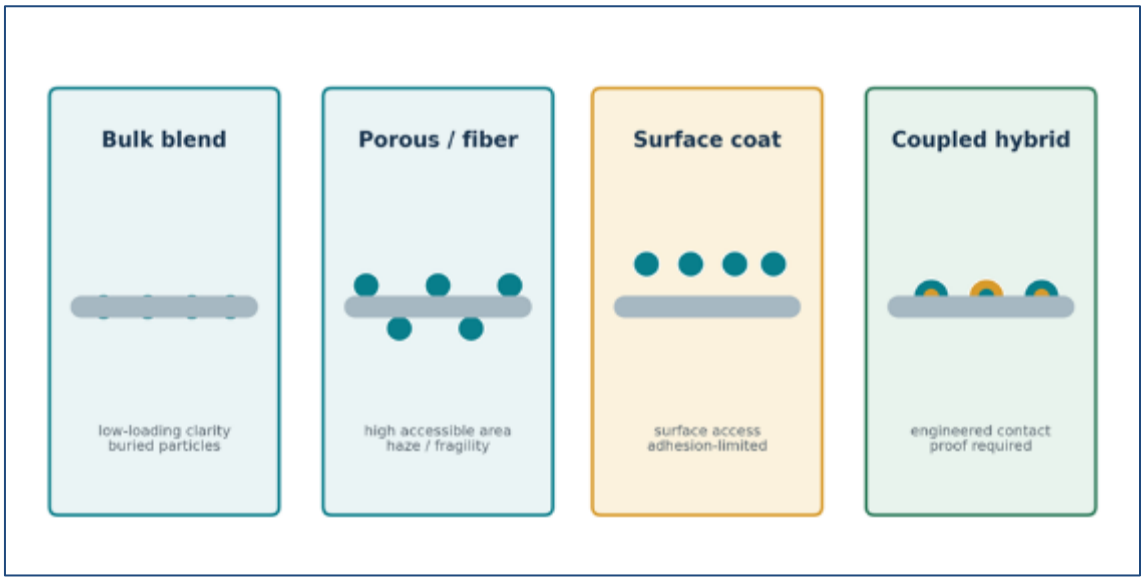


Figure 1: PMMA architectures and their principal trade-offs. Particle placement controls optical clarity, reactant access and interfacial stability; the schematic does not establish charge transfer.

These differences explain the impossibility of defending any universal optimum filler loading. UV protection should have little visible attenuation and haze for a transparent UV shield. A water-treatment support can take intentionally opacity to increase the reachable catalyst area. A self-cleaning cover with photocatalytic properties should satisfy optical and surface-cleaning requirements upon repeated exposure . Hence, each application needs to be benchmarked on a separate unfilled-PMMA or bare-substrate control.

4 DIRECT EVIDENCE FOR OPTICAL PROTECTION AND PHOTOCATALYSIS

4.1 Transparent and UV-shielding specimens

Xu et al. deposited a ~400 nm TiO2 coating on PMMA at 50 °C. Transmission at 250 nm was reduced from 62% to near zero while the transmission at 550 nm remained at 95% The normalised carbonyl signal at 1732 cm -1 was 0.90 and 0.18 for coated and uncoated PMMA, respectively, after 5 h UV irradiation. The reported degradation constant decreased

from 0.36 to 0.018 h -1 . Another adhesion challenge was water sonication with wiping [1]. These measurements support optical protection and short term integrity, but are not a service life test.

Choi and Lee embedded TiO 2 -core/PMMA-shell particles in a different optical adhesive. Visible transmission was about 95.3% and UVB and UVA blocking was about 25% and 14% at 0.05 wt % [2]. It is the result of a PMMA-shell/adhesive architecture. Yousefi et al. found that the 0.1 wt% formulation was more stable than the 0.2 wt% formulation in cast PMMA/TiO2 films after 720 h of exposure by FTIR [3]. A 1:1 TiO2:ZnO hybrid at 0.05 wt% total loading also showed good UV/FTIR properties [3]. More oxide thus does not necessarily improve preservation of the polymer.

ZnO quantum dots offer a further transparent regime. High PMMA transparency was achieved with ∼5 nm particles at <1 wt% [10]. Surface-modified ZnO quantum dots strongly attenuated below 340 nm [22]. PMMA/ZnO multilayers had about 80% transmission at 351 nm, describing near-UV rather than visible luminous transmission [21]. Optical and mechanical ageing evidence was contributed for ∼6 nm ZnO–PMMA composites for 200 h [23]. Cui et al. Earlier TiO2 and comparative-film reports extend the optical evidence but lack a common basis for haze, thickness and spectral-weighting [13,19–20].

4.2 Accessible TiO_2 supports

In one study, porous PMMA–titania decolorized methyl orange more than six times faster than a nonporous comparitor [11]. Kanth et al. [4] reported methylen blue disappearance constants of 0.116, 0.053 and 0.059 min-1 for D5, D10 and core–shell fibres with 36 wt% TiO2 in the active phase, respectively. Their fitted initial concentrations after adsorption were different (approximately 0.706, 2.466 and 2.545 mg L-1), so these constants cannot isolate geometry as the causal variable. Floating PMMA–titania spheres also removed > 96% of 60 mg L−1 tetracycline from 3.5 L pond water under solar exposure for 24 h, supporting a device-specific treatment format [12].

In the case of PMMA films loaded with 15 wt.% TiO2 nanotubes, the methylene-blue constant was reported to be (3.0 ± 0.1) × 10−3 min−1 with a photonic efficiency of 0.047 ± 0.007% and activity remained stable over five tests [5]. In the linked broad report [25] visible response required TCPP sensitisation . Sequential dye tests are performed on electrospun PMMA/anatase [6], whereas a porous PMMA–P25 study measures catalyst loss after a 1000 h UV/water-flow challenge [7]. Stable dye removal alone is not a means to demonstrate whether polymer erosion exposes new catalyst.

Thin coatings between optical and catalytic functions. Iesalnieks et al. reported 97% retention of the substrate transmission and more than 80% removal of rhodamine-B in 300 min. Microscopy revealed delamination in the five tests that maintained substantial activity. Inconsistent reported constants, 6 × 10-3 and 1.1 × 10-2 min-1, also preclude adoption of a single unqualified value [8]. Hence, a good reuse curve can be coupled with interfacial failure.

4.3 ZnO supports and PMMA-containing membranes

A ZnO layer of about 80 nm was deposited by low-temperature ALD on PMMA powder, which was then cast into a film of about 200 μm. The ZnO content was ∼0.14 wt% by weighing. A separate microscopy estimate was ∼0.2%. The powder and film degraded approximately 60 % and 40 % of methylene blue in 4 h with rate constants of $(4.1 \pm 0.2) \times 10^{-3}$ and $(2.6 \pm 0.1) \times 10^{-3}$ min^{-1}, respectively [9]. These tests were performed with different specimen bases, 100 mg powder and 1cm 2 film. Recoverable water treatment is supported by seven stable runs and phenol response, not transparent glazing.

A further investigation of a PMMA membrane with 2.5 wt% ZnO reported total removal of methylene blue in 80 min, although films with higher loadings attenuated light at 464 nm [36]. A study of 1-7 mass% showed Acid Red removal up to 99% under UV with a decrease in activity over four cycles [37]. These results further highlight the trade-off between catalytic throughput, visible transmission and sustained performance.

The 2026 PMMA/pPFPA study with formulations with polyethylene glycol (PEG) and polyvinylpyrrolidone (PVP) deserves a separate consideration, as it distinguishes pharmaceutical rejection, sorption and UV treatment. Rejection was less than 30%, sorption was 50-70% and the removal of the parent compound was reported to be 100% in 2 h under photocatalytic conditions [50]. In cross-flow testing, the formulation without PEG/PVP washed away, while the formulation with PEG/PVP permitted further testing. This provides direct evidence that chemical removal and mechanical integrity must be evaluated together; even complete parent disappearance does not confirm mineralisation. Other blend and grafted membranes support the evidence but entail other polymer-specific effects [51–52].

4.4 Hybrids and the limits of synergy claims

The TiO_2–ZnO/PMMA formula in [3] favours UV shielding and polymer stability, not photocatalytic synergy. Similarly, 1:1 SiO 2 /TiO 2 mixture of 1 wt% in PMMA led to a visible transmission of around 75–80% and a contact angle of nearly

12° after 120 min UV exposure [42]. This still evidences wettability without removal of deposited soil, abrasion or repeated cleaning.

The sequential ALD of ZnO and Ag on PMMA gave a non-monotonic loading response. Reported features with a peak size of 8.0 +/- 0.6 nm demonstrate about 20% improvement in methylene-blue activity relative to ZnO/PMMA at 150 Ag cycles. Removal of paracetamol and surfactant was close to 90% in 4 h with five stable tests. The activity was reduced by ~35% in comparison to the selected treatment when the Ag deposition was increased to 300–600 cycles [15]. Antibacterial activity in dark and under UV cannot independently validate the photocatalytic enhancement.

ZnO/SnO2–PMMA foils are reusable, but an unambiguous retained-removal percentage was not extracted [43]. ZnO–MoS_2–PMMA showed enhanced removal under the study lamp, but no detectable activity was observed under simulated visible light at 400–1100 nm and 1 kW m-2 [44]. TiO_2–MoS_2–PMMA enhanced the removal of methyl-orange and diclofenac in a white/grey film [45]. These contrasts caution against assigning visible activity to a smaller Tauc intercept. Microscopy can prove co-location but directional charge transfer needs further carrier sensitive evidence, consistent energetics and matched single component controls.

5 OPTICAL MEASUREMENTS AND DEFENSIBLE INTERPRETATION

Direct transmittance must be distinguished from total hemispherical transmittance. For uniform collection geometry, diffuse transmission is Tdiff = Ttot − Tdir. Haze is not 100 − T and requires a proper standardised geometry, e.g. ASTM D1003 [57]. If essentially all transmitted and reflected light is collected and fluorescence is negligible, stack absorptance is given by Astack = 1- Ttot - Rtot . The coating absorption coefficient is not obtained from this energy balance. Inversion of turbid films [58] also requires assumptions on the thickness, the refractive index, the interfaces and the scattering anisotropy.

In a homogeneous nonscattering medium, $\alpha = 4 \pi \kappa \lambda$, where κ is the extinction coefficient. By contrast, $-\ln(T_{dir})/d$ includes reflection and out-of-aperture scattering and should not be automatically identified as intrinsic absorption. Supported layers need a model of the full optical stack [59]. Swanepoel analysis requires well resolved interference fringes [60], while ellipsometry will still be dependent on thickness, roughness and dispersion model; for absorbing regions physically appropriate oscillator descriptions are required [61].

For the convention $(\alpha h\nu)^p = B(h\nu - Eg)$, p = 2 and p = ½ are often used for direct-allowed and indirect-allowed transitions, respectively [62]. Transition choice, baseline, fit interval and uncertainty must be justified . For multicomponent or scattering PMMA films, the intercept is an apparent optical edge unless contributions are resolved independently [63–65]. The transition mechanism is not proved by a high linear fit R^2.

A single value at 550 nm is not a full application metric. For glazing, defined visible and solar weighting is needed; ASTM G173 gives a reference solar spectrum and ASTM E903 concerns integrating-sphere optical measurements [66–67]. A spectrum that cuts off at 800 nm cannot achieve full solar transmission. Photovoltaic covers also require the throughput weighted by device spectral response and haze and colour change.

6 PHOTOCATALYSIS AND SELF-CLEANING REQUIRE DIFFERENT ENDPOINTS

Dye absorbance can be decreased by adsorption, direct photolysis, sensitisation, reduction and spectral shifts and photocatalytic transformation [68]. The tests require dark adsorption, light without catalyst, catalyst-containing PMMA in the dark and unfilled PMMA under identical illumination. Separation of parent disappearance from mineralisation requires the use of non-dye targets, product analysis and carbon balances. ISO 10678:2024 standardises a UV/aqueous methylene-blue surface test, and does not establish visible-light activity, direct-soiling performance or antimicrobial efficacy [69].

Under the given conditions, the monitored parent signal obeys the pseudo first order relation ln (C0 / Ct) = kapp t . Comparisons need the same definition of post-adsorption concentration, the same illumination, volume and catalyst basis. Reporting incident photon flux and exposed area improves interpretation; however, simply dividing a rate by area cannot remove mass-transfer or light field differences.

Self-cleaning is associated with a contaminant deposited on a surface. A known soil loading should be followed by quantified removal or optical recovery in a defined light, water, runoff or wiping procedure. Oleic-acid/contact-angle procedures related to ISO 27448 are limited for rough or initially hydrophobic surfaces [70]. Thus contact angle is to be an adjunct and not a substitute for direct removal of oily and particulate soils. Useful cleaning should be distinguished from a one-time change in wetting by repeated foul-clean cycles.

7 DURABILITY AND APPLICATION-SPECIFIC REPORTING

Parallel measurements of photocatalyst retention, substrate preservation and retained function have to be done. Falling activity may be due to fouling, loss, phase changes, or restricted access. Stable activity may mask PMMA oxidation. Transferable ZnO thin-film exhibits photodissolution dependent on the condition [71]. Therefore dissolved zinc and detached particles should be measured in PMMA systems and not assumed to be absent from a stable reuse curve.

The durability evidence available is valuable but fragmented, including 720 h FTIR tracking[3], 200 h optical/mechanical aging[23], a 1000 h UV/water challenge[7], delamination despite retained activity[8], and repeated activity tests[9,15]. The conversion of exposure hours into service lifetime requires spectrum, irradiance, temperature, humidity and wetting conditions. Relevant exposure frameworks are provided in ISO 4892-1, ISO 4892-3 and ASTM G154 [72–74]. Table 2: Measurements required before extrapolation of a laboratory response to an application claim.

Table 2: Minimum evidence linking the intended function to a defensible application claim

Function	Required measurements and controls
Transparent UV shield	Thickness and filler basis; total/direct transmission, reflection, haze and color; spectral weighting and substrate baseline; optical and chemical retention after declared weathering.
Recoverable photocatalyst	Lamp spectrum and irradiance at specimen; area/mass, pH, volume and concentration; dark, photolysis and neat-PMMA controls; non-dye target, products/carbon balance; cycle-resolved activity and release.
Visible-light hybrid	UV-cut illumination with measured residual spectrum; matched single-component controls; physical interface evidence; wavelength-dependent activity where possible. Band alignment or photoluminescence quenching alone is insufficient.
Photocatalytic self-cleaning	Defined oily and particulate soils; areal loading, removal and optical recovery; contact-angle/runoff protocol; repeated fouling/cleaning, abrasion and adhesion tests.
Material integrity	Before/after spectroscopy, molecular mass or suitable degradation markers, adhesion/mechanics and microscopy; dissolved-ion versus particle release by a sensitive method; distinguish pollutant oxidation from polymer oxidation.
Reproducibility	Independent specimen replicates; uncertainty and fitting interval; PMMA grade, particle/aggregate size and processing; exact loading denominator, geometry and test sequence. Select acceptance thresholds for the intended application.

A small factorial study crossing architecture, loading and surface-accessible fraction would be more informative than an uncontrolled loading series. Optical performance, non-dye transformation and polymer integrity should be measured on the same specimens. Barrier interlayers and outward-facing catalyst domains are promising hypotheses, but must preserve reactant access while limiting polymer attack. Negative results, including visible-only inactivity, excess-metal suppression and delamination, identify design boundaries and should be retained in the evidence base.

8 CONCLUSIONS

The inventory of 50 reports details identified evidence, not overall prevalence. Not all subscription databases were retrieved, and terminology, full-text availability, translation requirements and citation connectivity can affect inclusion and extraction. The qualitative appraisal is not a validated tool for risk of bias. Missing reporting ≠ missing experimental safeguards . Companion reports can overlap . Numerical examples remain source-specific . There is no pooled estimate or causal ranking . Negative statements regarding the field are restricted to the identified literature until 25 August 2026.

Direct evidence is provided for PMMA as a transparent UV-shielding host at appropriate loading or coating thickness and as a recoverable photocatalytic support when oxide accessibility is maintained. These roles are dictated by differing optical and mass-transfer requirements. Hybridization is useful if it improves a matched benchmark without sacrificing stability; co-presence of fillers does not show such improvement or its mechanism.

In this corpus, a persistent self-cleaning PMMA photocatalytic surface is under-validated. The next crucial step is paired testing of deposited-soil removal, optical recovery and material preservation after repeated cleaning and weathering.

The method translates isolated optical or dye removal results into evidence possibly relevant to an actual coating or treatment device.

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