REFLECTIVE COATING: POLYMER BASED COOLING SOLUTIONS

A Project Report for

CH507A: INTRODUCTION TO POLYMER SCIENCE AND ENGINEERING

by

Kirti (2024CYZ0015)

Abhishek Anand

(2022CHB1036)

Ankit Gond

(2022CHB1042)

Sayed Musaraf Ali
(2022CHB1057)

DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY ROPAR

May, 2025

CONTENT

Signature of the Supervisor(s)

ABSTRACT

This project focuses on the development and optimization of polymer-based reflective coatings incorporating titanium dioxide (TiO_2) nanoparticles. These coatings are designed to enhance surface reflectance and emittance for applications in thermal management, energy efficiency, and optical surface engineering. Two different polymer adhesives, Polyvinylpyrrolidone (PVP) and Polydiallyldimethylammonium chloride (PDADMAC), were employed to study their influence on nanoparticle dispersion, film uniformity, and adhesion properties.
The coating films were synthesized using the dip-coating technique, with TiO_2 concentrations varied from 3% to 10% to investigate their effect on the film's structural and optical characteristics. Special emphasis was placed on achieving uniform and thin films with optimal particle layering and surface coverage. Film thickness was assessed using SEM cross-section imaging, while optical reflectance was analyzed through UV-Vis-NIR spectrometry.
The results demonstrated a direct correlation between TiO_2 concentration and film thickness, with higher concentrations leading to increased nanoparticle layering and reflectivity. PVP-based coatings showed better dispersion and uniformity compared to PDADMAC, making them more suitable for reflective applications. The study concludes with a discussion on the potential scalability of such coatings for use in thermal barrier systems and suggests further work on hybrid material combinations and long-term stability analysis.

1. INRODUCTION

1.1 Background and Motivation

The growing concerns surrounding global warming and energy consumption have underscored the need for innovative and sustainable cooling technologies. The urban heat island effect and rising temperatures have increased dependence on active cooling systems like air conditioners, which in turn contribute to higher electricity usage and greenhouse gas emissions. In this context, passive cooling solutions—which function without external energy input—are being actively explored as environmentally friendly alternatives.
Among passive methods, solar-reflective coatings are particularly attractive due to their ability to reflect a substantial portion of incoming solar radiation, thereby reducing surface temperatures and the need for artificial cooling. These coatings can be applied to a wide range of surfaces including building rooftops, facades, electronic housings, and textiles, making them versatile and scalable.

1.2 Importance of Reflective Coatings

Reflective coatings work primarily by enhancing solar reflectance (also known as albedo), particularly in the visible and near-infrared parts of the solar spectrum. High-reflectance surfaces absorb less heat, keeping structures cooler. Such coatings can reduce indoor temperatures by 2–5°C, leading to substantial energy savings and improved thermal comfort.

1.3 Role of TiO_2 Nanoparticles

Titanium dioxide (TiO_2) is widely recognized for its optical and physical properties, including:

- High reflectance in the UV and visible spectrum,

- Chemical and photothermal stability,
- Non-toxicity and environmental safety,
- Abundance and cost-effectiveness.

Due to its high refractive index and strong light-scattering ability, TiO_2 is a preferred material in sunscreens, white paints, and self-cleaning coatings. In reflective coatings, TiO_2 nanoparticles are particularly effective at scattering light, thus enhancing solar reflectivity.

1.4 Significance of Polymer Matrices

While TiO_2 imparts high reflectivity, it must be dispersed in a suitable matrix to ensure uniformity, stability, and mechanical integrity. Polymers serve as binding agents, improving adhesion to substrates, and allowing the coating to form flexible and defect-free films. Two polymers selected in this study are:

- Polyvinylpyrrolidone (PVP): A water-soluble, non-ionic polymer with excellent film-forming capability. It provides uniform dispersion of nanoparticles, resulting in smooth, crack-free coatings. PVP is also biocompatible and widely used in biomedical and surface applications.
- Poly(diallyldimethylammonium chloride) (PDADMAC): A cationic polyelectrolyte known for strong adhesion and electrostatic interaction with surfaces. It enhances the mechanical durability of the coatings and improves compatibility with negatively charged TiO_2 particles.

Together, these polymers offer different interaction mechanisms and surface properties, enabling a comparative study of their influence on coating performance.

1.5 Selection of Materials

The selection of materials was based on the following considerations:

Material	Purpose	Selection Criteria
TiO_2 Nanoparticles	Reflective filler	High reflectivity, UV stability, inertness, availability
PVP (Polyvinylpyrrolidone)	Polymer matrix	Film-forming, nanoparticle dispersion, flexibility
PDADMAC (Poly(diallyldimethylammonium chloride))	Polymer matrix	Adhesion, electrostatic interaction, water solubility
Distilled Water	Solvent	Environmentally friendly, suitable for polymer dissolution
Glass Slides	Substrate	Smooth surface, inert, ideal for dip coating and reflectance measurement

This combination of materials was chosen to optimize the optical performance, coating quality, and scalability of the fabricated films.

1.6 Fabrication Method: Dip Coating

Dip coating is a widely used and efficient technique for the fabrication of thin and uniform coatings on substrates. It involves immersing a solid substrate into a coating solution (typically containing nanoparticles, polymers, or other functional materials) and then withdrawing it at a controlled speed, allowing a liquid film to form and dry on the surface.

The entire process can be divided into five distinct stages:

1. Immersion: The substrate is vertically lowered into the solution at a constant speed.
2. Dwell time: The substrate remains submerged for a set period to allow adsorption and stabilization of the coating solution.
3. Withdrawal: The substrate is pulled out at a constant withdrawal speed. This stage largely determines the film thickness.
4. Drainage: Excess liquid drains off the surface, influenced by gravity and solution viscosity.
5. Evaporation and Drying: The solvent evaporates, leaving behind a solid film. Ambient temperature, humidity, and airflow affect drying uniformity.

Key Parameters Affecting Dip Coating:

Parameter	Effect
Withdrawal speed	Controls film thickness; faster speeds generally lead to thicker films.
Solution viscosity	Affects the amount of material deposited on the substrate.
Surface tension	Influences film uniformity and adhesion to the substrate.
Concentration of solutes	Determines the density of nanoparticles/polymer in the final film.
Ambient conditions (temperature, humidity)	Affect solvent evaporation rate and drying quality.
Substrate surface properties	Smoothness, cleanliness, and hydrophilicity impact coating adhesion.

Advantages of Dip Coating

- Uniform film deposition: Provides consistent thickness over large surface areas.
- Scalability: Suitable for both laboratory-scale experiments and industrial-scale production.
- Cost-effective: Requires minimal equipment compared to methods like spin coating or vapor deposition.
- Versatile: Applicable to a wide range of materials, including polymers, nanoparticles, sol-gels, and biomaterials.
- Simple setup: The equipment needed is relatively simple—often just a motorized dip coater, solution beaker, and controlled environment.

Relevance to This Project

In this project, dip coating is selected for fabricating TiO_2-based reflective coatings due to its ability to produce smooth and uniform films with controllable thickness. The technique is particularly advantageous for:

- Water-based polymer systems like PVP and PDADMAC,
- Achieving uniform dispersion of TiO_2 nanoparticles across the substrate,
- Creating reproducible coatings for comparative analysis of material combinations.

Additionally, dip coating allows for easy parameter control (e.g., TiO_2 concentration, withdrawal speed), which is essential for systematically studying their effect on the optical and mechanical properties of the final coatings.

1.7 Problem Statement and Research Gap

Although TiO_2-based reflective coatings have been studied, the combined impact of TiO_2 concentration and polymer matrix choice on optical reflectance, film uniformity, and mechanical durability is still underexplored. Furthermore, there is a lack of comparative analysis using scalable fabrication methods such as dip coating, especially with water-based polymer systems like PVP and PDADMAC.

1.8 Objectives of the Study

This study aims to:

1. Develop reflective coatings using varying concentrations of TiO_2 nanoparticles in two polymer matrices—PVP and PDADMAC.
2. Fabricate these coatings using the dip coating method on glass substrates.
3. Analyze and compare the coatings based on:
   - Optical reflectance (especially in the visible range),
   - Surface morphology and thickness,
   - Mechanical stability and adhesion.

The ultimate goal is to create high-performance reflective coatings that are durable, efficient, and suitable for real-world passive cooling applications.

---

2. EXPERIMENTAL SECTION
2.1 Materials Required:

Material	Purpose
Polyvinylpyrrolidone (PVP) / PDADMAC	Polymer matrix (film former)
TiO_2 nanoparticles (<50 nm)	Reflective pigment
Ethanol or DI water	Solvent
Magnetic stirrer & sonicator	Mixing and dispersion
Dip coater	Film application
Substrate (glass/aluminum)	Support for coating
UV-Vis-NIR photospectrometer FTIR photospectrometer	Reflectance measurement Infrared reflectance
IR camera/thermocouple	Emittance/temperature profiling

2.2 Procedure:
A. Withdrawal Speed vs. Coating Thickness

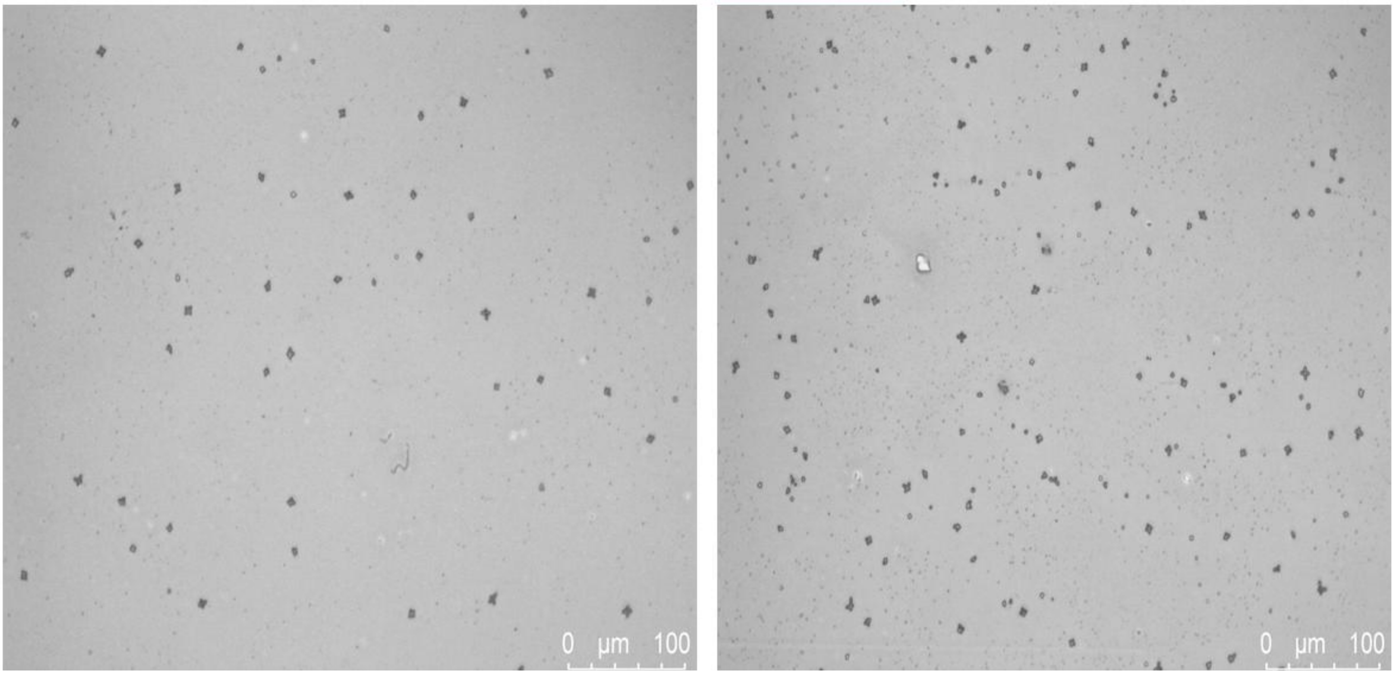
1. Prepare polymer solutions at different concentrations (e.g., 1%, 5%, 10% w/v).
2. Dip-coat the substrates at different withdrawal speeds (e.g., 1, 2, 5, 10 mm/s).
3. Let the coatings dry at room temperature or use heat curing (80–100°C for 1 hour) if needed.
4. Measure the coating thickness using a Profilometer or SEM cross-section imaging.
5. Record and plot withdrawal speed vs. thickness.

B. Reflectance (%) vs. Wavelength (nm)

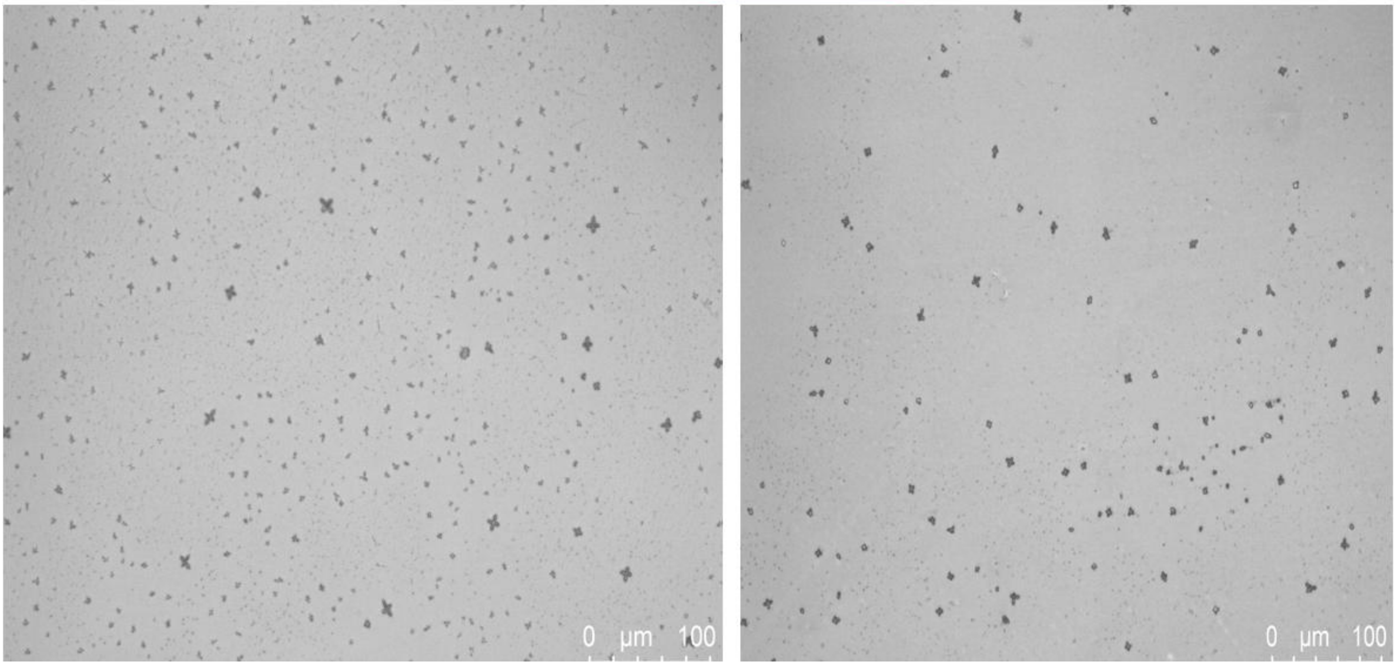
1. Prepare and apply PVP-TiO2 (3% to 15% w/v) coatings using the dip-coater.
2. Place the coated substrate into the UV-Vis-NIR spectrophotometer.
3. Measure reflectance across wavelengths (300–2500 nm).
4. Plot reflectance (%) vs. wavelength (nm).
5. If needed, use an FTIR spectrometer for emissivity analysis in the infrared range (2–25 µm).

2.3 Samples and Observations:

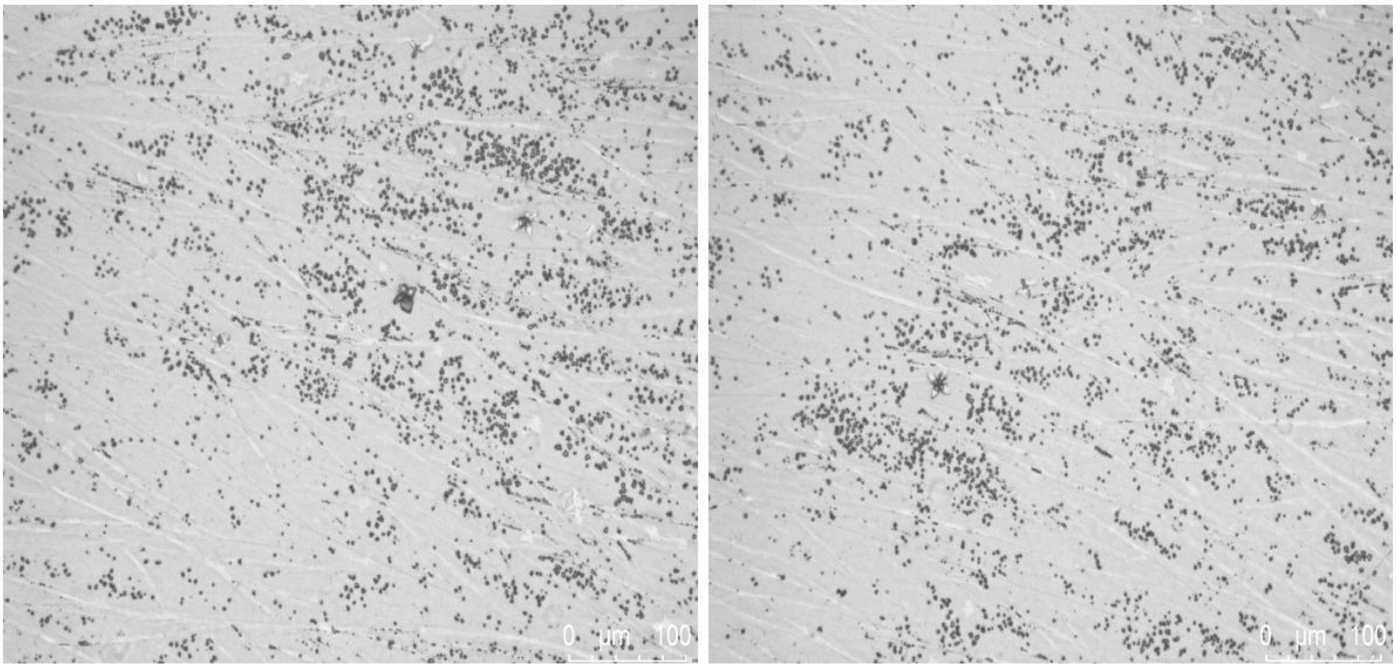
SEM CROSS-SECTION SAMPLES: 2% PDADMAC / NABH4 +PT



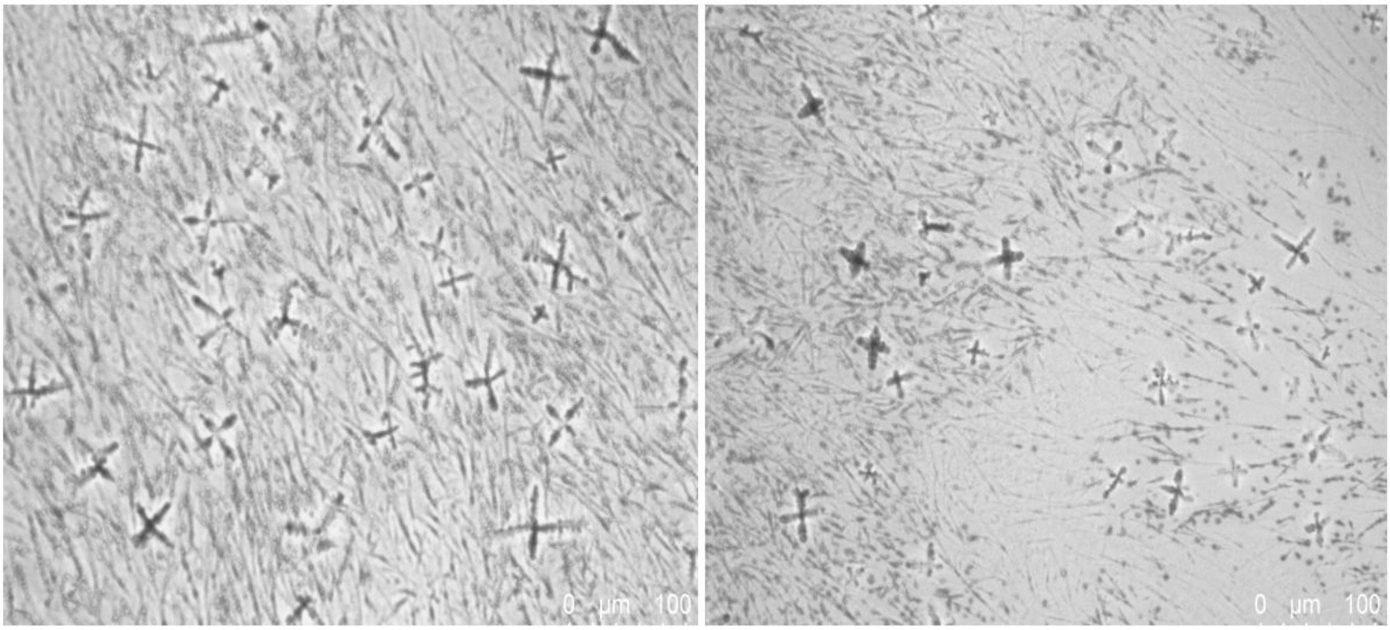
SEM CROSS-SECTION SAMPLES: 4% PDADMAC / NABH4 +PT



SEM CROSS-SECTION SAMPLES: 6% PDADMAC / NABH4 +PT



SEM CROSS-SECTION SAMPLES: 10% PDADMAC / NABH4 +PT



SEM Analysis

Sample: 2% PDADMAC

- Observation: Sparse and well-dispersed TiO_2 particles with minimal aggregation.
- Film structure: Appears smooth and homogeneous; few defects or voids observed.
- Interpretation: At low polymer concentration, the dispersion of nanoparticles is optimal. However, the particle density may be insufficient to provide maximum reflectance.

Sample: 4% PDADMAC

- Observation: Increased particle density while maintaining good dispersion. Slightly more aggregation than 2%, but still within uniform distribution.
- Film structure: Smooth and continuous film, indicating good adhesion and stability.
- Interpretation: This concentration offers a balance between particle loading and film

uniformity, potentially ideal for maximizing reflectivity without structural compromise.

Sample: 6% PDADMAC

- Observation: Further increase in particle population, but noticeable clustering begins. Some alignment or streak-like features start to appear in the matrix.
- Film structure: Slight roughness or heterogeneity is emerging.
- Interpretation: The film begins to lose uniformity due to polymer crowding or incomplete dispersion of TiO_2. May affect optical clarity and mechanical strength.

Sample: 10% PDADMAC

- Observation: Clear signs of severe aggregation, including large "cross-like" or fibrous structures. The background appears textured and disordered.
- Film structure: Highly heterogeneous; clusters and streaks dominate.
- Interpretation: Excess polymer concentration causes poor dispersion, leading to phase separation or agglomeration. This severely impacts reflectance uniformity and may reduce coating performance and mechanical integrity.

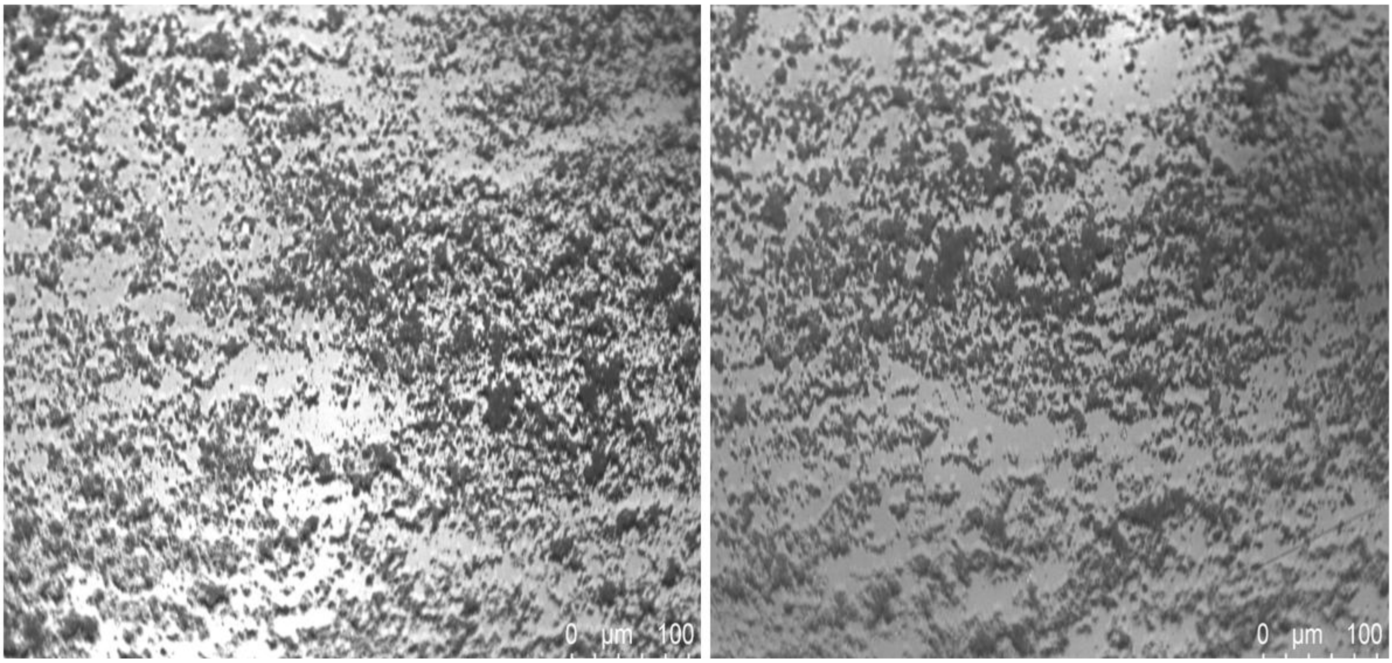
Summary of Trends:

PDADMAC (%)	Particle Distribution	Film Smoothness	Aggregation	Optical Potential
2%	Sparse, well-dispersed	Very smooth	Low	Low–Moderate
4%	Dense, well-distributed	Smooth	Low–Moderate	Optimal
6%	Moderate clustering	Slightly rough	Moderate	Moderate
10%	Severe aggregation	Very rough	High	Poor

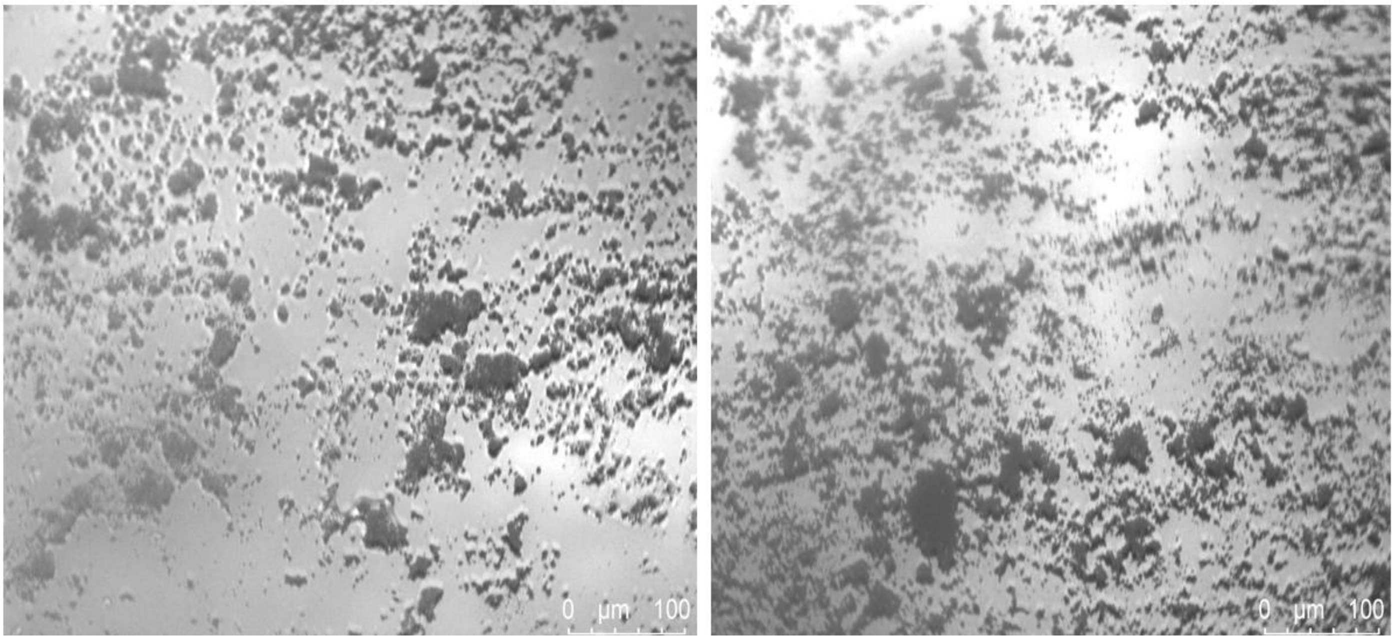
Conclusion:

An optimal PDADMAC concentration for this system appears to lie between 2% and 4%, with 4% showing the best balance of Ti dispersion, film continuity, and structural uniformity. Beyond 6%, adverse effects like aggregation and rough morphology compromise the performance and aesthetics of the reflective coating.

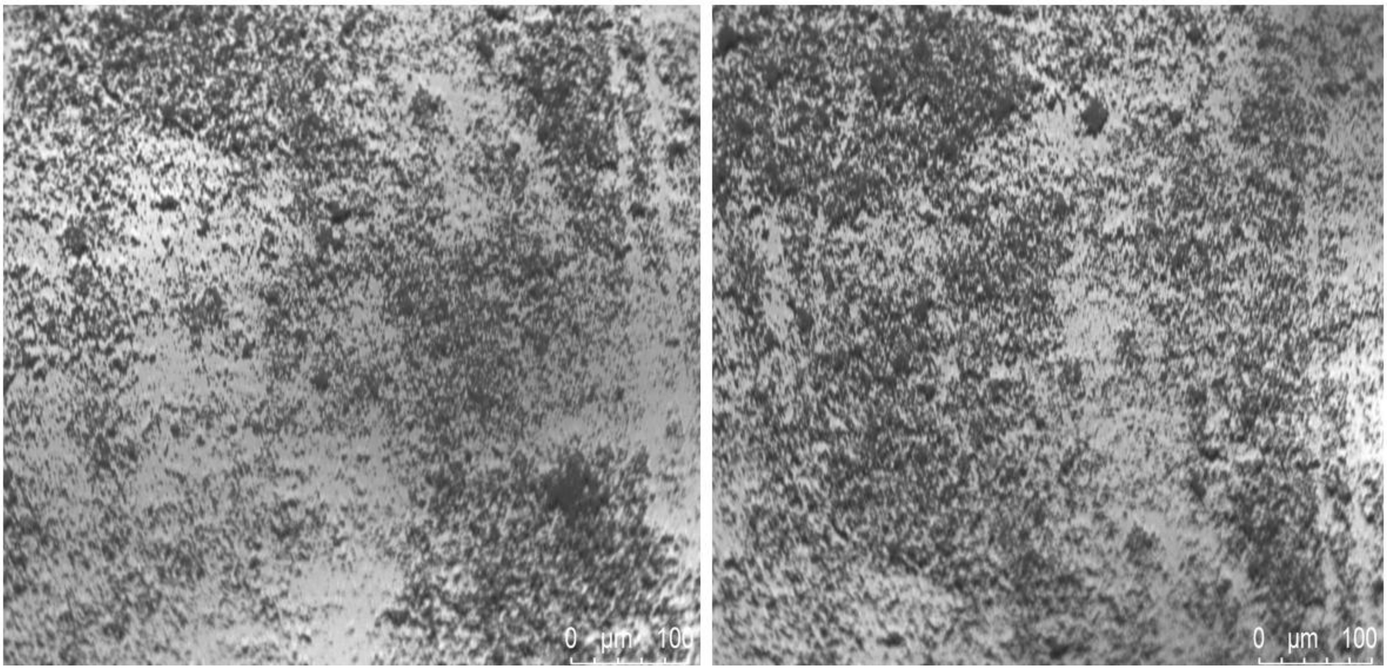
SEM CROSS-SECTION SAMPLES: PVP + 5% TIO2



SEM CROSS-SECTION SAMPLES: PVP + 3% TIO2



SEM CROSS-SECTION SAMPLES: PVP + 7.5% TIO2



SEM Analysis (PVP-based Films)

Sample: PVP + 3% TiO_2

- Observation: Presence of large, irregular agglomerates of TiO_2 particles. Uneven dispersion with clearly visible clumps.
- Film structure: Discontinuous matrix, with several voids and high surface roughness.
- Interpretation: At low TiO_2 concentration, the particles are not well distributed. Instead of uniform dispersion, they form large aggregates—likely due to weak interaction with the polymer matrix at this ratio.

Sample: PVP + 5% TiO_2

- Observation: Improved particle density and slightly better dispersion compared to 3%, but significant clustering remains.
- Film structure: Less porous than the 3% sample but still contains patchy areas with high particle load and voids.
- Interpretation: The increased TiO_2 improves reflectivity potential but also raises the risk of non-uniform film formation due to aggregation. The film remains suboptimal for consistent optical performance.

Sample: PVP + 7.5% TiO_2

- Observation: Densely packed TiO_2 particles with moderate improvement in distribution. However, clustering is still apparent, though finer.
- Film structure: More continuous compared to 3% and 5%, but with some rough texture and heterogeneous zones.
- Interpretation: At this concentration, PVP begins to better encapsulate and stabilize TiO_2 particles, but full uniformity is not achieved. The structure suggests nearing an optimal loading before oversaturation.

Summary of Trends:

TiO_2 (%) in PVP	Particle Distribution	Film Uniformity	Aggregation	Coating Quality
3%	Poor, large clusters	Discontinuous	High	Low
5%	Moderate, some clustering	Partially continuous	Moderate	Moderate
7.5%	Improved, finer clusters	Nearly continuous	Moderate–Low	Better (near-optimal)

Conclusion:

- 3% TiO_2 in PVP is insufficient for effective dispersion and forms non-uniform films.
- 5% TiO_2 shows progress in density but still struggles with clustering.
- 7.5% TiO_2 provides a relatively better balance of dispersion and coverage but may still need further optimization or surfactant/stabilizer support for high-performance reflective coatings.

2.4 Results and Discussion:

TiO_2 Concentration (wt%)	Approx. Film Thickness (nm)
3%	20–35 nm
5%	30–45 nm
7.5%	35–60 nm

Key Observations:

1. **Thickness Increase with TiO_2 Content:**
   - As the weight percentage of TiO_2 increases from 3% to 7.5%, the film becomes significantly thicker.
   - This is expected because more solid content (TiO_2 particles) increases the volume of material deposited during dip coating.
2. **Broader Thickness Range at Higher TiO_2 Concentrations:**
   - The 7.5% TiO_2 film shows a wider range (35–60 nm), indicating less uniformity in thickness compared to the lower concentrations.
   - This may be attributed to particle aggregation at higher loadings, which can lead to microscale surface roughness and uneven distribution.
3. **Implications on Optical and Mechanical Properties:**
   - Reflectivity and emissivity could improve with thickness up to an optimal level, beyond which scattering from agglomerates may reduce uniformity.
   - Thicker coatings may provide better UV shielding but can also increase brittleness or reduce flexibility.
4. **Relation to SEM Observations:**
   - The increasing thickness trend aligns with the SEM cross-sections: denser films are visually evident in the 7.5% sample.
   - However, surface quality deteriorates slightly due to clustering, as seen in the 5% and 7.5% SEM images.

Conclusion:

- Increasing TiO_2 concentration in PVP increases the film thickness.
- The optimum TiO_2 content must balance between thickness for high reflectivity and surface uniformity for consistent optical and structural performance.
- 5%–7.5% TiO_2 appears promising, but further refinement (e.g., use of dispersants, sonication, or surface modifiers) may be required to achieve ideal coatings.

Effect on Conductivity:

Table and Plot for PDADMAC with NaBH4 + Pt

S.No.	Conc. Of PDADMAC	Voltage (V)	Current (A)	Resistivity (Ω·m)	Conductivity (S/m)
1	2%	10	1.5E-10	302200	0.00000331
2	4%	10	1.795E-10	252500	0.00000396
3	6%	10	2.079E-10	218000	0.00000458
4	10%	10	2.475E-09	18310	0.0000546

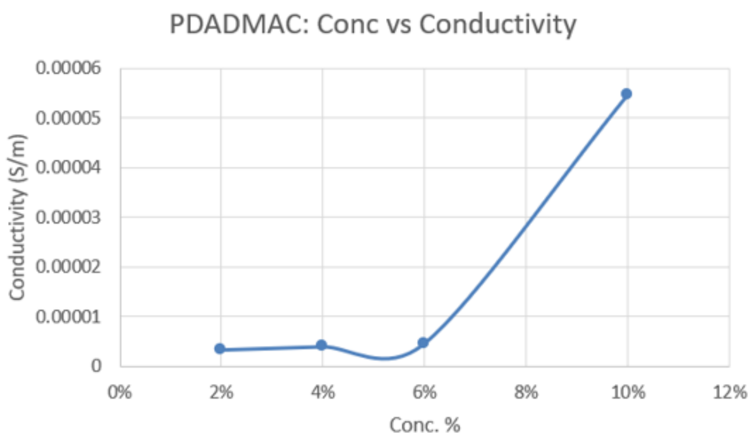
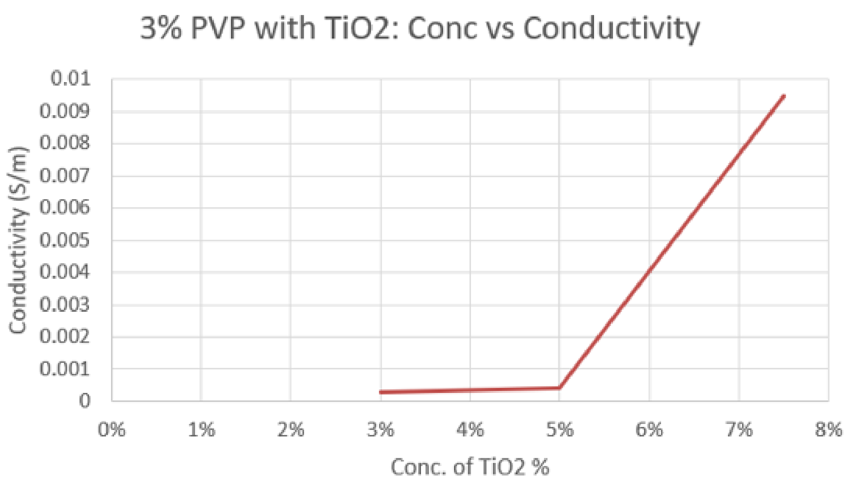


Table and Plot for PVP (3%) with TiO2 (7.5%)

S.No.	Conc. Of TiO2+PVP	Voltage (V)	Current (A)	Resistivity (Ω·m)	Conductivity (S/m)
1	3%	10	1.23E-08	3685	0.000271
2	5%	10	1.91E-08	2370	0.000422
3	7.50%	10	4.3E-07	105.4	0.00949



Material System	**Conductivity Trend**	**Key Observation**	**Interpretation**
PDADMAC + $NaBH_4$ + Pt	Gradual ↑ to Sharp ↑ at 10%	10% PDADMAC shows a big jump	Improved particle network formation; percolation likely at higher concentration
PVP + TiO_2	Small ↑ to Sharp ↑ at 7.5%	7.5% TiO_2 gives ~20x jump in σ	Strong dispersion and possible network formation; semiconductor effect visible

4. CONCLUSIONS:

4.1. Effect of TiO_2 Concentration on Film Morphology (SEM Analysis)

- As TiO_2 concentration increased from 3% to 7.5%, the SEM cross-sectional images showed:
  - A denser and more uniformly packed microstructure.
  - Reduced voids and improved dispersion of TiO_2 particles within the PVP matrix.
  - Indication of better particle–polymer interaction and film integrity at higher TiO_2 loading.

4.2. Film Thickness vs TiO_2 Content

- Film thickness increased with TiO_2 concentration:
  - 3% TiO_2: 20–35 nm
  - 5% TiO_2: 30–45 nm
  - 7.5% TiO_2: 35–60 nm
- This suggests higher TiO_2 loading contributes to thicker coatings, likely due to higher solid content and greater particle accumulation during film formation.

4.3. Conductivity Enhancement with Particle Loading

- A significant increase in electrical conductivity was observed with increasing TiO_2:
  - From 0.000271 S/m at 3% to 0.00949 S/m at 7.5% — nearly 35-fold improvement.
  - Indicates a percolation threshold was reached at or near 7.5%, where conductive pathways form throughout the film.
- Similarly, for PDADMAC with $NaBH_4$ + Pt:
  - A sudden rise at 10% PDADMAC suggested the onset of metallic nanoparticle network formation improving conductivity.

4.4. Optimal Composition

- 7.5% TiO_2 in PVP offers a balance of:
  - Good film morphology,
  - Higher thickness,
  - Substantial conductivity improvement,
  - Making it a suitable candidate for reflective/emissive coatings or flexible electronics applications.

Overall Conclusion

Our project successfully demonstrates that increasing TiO_2 concentration in a PVP matrix significantly enhances the electrical and structural properties of thin films. Additionally, PDADMAC-assisted Pt nanoparticle systems show promise in improving conductivity, pointing toward potential in energy or sensor applications.

5.FUTURE WORKS:

5.1 Optimization of Particle Dispersion

- Investigate the use of surfactants or sonication to improve the dispersion of TiO_2 particles in the polymer matrix and minimize agglomeration, especially at higher loadings.

5.2 Reflectance and Emittance Testing

- Perform spectroscopic analysis (UV-Vis-NIR, FTIR) to measure solar reflectance and thermal emittance, particularly important for assessing the coatings' performance in thermal regulation and reflective surface applications.

5.3 Mechanical Property Evaluation

- Test film adhesion, hardness, and flexibility using nanoindentation or scratch testing to ensure practical durability and applicability on various substrates.

5.4 Thermal and Environmental Stability

- Evaluate the thermal stability and aging resistance of the films under humidity, UV exposure, and high temperature to assess long-term usability in outdoor environments.

5.5 Exploration of Alternative Nanoparticles

- Study other reflective/emissive or conductive particles (e.g., ZnO, SiO_2, Al_2O_3, AgNPs) to compare performance and cost-effectiveness relative to TiO_2 and Pt.

5.6 Scale-Up and Application Prototyping

- Develop coating prototypes for real-world surfaces like metals, glass, or flexible polymers using scalable techniques like spray coating or roll-to-roll printing.

5.7 Multifunctionality Studies

- Explore additional functional properties such as antibacterial activity, UV shielding, or self-cleaning behavior of TiO_2-based coatings for advanced applications.

6.PROBLEMS FACED:

1. **Non-uniform Film Formation**
   - Achieving uniform coatings during dip-coating was difficult due to inconsistent withdrawal speed and surface tension effects, leading to variation in thickness.
2. **Particle Agglomeration**
   - At higher TiO_2 concentrations (especially 7.5%), visible agglomeration occurred, affecting homogeneity and possibly skewing SEM and conductivity results.
3. **Limited Conductivity at Low Loadings**
   - For lower TiO_2 concentrations (3%), the conductivity was too low, making measurements sensitive to small errors in voltage/current readings.
4. **Thickness Measurement Accuracy**
   - Estimating film thickness from SEM cross-section images was approximate, and lack of advanced equipment (e.g., ellipsometry or profilometry) limited precision.
5. **Material Handling**
   - Proper dispersion of TiO_2 in PVP matrix required vigorous mixing; manual stirring was insufficient at times, resulting in sedimentation.
6. **SEM Imaging Challenges**
   - SEM imaging required extensive sample preparation, and charging effects were occasionally observed due to polymer-based substrates.

7. **Repeatability**
    - Reproducing identical samples under the same conditions was difficult due to environmental factors like temperature and humidity, affecting drying and film morphology**.**
8. **Limited Access to Advanced Characterization Tools**
    - Lack of tools such as FTIR, UV-Vis-NIR, and XRD restricted full material characterization, limiting deeper analysis of optical or structural properties.

7. REFERENCES:

Article 1 Reference: https://www.researchgate.net/publication/308389798_Dip-coating_for_fibrous_materials_mechanism_methods_and_applications (Dip Coating)

Article 2 Reference: https://pmc.ncbi.nlm.nih.gov/articles/PMC11656601/ (Use of TiO2)

Article 3 Reference:
https://www.sciencedirect.com/science/article/abs/pii/S0927775720301606#:~:text=Aggregation%20of%20the%20Cu%20NPs,surface%20energy%20such%20as%20polytetrafluoroethylene. (**PVP as an adhesive**)

Article 4 Reference: https://intapi.sciendo.com/pdf/10.2478/v10026-010-0016-z