

**INVESTIGATION OF SIZE AND SHAPE EFFECTS OF ZINC OXIDE
PARTICLES ON OPTICAL PROPERTIES**

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Master's Thesis

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FINAL APPROVAL FOR THESIS

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ABSTRACT

INVESTIGATION OF SIZE AND SHAPE EFFECTS OF ZINC OXIDE PARTICLES ON OPTICAL PROPERTIES

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Materials such as ZnO (macro to nanoparticles) are valuable in a broad range of scientific domains. ZnO has gained appeal in cosmetics due to its low toxicity, higher biodegradability, superior antibacterial property, and excellent UV blocking capability in sunscreens. The use of ZnO particles, leveraging its optical property in sunscreens for skin protection against harmful UV radiation, has advanced technologically. The amount of radiation blocked by ZnO is dependent on scattering and absorption, and it has been shown in the literature that size and shape have a significant impact on the optical properties of micro and nanoparticles. The scientific objective of this thesis was to investigate the scattering and absorption of ZnO micro, and nanoparticles based on their shapes and sizes. A UV-VIS-NIR spectrophotometer was used to examine the optical characteristics of five ZnO solid powders with different particle sizes and shapes. The technological objective of this thesis was to contribute to the optimization of sunscreen products in terms of ZnO particle size ranges and shapes. As a result, sunscreens were formulated using the five ZnO samples. The solid ZnO powders results demonstrated that size and shape have a strong impact on optical characteristics of the powders. Compared to the other powders used, the MicNo-ZnO solid powder sample with a thickness of 0.0769 mm had the highest UV absorbance and transparency in the visible region, with absorption and extinction coefficients of 1015 cm^{-1} and 0.00207, respectively. Some of the outstanding optical characteristics seen in the solid ZnO powders were hidden in the formulation system used. Higher SPF values of 68.22 and 73.22 were nevertheless observed for reduced size MicNo-ZnO and 30-50nm spherical ZnO, respectively.

Keywords: Zinc oxide, Inorganic UV filter, Optical property, Sunscreen formulation.

ÖZET

ÇINKO OKSİT PARTİKÜLLERİN BOYUT VE ŞEKLİNİN OPTİK ÖZELLİKLERE ETKİLERİNİN İNCELENMESİ

Adekunle Olatunde ADESANYA

Malzeme Bilimi ve Mühendisliği Anabilim Dalı

Malzeme Bilimi ve Mühendisliği Bilim Dalı

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ZnO partiküller gibi malzemeler çok çeşitli bilimsel alanlarda değerlidir. ZnO, düşük toksisitesi, daha yüksek biyolojik olarak parçalanabilirliği, üstün antibakteriyel özelliği ve güneşten koruyucularda mükemmel UV engelleme özelliği nedeniyle kozmetikte çekicilik kazanmıştır. Zararlı UV radyasyonuna karşı cilt koruması için güneş kremlerinde optik özelliğinden yararlanan ZnO parçacıklarının kullanımı teknolojik olarak ilerlemiştir. ZnO tarafından bloke edilen radyasyon miktarı saçılma ve absorpsiyona bağlıdır ve boyut ve şeklin mikro ve nanopartiküllerin optik özellikleri üzerinde önemli bir etkiye sahip olduğu literatürde gösterilmiştir. Bu tezin bilimsel amacı ZnO mikro ve nanoparçacıklarının saçılma ve absorpsiyonunu şekil ve boyutlarına göre araştırmaktır. Farklı parçacık boyutlarına ve şekillerine sahip beş ZnO katı tozunun optik özelliklerini incelemek için bir UV-VIS-NIR spektrofotometresi kullanılmıştır. Bu tezin teknolojik amacı güneşten koruyucu ürünlerin ZnO partikül boyutu aralıkları ve şekilleri açısından optimizasyonuna katkıda bulunmaktır. Sonuç olarak; güneşten koruyucular beş ZnO numunesi kullanılarak formüle edildi. Katı ZnO tozları sonuçları, boyut ve şeklin tozların optik özellikleri üzerinde güçlü bir etkisi olduğunu göstermiştir. Kullanılan diğer tozlarla karşılaştırıldığında, 0.0769 mm kalınlığa sahip MicNo-ZnO katı toz numunesi, sırasıyla 1015 cm^{-1} ve 0.00207 absorpsiyon ve sönme katsayıları ile görünür bölgede en yüksek UV absorbansına ve şeffaflığına sahiptir. Katı ZnO tozlarında görülen olağanüstü optik özelliklerden bazıları kullanılan formülasyon sisteminde gizlenmiştir. Yine de sırasıyla küçültülmüş boyutlu MicNo-ZnO ve 30-50nm küresel ZnO için 68.22 ve 73.22'lik daha yüksek SPF değerleri gözlenmiştir.

Anahtar Sözcükler: Çinko oksit, İnorganik UV filtresi, Optik özellik, Güneş kremi.

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Adekunle Olatunde ADESANYA

STATEMENT OF COMPLIANCE WITH ETHICAL PRINCIPLES AND RULES

I hereby truthfully declare that this thesis is an original work prepared by me; that I have behaved in accordance with the scientific ethical principles and rules throughout the stages of preparation, data collection, analysis and presentation of my work; that I have cited the sources of all the data and information that could be obtained within the scope of this study, and included these sources in the references section; and that this study has been scanned for plagiarism with “scientific plagiarism detection program” used by Eskişehir Technical University, and that “it does not have any plagiarism” whatsoever. I also declare that, if a case contrary to my declaration is detected in my work at any time, I hereby express my consent to all the ethical and legal consequences that are involved.

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CONTENTS

	<u>Page</u>
HEADER PAGE	i
FINAL APPROVAL FOR THESIS	ii
SUPERVISOR APPROVAL	iii
ABSTRACT.....	iv
ÖZET	v
ACKNOWLEDGEMENTS	vi
STATEMENT OF COMPLIANCE WITH ETHICAL PRINCIPLES AND RULES	vii
CONTENTS	viii
LIST OF TABLES	xiii
LIST OF FIGURES	xv
GLOSSARY OF SYMBOLS AND ABBREVIATIONS	xxii
1. INTRODUCTION	1
2. OVERVIEW AND LITERATURE REVIEW	4
2.1. Sun Protection	4
2.1.1. Sun radiation and its damaging effects	4
2.1.2. The ozone layer	5
2.1.3. Relationship between sun exposure and skin cancer	7
2.1.4. Damaging effects of UV-rays on the human skin	7
2.2. Sunscreens.....	9
2.2.1. The history of sunscreen development and usage	10
2.2.2. General features of a good sunscreen	14
2.2.3. Organic (chemical) sunscreens.....	15
2.2.3.1. Mechanism of absorption of organic UV filters.....	17
2.2.3.2. Disadvantages of organic UV filters	21
2.2.4. Inorganic (mineral) sunscreens	24
2.3. Zinc Oxide (ZnO)	24

2.3.1. Crystal structure of zinc oxide (ZnO).....	25
2.4. Optical Properties of Particle Materials	27
2.4.1. Light-material interaction processes	27
2.4.2. Light-ZnO powder interaction.....	30
2.4.2.1. <i>Scattering</i>	30
2.4.2.2. <i>Absorption</i>	32
2.5. UV Filters Available in the Market	34
2.5.1. Micron-sized ZnO.....	34
2.5.1.1. <i>Mechanism of scattering of visible light by micron-sized ZnO</i>	35
2.5.2. Nano-sized ZnO	36
2.5.3. MicNo-ZnO® particle	37
2.6. Previous Studies and Research Objectives	40
3. SUNSCREEN FORMULATION	42
3.1. Sunscreens Available in the Market.....	42
3.1.1 Emulsions	42
3.1.2. Sticks.....	44
3.1.3. Mousses.....	44
3.1.4. Aerosols	45
3.1.5. Ointments	45
3.1.6. Oils	45
3.1.7. Gels	45
3.1.7.1. <i>Aqueous gel</i>	46
3.1.7.2. <i>Microemulsion gel</i>	46
3.1.7.3. <i>Oleaginous gel</i>	47
3.1.7.4. <i>Hydro-alcoholic gel</i>	47
3.1.8. Wipes	47
3.2. Sunscreen Compositional Ingredients.....	47
3.2.1. UV filters	48
3.2.2. Emollients.....	48
3.2.3. Emulsifier system	49
3.2.4. Rheology modifiers.....	49
3.2.5. Boosting ingredients	50

3.2.6. Sensory enhancers	50
3.3. Formulating Sunscreens with ZnO	50
3.3.1 Factors affecting film-forming	52
3.3.1.1 Rheological behaviour.....	52
3.3.1.2. De-emulsification.....	53
3.3.2. Basic criteria for obtaining optimum performance	53
3.3.3. Formulation basic principles.....	54
3.3.3.1. Formulating sunscreen with ZnO dispersed in the water phase	57
3.3.3.2. Formulating sunscreen with ZnO in the oil phase.....	59
3.3.4. Techniques for optimizing the performance of zinc oxide (ZnO) in sunscreen formulations.....	59
3.3.4.1. Dispersion	59
3.3.4.2. Dispersion of ZnO in oil phase	60
3.3.4.3. Dispersion of ZnO in water phase.....	60
3.3.4.4. Selection of emollient	60
3.3.4.5. Choice of rheology modifier.....	61
3.3.4.6. Emulsion type and choice of emulsifier.....	61
3.4. Sunscreen Testing	62
3.4.1. Important terminologies	62
3.4.1.1. Sun protection factor (SPF)	62
3.4.1.2. Broad spectrum protection	64
3.4.1.3. Critical wavelength	64
3.4.2. Method of testing sunscreen	64
3.4.2.1. In vivo methods of testing sunscreen (ISO 24442: 2011)	65
3.4.2.2. In vitro methods of testing sunscreen (ISO 24443: 2012).....	65
3.4.2.3. In silico methods of testing sunscreen	66
4. MATERIALS AND METHOD	67
4.1. Experimental Design and the ZnO Powder Procurement	68
4.1.1. Procurement of the ZnO powder	68
4.1.2 Size reduction of the original MicNo-ZnO powder	69
4.1.3. ZnO powder utilized for the study.....	70
4.2. Characterization of the ZnO Powder Samples.....	70

4.2.1. Morphology of powder samples	71
4.2.1.1. Scanning electron microscopy (SEM)	71
4.2.1.2. Particle size analysis	71
4.2.2. X-ray diffraction analysis (XRD)	72
4.2.3. Thermogravimetric Analysis (TGA)	72
4.2.4. Fourier transform infrared spectroscopy (FTIR)	72
4.3. Optical Properties Measurements of ZnO Solid Samples	72
4.3.1. Designed method to measure absorbance and transmittance of ZnO solid powder	73
4.3.1.1. Optical microscopy analysis of ZnO decorated PMMA plates.....	75
4.3.1.2. Absorbance and transmittance measurements of ZnO solid powder samples	75
4.3.1.3. Measurement of sample thickness for extinction coefficient determination	78
4.3.1.4. ZnO samples weighing after absorbance and transmittance measurements	79
4.3.2. Concept of reflectance measurement of solid samples.....	79
4.3.2.1. Reflectance measurement of ZnO solid samples	79
4.3.2.2. Relative diffuse reflectance of ZnO solid samples.....	81
4.3.2.3. Relative total reflectance of ZnO samples	82
4.4. Sunscreen Formulations	83
4.4.1. Formulation procedures	84
4.4.2. SPF and optical measurements of formulated sunscreens	87
4.4.2.1. Measuring procedure.....	87
5. RESULTS AND DISCUSSIONS	89
5.1. Powder Particles Characterization Results	89
5.1.1. X-ray powder diffraction analysis results	89
5.1.2. SEM and EDX results	96
5.1.3. Particle size results	100
5.1.4. Thermogravimetric analysis result of 30-50 nm spherical ZnO (TGA-DTA)	102

5.1.5 Fourier transform infrared spectroscopy result of 30-50 nm spherical ZnO	103
5.2 Optical Properties Measurement Results of ZnO Solid Samples	104
5.2.1 Optical microscopy images of ZnO PMMA plates.....	104
5.2.2. ZnO PMMA plates weighing results	106
5.2.3 Absorbance measurement results	107
5.2.3.1 Absorbance results for the first set of data obtained.....	107
5.2.3.2 Absorbance results for the second set obtained.....	108
5.2.3.3 Comparison of the first and second set of absorbance data.....	108
5.2.3.4. Extinction coefficient determination from absorbance data	109
5.2.4 Transmittance results.....	115
5.2.4.1. Transmittance results obtained for the first data set.....	116
5.2.4.1. Transmittance results obtained for the second data set	116
5.2.4.3. Comparison of the first and the second set of transmittance data.....	116
5.2.5. Reflectance measurement results.....	119
5.2.5.1. Relative diffuse reflectance measurement results	119
5.2.5.2. Relative total reflectance measurement results	122
5.2.5.3 Comparison of relative diffuse and relative total reflectance results	123
5.3. Results of Formulated Sunscreens.....	125
5.3.1 SPF and optical measurement results of formulated sunscreens.....	125
6. CONCLUSIONS AND RECOMMENDATIONS.....	128
REFERENCES.....	129
APPENDIX	
CURRICULUM VITAE	

LIST OF TABLES

	<u>Page</u>
Table 2.1. Six locations that have enacted regulations prohibiting the use of organic UV filters	14
Table 2.2. FDA's UV filters and their concentrations	17
Table 2.3. Limiting scenarios of Lorenz-Mie Theory	30
Table 2.4. MicNo-ZnO [®] characteristics	39
Table 3.1. UVB penetration reduction in percentage based on sunscreen SPF value	63
Table 4.1. ZnO powders obtained	67
Table 4.2. Other reagents utilized	67
Table 4.3. Other materials utilized	67
Table 4.4. ZnO powders utilized	70
Table 4.5. List of instruments utilized	70
Table 4.6. UV-VIS-NIR Shimadzu device configuration for absorbance/transmittance measurements	76
Table 4.7. Sunscreen formulation constituents	84
Table 5.1. Experimentally observed XRD data of MicNo-ZnO data	93
Table 5.2. Experimentally observed XRD data of reduced size MicNo-ZnO data.....	93
Table 5.3. Experimentally observed XRD data of nano ZnO data	94
Table 5.4. Experimentally observed XRD data of submicron ZnO data	94
Table 5.5. Experimentally observed XRD data of 30-50 nm spherical ZnO data	95
Table 5.6. Crystallite size calculated using Scherer's equation	96
Table 5.7. Elemental composition of 30-50 nm spherical ZnO	100
Table 5.8. D(0.1), d(0.5) and d(0.9) values obtained from the Mastersizer particle size analyzer	101
Table 5.9. Average particle size of nano powders obtained from Zetasizer particle size analyzer	102
Table 5.10 Total Mass of ZnO PMMA samples prepared for absorbance and transmittance measurements	106
Table 5.11. Mass of ZnO PMMA samples after absorbance and transmittance measurements.....	106

Table 5.12. Mass of ZnO powder remaining after absorbance and transmittance measurements.....	107
Table 5.13. Average thickness of two PMMA plates without ZnO powder.....	110
Table 5.14. Estimated average thickness of ZnO powder samples.....	110
Table 5.15. SPF and optical properties measurement results.....	126
Table 5.16. Repeated SPF and optical properties measurement results of initial formulated sunscreens.....	126



LIST OF FIGURES

	<u>Page</u>
Figure 2.1. Electromagnetic spectrum	5
Figure 2.2. Sun's radiations that reach the surface of the earth	6
Figure 2.3. Ozone depletion reactions	6
Figure 2.4. (a) Human skin with soft tissues (b) layers of epidermis	8
Figure 2.5. UV-Rays wavelength-dependent penetration into the skin	9
Figure 2.6. Classification of Sunscreens	16
Figure 2.7. Absorption mechanism of organic UV filters	18
Figure 2.8. Molecule absorption of organic UV-filters	19
Figure 2.9. Absorption band of an organic UV filter	19
Figure 2.10. Absorption range of organic UV filters	20
Figure 2.11. A Jablonski diagram simplified to depict the energies associated with ground state and	21
Figure 2.12. Impacts of organic UV filters on health and environment	23
Figure 2.13. ZnO crystal structures (a) wurtzite hexagonal (b) cubic zinc blend structures	25
Figure 2.14. Rocksalt ZnO crystal structure	26
Figure 2.15. Wurtzite hexagonal structure	27
Figure 2.16. Reflected, propagated, and transmitted light through a medium	28
Figure 2.17. Optical processes that can occur as light propagates across an optical medium	28
Figure 2.18. Rayleigh and Mie scattering patterns	31
Figure 2.19. Comparison of the scattering efficiencies of ZnO and TiO ₂	32
Figure 2.20. ZnO and TiO ₂ band gap energy representation	33
Figure 2.21. Particle size dependent UV characteristics of TiO ₂	34
Figure 2.22. Multiple scattering of micron-sized ZnO particles	35
Figure 2.23. Back scattered light rays appearing white in the eyes	36
Figure 2.24. Scattering of convectional micron-sized ZnO	36
Figure 2.25. MicNo-ZnO [®] hexagonal platelet with spherical fine primary particles	37
Figure 2.26. Morphology and particle size distribution	38
Figure 2.27. Correlation of MicNo-ZnO [®] amount in formulations and SPF	39

Figure 2.28. Excellent broad-spectrum protection of MicNo-ZnO®	39
Figure 2.29. Particle geometries studied by Penttilä and Lumme	41
Figure 3.1. General cosmetic dosage forms	43
Figure 3.2. Oil-in-water emulsion.....	44
Figure 3.3. Sunscreen ingredients and their functions	48
Figure 3.4. Homogeneous distribution of sunscreen on skin surface under ideal situation.....	51
Figure 3.5. Non-uniform sunscreen coverage on the skin's surface	51
Figure 3.6. The pH effect on the overall charge on the surface of particles	56
Figure 3.7. Evaporation of the water phase in water dispersed ZnO emulsion	58
Figure 3.8. Discontinuous coverage resulting water phase evaporation.....	58
Figure 3.9. Better skin coverage achieved through the incorporation of liquid crystalline structure	59
Figure 3.10. Filtered and transmitted UV rays based on SPF value	64
Figure 4.1. Chemical formula of paracetamol	68
Figure 4.2. Schematic diagram of the particle size reduction experiment.....	69
Figure 4.3. The absorbance and transmittance sample preparation process	73
Figure 4.4. Prepared absorbance and transmittance reference samples	74
Figure 4.5. Prepared absorbance and transmittance ZnO samples	74
Figure 4.6. Separated ZnO-decorated PMMA plates.....	75
Figure 4.7. MPC-603A integrated sphere compartment interior	76
Figure 4.8. Positioning the PMMA plates for baseline correction and absorbance/transmittance	77
Figure 4.9. Absorbance/transmittance measurements: (a) Sample position (b) points on the PMMA plate	78
Figure 4.10. (a) Thickness measurement using Mitutoyo micrometer (b) points on the PMMA plates	78
Figure 4.11. Types of light reflected from solid sample.....	79
Figure 4.12. Integrating sphere powdered sample holder	80
Figure 4.13. Sample holders filled with ZnO samples.....	80
Figure 4.14. Schematic diagram of reference and sample positions in the integrated sphere compartment	81

Figure 4.15. Experimental diagram showing the reference and sample positions in integrated sphere	82
Figure 4.16. Schematic diagram showing the reference and sample positions in integrated sphere	83
Figure 4.17. Experimental diagram showing the reference and sample positions in integrated sphere	83
Figure 4.18. Separately measured formulation phases	85
Figure 4.19. A and B phases placed in a digital water bath at 80°C	85
Figure 4.20. (a) A and C phases under mechanical stirrer (b) homogenization of phases A, C and B (c)	86
Figure 4.21. Formulated sunscreens from the five powder systems.....	88
Figure 4.22. Rubbing directions of formulated sunscreens on PMMA plates.....	88
Figure 5.1. X-ray diffraction patterns (a) Original MicNo-ZnO (b) reduced size MicNo-Zno (c) submicron ZnO (d) 25-35nm nano ZnO (e) 30-50nm spherical ZnO.....	92
Figure 5.2. X-ray diffraction pattern of the combined five powder systems.....	92
Figure 5.3. X-ray diffraction pattern of silicon powder.....	95
Figure 5.4. Plot of FWHM vs 2 θ for silicon powder	96
Figure 5.5. (a) Original MicNo-ZnO (b) reduced size MicNo-ZnO (c) submicron ZnO (d) 25-35nm nano ZnO (e) 30-50nm spherical ZnO	99
Figure 5.6. EDX Analysis result of the 30-50 nm spherical ZnO powder sample.	100
Figure 5.7. Particle size distributions (a) original MicNo-ZnO, (b) reduced size MicNo-ZnO, and (c) submicron ZnO	101
Figure 5.8. Nanoparticle size distributions of (a) 25-35 nm nano ZnO and (b) 30-50 nm spherical ZnO.....	102
Figure 5.9. TGA-DTA graphs of 30-50nm spherical ZnO	103
Figure 5.10. Analyzed FTIR transmittance spectrum of 30-50nm spherical ZnO	103
Figure 5.11. Optical microscopy images of MicNo- ZnO (a) PMMA 1 st face (b) PMMA 2 nd face	104
Figure 5.12. Optical microscopy images of reduced size MicNo-ZnO (a) PMMA 1 st face (b) PMMA 2 nd	104
Figure 5.13. Optical microscopy images of 25-35 nano ZnO (a) PMMA 1 st face (b) PMMA 2 nd face	105

Figure 5.14. Optical microscopy images of 30-50 nm spherical ZnO (a) PMMA 1 st face (b) PMMA 2 nd face	105
Figure 5.15. Optical microscopy images of submicron ZnO (a) PMMA 1 st face (b) PMMA 2 nd face	105
Figure 5.16. Mass of ZnO samples placed vs mass remaining after measurements....	107
Figure 5.17. Absorbance graph comparison (a) first data set 1 st face (b) second data set	108
Figure 5.18. Absorbance graph comparison (a) first data set 2 nd face (b) second data set	109
Figure 5.19. Absorbance graph comparison (a) first data set 1 st and 2 nd faces combined (b) second data	109
Figure 5.20. Cross section of the prepared samples during absorbance and transmittance measurements	110
Figure 5.21. Absorption coefficient (a) first data set 1 st face and second data set (b) 2 nd face and second.....	111
Figure 5.22. Extinction coefficient (a) first data set 1 st face and second data set (b) 2 nd face and second.....	112
Figure 5.23. Transmittance graphs of 1 st face of the first data set	116
Figure 5.24. Transmittance graphs of 2 nd face of the first data set	117
Figure 5.25. Transmittance graphs of combined 1 st and 2 nd faces of the first data set	117
Figure 5.26. Transmittance graphs of the second data set (taken from the two faces)	118
Figure 5.27. Relative diffuse reflectance graphs of the average values of each ZnO sample (first data)	120
Figure 5.28. Relative diffuse reflectance graphs of the average values of each ZnO sample (second data)	120
Figure 5.29. Relative diffuse reflectance comparison of 1 st and 2 nd measurements of each powder	121
Figure 5.30. Relative diffuse reflectance graphs of the average values of each sample (1 st and 2 nd data).....	122
Figure 5.31. Relative total reflectance graphs (average values) of the five powder systems.....	122

Figure 5.32. Graphs of relative total reflectance and the 1 st relative diffuse reflectance data	123
Figure 5.33. Graphs of relative total reflectance and the 2 nd relative diffuse reflectance data	124
Figure 5.34. Initial vs repeated SPF measurements	127
Figure 0.1. Optical microscopy images of MicNo-ZnO PMMA 1 st face	144
Figure 0.2. Optical microscopy images of MicNo-ZnO PMMA 2 nd face	145
Figure 0.3. Optical microscopy images of reduced size MicNo-ZnO PMMA 1 st face	145
Figure 0.4. Optical microscopy images of reduced size MicNo-ZnO PMMA 2 nd face	146
Figure 0.5. Optical microscopy images of 25-35 nano ZnO PMMA 1 st face	146
Figure 0.6. Optical microscopy images of 25-35 nano ZnO PMMA 2 nd face	147
Figure 0.7. Optical microscopy images of 30-50nm spherical ZnO PMMA 1 st face	148
Figure 0.8. Optical microscopy images of 30-50nm spherical ZnO PMMA 2 nd face	148
Figure 0.9. Optical microscopy images of submicron ZnO PMMA 1 st face	149
Figure 0.10. Optical microscopy images of submicron ZnO PMMA 2 nd face	149
Figure 0.11. Absorbance graphs of original MicNo- ZnO PMMA plate (1 st face)	150
Figure 0.12. Absorbance graphs of original MicNo- ZnO PMMA plate (2 nd face).....	150
Figure 0.13. Absorbance graphs of reduced size MicNo-ZnO PMMA plate (1 st face).....	150
Figure 0.14. Absorbance graphs of reduced size MicNo-ZnO PMMA plate (2 nd face).....	151
Figure 0.15. Absorbance graphs of 25-35 nm nano ZnO PMMA plate (1 st face)	151
Figure 0.16. Absorbance graphs of 25-35 nm nano ZnO PMMA plate (2 nd face)	151
Figure 0.17. Absorbance graphs of 30-50 nm spherical ZnO PMMA plate (1 st face).....	152
Figure 0.18. Absorbance graphs of 30-50nm spherical ZnO PMMA plate (2 nd face).....	152
Figure 0.19. Absorbance graphs of submicron ZnO PMMA plate (1 st face).....	152
Figure 0.20. Absorbance graphs of submicron ZnO PMMA plate (2 nd face).....	153

Figure 0.21. Absorbance graphs of original MicNo-ZnO PMMA plate (taken from the two faces)	154
Figure 0.22. Absorbance graphs of reduced size MicNo- ZnO PMMA plate (taken from the two faces)	154
Figure 0.23. Absorbance graphs of 25-35 nm nano ZnO PMMA plate (taken from the two faces)	154
Figure 0.24. Absorbance graphs of 30-50 nm spherical ZnO PMMA plate (taken from the two faces)	155
Figure 0.25. Absorbance graphs of submicron ZnO PMMA plate (taken from the two faces)	155
Figure 0.26. Transmittance graphs of original MicNo PMMA for first data set (a) 1 st face (b) 2 nd face	156
Figure 0.27. Transmittance graphs of reduced MicNo PMMA for first data set (a) 1 ^s face, (b) 2 nd face	157
Figure 0.28. Transmittance graphs of nano ZnO PMMA for first data set (a) 1 ^s face, (b) 2 nd face	157
Figure 0.29. Transmittance graphs of 30-50m spherical ZnO PMMA for first data set (a) 1 ^s face, ...	158
Figure 0.30. Transmittance graphs of submicron ZnO PMMA for first data set (a) 1 ^s face, (b) 2 nd face	159
Figure 0.31. Transmittance graphs of original MicNo- ZnO PMMA plate (taken from the two faces)	160
Figure 0.32. Transmittance graphs of reduced size MicNo- ZnO PMMA plate (taken from the two faces)	160
Figure 0.33. Transmittance graphs of nano ZnO PMMA plate (taken from the two faces)	160
Figure 0.34. Transmittance graphs of 30-50nm spherical ZnO PMMA plate (taken from the two faces)	161
Figure 0.35. Transmittance graphs of submicron ZnO PMMA plate (taken from the two faces)	161
Figure 0.36. Relative diffuse reflectance graphs of MicNo ZnO (first measurement)	162

Figure 0.37. Relative diffuse reflectance graphs of reduced size MicNo ZnO (first measurement)	162
Figure 0.38. Relative diffuse reflectance graphs of nano ZnO (first measurement)....	162
Figure 0.39. Relative diffuse reflectance graphs of 30-50 nm spherical ZnO (first measurement)	163
Figure 0.40. Relative diffuse reflectance graphs of submicron ZnO (first measurement)	163
Figure 0.41. Relative diffuse reflectance graphs of MicNo ZnO (second measurement)	164
Figure 0.42. Relative diffuse reflectance graphs of reduced size MicNo ZnO (second measurement)	164
Figure 0.43. Relative diffuse reflectance graphs of nano ZnO (second measurement)	164
Figure 0.44. Relative diffuse reflectance graphs of 30-50 nm spherical ZnO (second measurement)	165
Figure 0.45. Relative diffuse reflectance graphs of submicron ZnO (second measurement)	165
Figure 0.46. Relative total reflectance graphs of MicNo ZnO	166
Figure 0.47. Relative total reflectance graphs of reduced size MicNo ZnO.....	166
Figure 0.48. Relative total reflectance graphs of nano ZnO	166
Figure 0.49. Relative total reflectance graphs of 30-50 nm spherical ZnO	167
Figure 0.50. Relative total reflectance graphs of submicron ZnO	167

GLOSSARY OF SYMBOLS AND ABBREVIATIONS

PMMA	:	Polymethyl methacrylate
ISO	:	International Organization for Standardization
Abs.	:	Absorbance
COLLIPA	:	The European Cosmetic, Toiletry and Perfumery Association
% T	:	Percentage Transmittance
% R	:	Percentage Reflectance
COV	:	Coefficient of Variance
UV _A PF	:	UV _A Protection Factor
VIS	:	Visible light
NIR	:	Near infrared
OHI	:	Ocean Health Index

1. INTRODUCTION

There is an increasing concern over the issue of skin cancers and other skin diseases associated with the sun's harmful rays resulting from the depletion of the Ozone layer. The radiation from the sun covers a wide spectral range, consisting of ultraviolet (UV), visible, and infrared (IR) radiation. Ultraviolet (UV) is divided into UV_A, UV_B, and UV_C radiation. In terms of its skin penetration level and the amount of UV_A entering the earth, UV_A is considered to be the most dangerous of the UV rays reaching the earth [1]. Year round, UV_A rays maintain the same level of intensity throughout the daytime hours. This implies everyone is exposed to a high level of UV_A rays throughout their life ([http-1](#)).

According to World Health Organization (WHO) report in July 2002, 2-3 million non-melanoma skin cancers and at least 132,000 malignant melanomas occur across the globe each year ([http-2](#)). In terms of new cases of cancers in 2020, skin cancer (non-melanoma) was one of the most common cancers, accounting for 1.20 million new cases worldwide ([http-3](#)). In the United States of America, more patients are diagnosed with skin cancer than all other cancers combined each year, and in 2012, more than 5.4 million cases of non-melanoma skin cancer were diagnosed and given treatment in over 3.3 million people . Also, in the United States, 99,780 and 97,920 new cases of invasive and in situ melanoma are estimated to be diagnosed respectively for the year 2022 and would result in 7,650 deaths ([http-4](#)).

Australia has one of the highest rates of skin cancer in the globe. Approximately two in three Australians will have skin cancer at the age of 70 years ([http-5](#)). According to Cancer Council Australia, skin cancers account for about 80 percent of all newly diagnosed cancers in the country ([http-6](#)). Melanoma is the most common cancer diagnosed between the ages of 15-29 years, accounting for 75 percent of skin cancer related deaths in Australia ([http-7](#)). Melanoma of skin is one of the 35 common types of cancers in Turkey. According to GLOBOCAN 2020 report for Turkey, it accounts for 1,756 out of 233,834 totals of the different kinds of cancer cases with mortality of 888 out of 126,335 total deaths ([http-8](#)).

The vast majority of both non-melanoma and melanoma skin cancers are caused by exposure to the sun's UV rays. About 90 percent of non-melanoma skin cancers occur due to the exposure to UV radiation ([http-9](#)). In another study in the United Kingdom, 86 percent of melanoma skin cancer can be associated to the sun's ultraviolet radiation [2].

The treatment of skin cancer comes at an expensive rate. According to statistics from the Skin Cancer Foundation, the U.S annual cost of treating skin cancers is estimated at \$8.1 billion (about \$4.8 billion for non-melanoma and \$3.3 billion for melanoma skin cancer) ([http-10](#)).

Protecting ourselves from these harmful effects of the UV rays is very critical to our wellbeing in our contemporary environments. The United States Food and Drug Administration (US FDA) has recommended the use of sunscreen in addition to wearing of clothes, most especially when the sun is at its peak to minimize the effect of the dangerous ultraviolet rays from the sun. Regular daily use of sunscreen with Sun Protective Factor (SPF) value of 15 or higher reduces the risks of developing non-melanoma (Squamous Cell Carcinoma) and melanoma by about 40 and 50 percent respectively ([http-1](#)). As a result, wearing cosmetic products (primary and secondary sunscreens) with sun protection ingredients (active filters) on a daily basis is not only recommended but also obligatory for protecting ourselves against the sun's harmful rays.

The active filters in sunscreens (primary and secondary) are categorized into organic and inorganic filters based on their sun blocking mechanism. Organic filters have narrow wavelength range of UV absorption, and they exhibit molecular absorption ([http-10](#)). They are often combined to give broad spectrum protection (both UV_A and UV_B) in the UV region. Moreover, organic filters have low photostability under the sun and can trigger allergic reaction when applied on the skin [3]. These adverse effects are disadvantages of the organic filters. On the other hand, inorganic filters have wide wavelength range of UV absorption while eliminating the adverse effect of the organic filters.

As of the time of this thesis, the use of inorganic filters in sunscreens is limited by the regulatory authorities due to safety concerns. The U.S. FDA has only accepted two active inorganic filters; Zinc Oxide (ZnO) and Titanium dioxide (TiO₂); therefore, these two ingredients are now being widely utilized in commercial sunscreens. From the two active filters accepted, ZnO is the only active inorganic filter that can provide broad spectrum (i.e., both in UV_A and UV_B) although TiO₂ is great in achieving high SPF protection which is mainly involving protection in UV_B range. Extensive research has been conducted using zinc oxide of different sizes and shapes. The previous studies concluded that micron-sized zinc oxide exhibits a higher level of visible light scattering and reflection when utilized in sunscreens, leading to whitening effect when applied on

the skin. For this reason, consumers are not comfortable using such sunscreens. This concern has led to the development of nanosized zinc oxide UV filters. Although nanosized zinc oxide in sunscreens has good transparency due to its reduced particle size, which scatters and reflects less visible light, there have been some reports on its skin penetration potential, which can result in some adverse effects in the body [4]–[6]. However, it has to be emphasized that the level of penetration through the skin layers and its potential to wreak havoc on the body system is a matter of controversy in the literature.

Recent advancement in sunscreen technology has shown the use of a designed micron-sized and platelet-shaped zinc oxide with primary nanoparticles (MicNo) developed by Entekno Materials Inc. (Suvaci Research Group, Materials Science and Engineering Department, Eskisehir Technical University, Turkey). MicNo is known to combine the advantages of both the micron-sized and the nano-sized zinc oxide while eliminating their negative effects. It has been shown in the literature that the size and shape have a strong impact on nanoparticles optical and chemical properties. The optical properties (most especially, scattering and absorption) of ZnO particles play a vital role in its sun blocking ability. Formulating sunscreens with high efficacy for optimum sun protection comes with a lot of challenges such as determining the optimum particle size and shape of the particles, retaining the particle size both in formulations and in the final films when they are being applied on skin, to name but a few. For an optimum design of sunscreen, it is imperative to have a size range of the UV- blocking particles (d) to be compatible with the wavelength of the incident light (λ) [7]. The studies [7], [8] reveal that the scattering coefficient and scattering efficiency depends strongly on the size and shape of the nanoparticles used and experiences a decrease after reaching a maximum.

Accordingly, it is vital to investigate ZnO nanoparticles' scattering and absorption behaviors based on their shapes and sizes to assess their utility in sunscreen products in detail. Therefore, the scientific research objective of this study was to evaluate the optical properties of ZnO particles of different shapes and sizes (i.e., ZnO micro-particles (MicNo-ZnO) produced with size and morphology control and smaller-sized versions of MicNo-ZnO, as well as submicron sized ZnO, 25-35nm and 30-50 nm ZnO nanoparticles) using a UV/VIS/NIR spectrophotometer. Therefore, the technological objective of this study was to contribute to the optimization of sunscreen products in terms of ZnO particle size ranges and shapes by using the fundamental understanding to be generated in this study.

2. OVERVIEW AND LITERATURE REVIEW

2.1. Sun Protection

2.1.1. Sun radiation and its damaging effects

The sun is an essential part of the ecosystem which serves as the ultimate source of energy to the earth. It is well established in the literature that sunlight is an essential ingredient needed for the synthesis of vitamin D in the skin. However, excessive exposure to sun's radiation causes deleterious effects such as skin cancer and other skin diseases. The electromagnetic waves from the sun's radiation consist of radio waves, microwaves, infrared rays, visible rays, ultraviolet rays, x-rays, and gamma-rays. The electromagnetic spectra are often classified based on their wavelengths, frequencies, and energies. These spectra include, from the shortest to the longest wavelength (i.e., from the highest to the lowest frequency): gamma-rays, x-rays, ultraviolet (UV), visible (VIS), infrared (IR), microwaves, and radio waves. In terms of energy, radio waves have the lowest and the energy increases from microwaves to gamma-rays following the order stated (Figure 2.1). Gamma-rays and x-rays, both of which are life threatening, are not found on the earth's surface [9]. Only visible light, some amount of infrared rays (near-infrared light), a fraction of ultraviolet rays and radio waves reach humans as electromagnetic waves (Figure 2.2). Ultraviolet (UV) radiation is the most energetic of all the wavelengths of radiation that reach the earth's surface. As a result, it is of the utmost importance in terms of sun exposure [9]. The ultraviolet radiation from the sun consists of three parts: UV_A (320-400 nm), UV_B (280-320 nm) and UV_C (200-280 nm). UV_C being the most energetic among them is fatal, although ozone and oxygen in the atmosphere absorb nearly all of it. UV_B (280-320 nm) and UV_A (320-400 nm) both reach the surface of the earth and are harmful to living organisms (http-11). According to OHI, UV-Rays account for 9% of solar radiation and since ozone (O₃) in the stratosphere strongly absorbs UV-Rays, lesser amount reaches the earth (http-11). As reported by Brugè [10], the Ultraviolet (UV) radiation accounts for 5% of the total sun's radiation entering the earth's surface. UV_A makes up the majority of the UV radiation that gets to the Earth's surface (96%), with a little amount of UV_B (4%). In other research studies [11]–[13] and (http-12 and http-13), 95% and 5% were reported for UV_A and UV_B respectively.

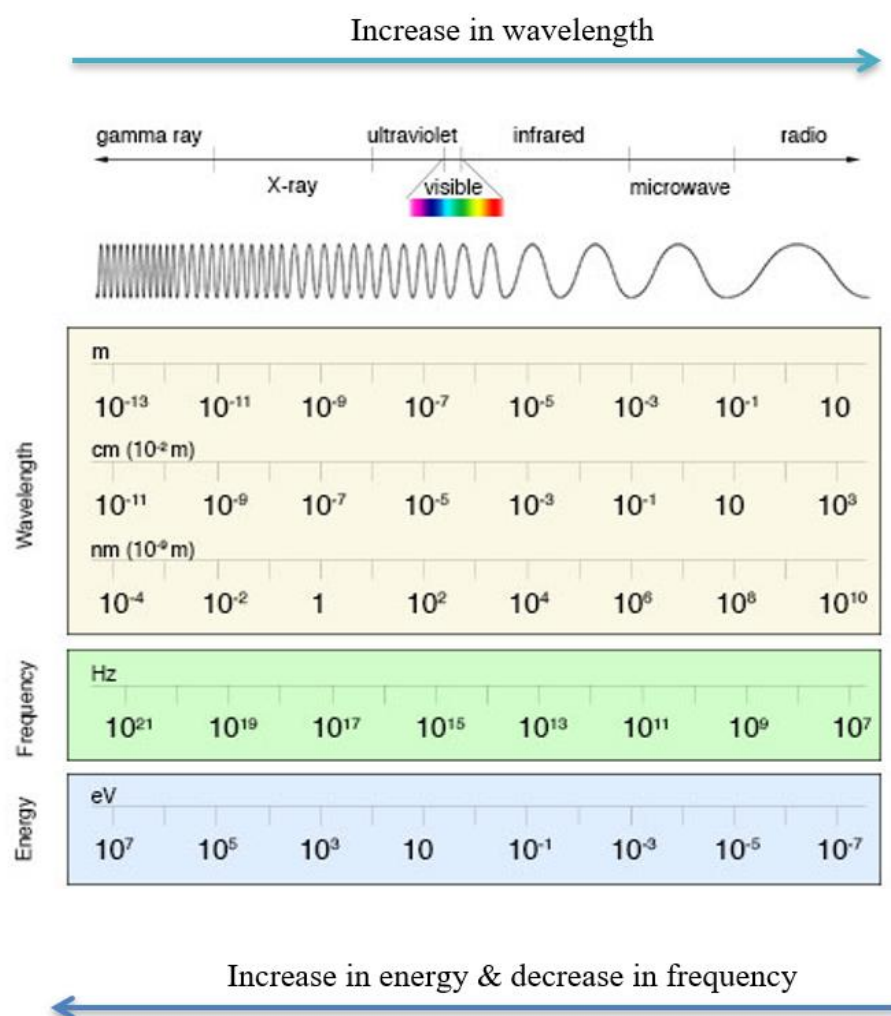


Figure 2.1. Electromagnetic spectrum ([http-14](#))

2.1.2. The ozone layer

Ozone is a kind of oxygen that has three atoms rather than two in each molecule. Ozone can be found in the troposphere, which is the lower ten kilometers of the atmosphere, and the stratosphere, which is ten to fifty kilometers above the ground. Ozone works as a shield, shielding us from the sun's harmful UV rays. Chlorine (chlorofluorocarbon, CFC) and bromine (halon) compounds, which were widely employed in the past in items such as aerosol spray can propellants, insecticides, solvents, refrigerants, and fire extinguishers, have been known to deplete the ozone layer. When these compounds reach the stratosphere, they are broken apart by UV radiation from the Sun, releasing chlorine and bromine atoms, which react with ozone. These reactions set off ozone-depleting chemical cycles, which erode the protective ozone layer ([http-15](#))

(see Figure 2.3). As a result of these chemical reactions, the ozone protective layer is depleted and consequently, more life-threatening UV-rays penetrate to the earth's surface.

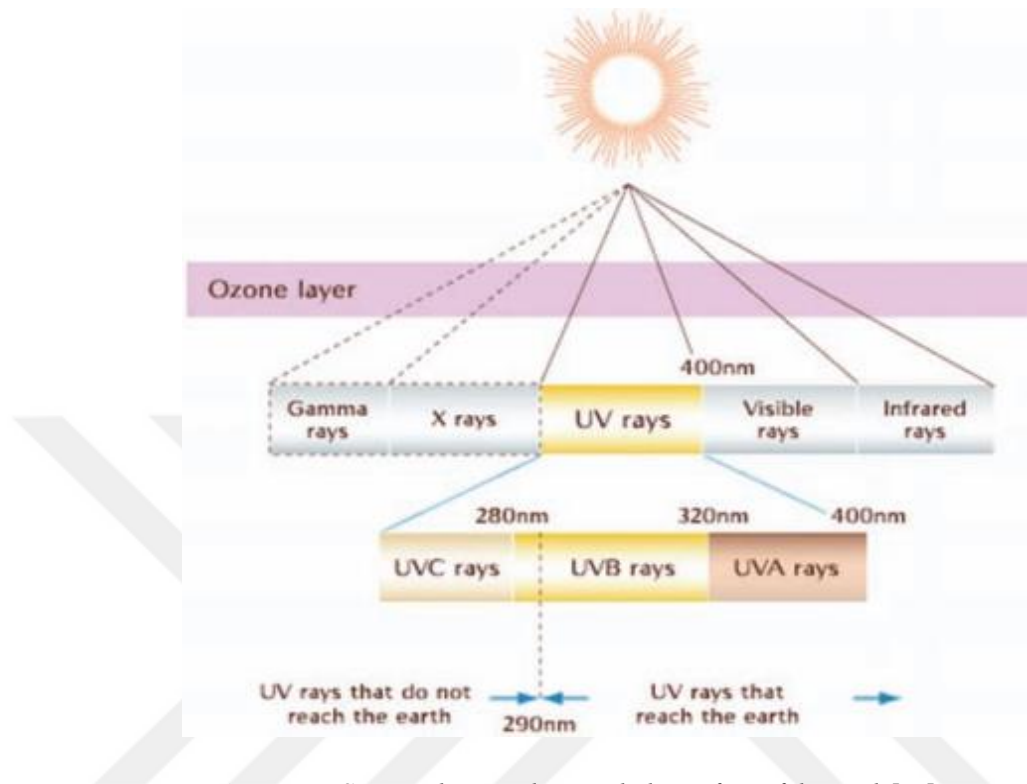


Figure 2.2. Sun's radiations that reach the surface of the earth [14]

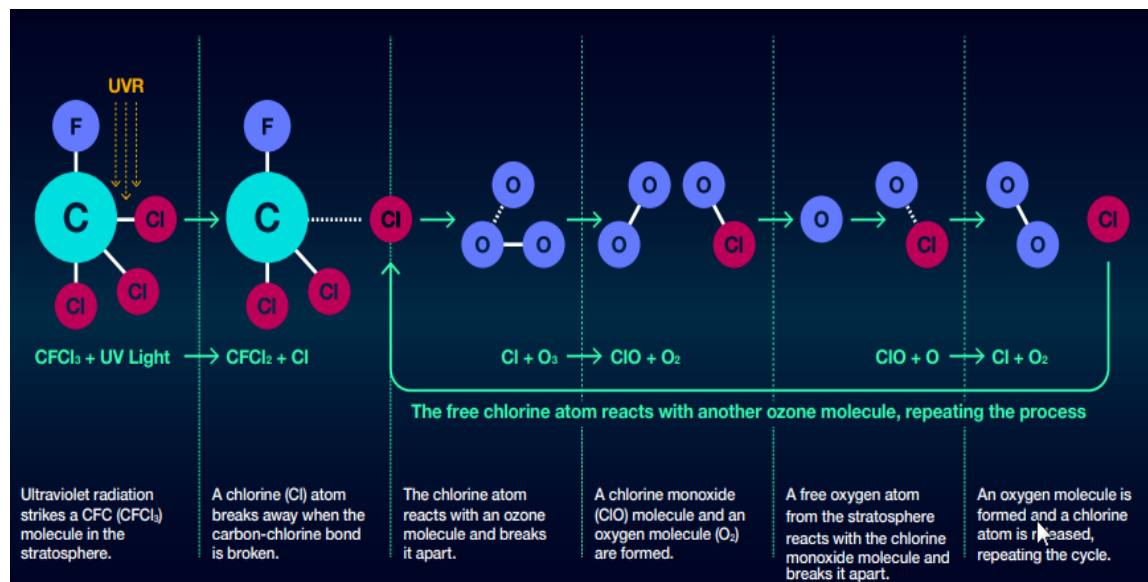


Figure 2.3. Ozone depletion reactions (<http-11>)

2.1.3. Relationship between sun exposure and skin cancer

Physicians hypothesized a link between skin cancer and regular sun exposure in the late nineteenth century, which was later confirmed in animal tests in the early twentieth century [15]. Similarly, it was reported by Hollaender and Emmons [16] in 1941 that the wavelength dependency of fungi mutagenicity corresponded to UV absorption by DNA. Epidemiological research conducted in the latter half of the twentieth century considerably increased the understanding of the aetiology of skin cancers and UV radiation was identified as the cause of gene alterations in skin carcinomas, according to research [15]. Although sunlight is the primary source of UV radiation we receive, solariums are a source of UV radiation that is produced artificially (http-16), [17]. Skin cancers such as squamous cell carcinoma (SCC), cutaneous malignant melanoma and basal cell carcinoma (BCC) are caused by exposure to UV-Rays [17].

2.1.4. Damaging effects of UV-rays on the human skin

The human skin which is known as the largest organ in the body serves as a protective barrier, shielding the body from various harmful substances (microbes and elements) in the environment while maintaining the inner body temperature. The total area of the skin is about 20 Sq. feet (1.86 m²), and it enables us to feel the sensation of heat, cold and touch (http-17). The human skin comprises of three layers; epidermis, dermis, and hypodermis (Figure 2.4a). The epidermis, or outermost layer of skin, determines the skin tone and serves as a waterproof barrier (http-17). The epidermis layer thickness varies at different body sites. According to a study conducted on seventy-one volunteers, the mean thickness of the stratum corneum (one of the strata of the epidermis as shown in Figure 2.4b) was measured at 18.3 μm , 11 μm , and 14.9 μm at the forearm, shoulder, and buttock, respectively. The corresponding thickness of the cellular epidermis was measured at 56.6 μm , 70.3 μm , and 81.5 μm , respectively [18]. In another study conducted at six different body sites on 180 Anatolian Turkish people of equal gender revealed that the thickness of the epidermis varies largely from one body site to another, and the thinnest and thickest epidermis were measured in the female breast and dorsum foot. Their corresponding mean values were $76.9 \pm 26.2 \mu\text{m}$ and $267.4 \pm 120.6 \mu\text{m}$, respectively [19]. Melanocytes, which produce the pigment melanin, are responsible for the skin's color. Melanocytes are pigmented cells found in the epidermis (http-17). Tough connective tissue, blood vessels, sweat glands and hair follicles are found in the dermis. The thickness of the dermis also varies. It has a thickness of approximately 1 cm on the

back, and the eyelid's dermis is very thin (http-18). According to the earlier report [19], the thinnest and thickest dermis were measured in the female dorsum of the hand and the breast of the male, respectively. Their corresponding mean values were $2115 \pm 946.4 \mu\text{m}$ and $5888 \pm 2422.3 \mu\text{m}$, respectively. The hypodermis (deeper subcutaneous tissue) is made up of fat and connective tissue. It offers buoyancy to the body, maintains the body heat and serves as an energy storage facility (http-17 and http-18). It is no doubt that skin exposure to sunlight has some benefits; however, sunburns, skin cancers, tanning and photoaging are some of the life-threatening effects of sunlight exposure. Some of these effects appear immediately, while others take time to manifest [20], [21]. The common skin cancer conditions associated with UV exposure from the sun include squamous cell carcinoma (SCC), basal cell carcinoma (BCC) and cutaneous malignant melanoma [20].

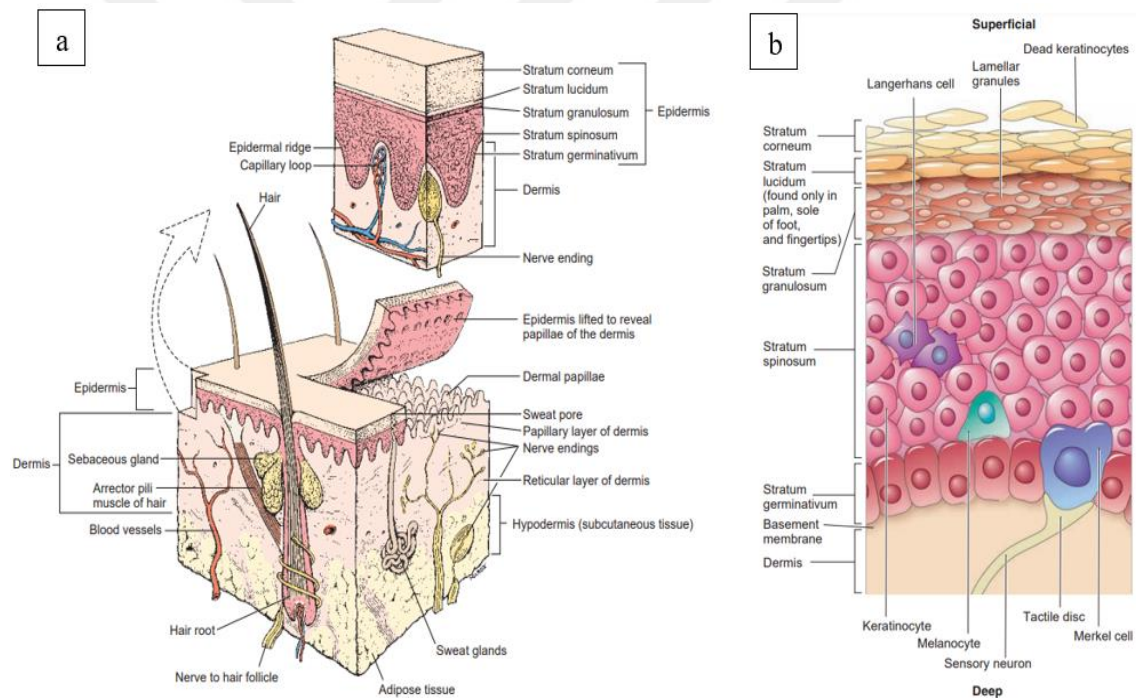


Figure 2.4. (a) Human skin with soft tissues (b) layers of epidermis [22]

The level of UV_A (320-400 nm) and UV_B (280-320 nm) penetration into the skin varies. UV_B -rays generally penetrate into the epidermis, the skin's outermost layer (Figure 2.5). Sunburn is a type of acute skin damage that manifests as redness and is caused by UV_B radiation. UV_B radiation has also been linked to the development of skin cancer. The redness and potential pain associated with sunburns diminish over a short period of time, but the underlying damage cumulates over time. As a result, several types of skin cancer

develop. UV_B-ray also has immunosuppressive capabilities and contributes to photoaging and tanning. UV_B radiation is responsible for the creation of vitamin D in the skin, which is a beneficial effect [9]. UV_A-rays penetrate deeper into the epidermis, all the way to the dermis, due to their longer wavelength (Figure 2.5). UV_A II (320–340 nm) and UV_A I (340–400 nm) are two subgroups of these rays. Skin tanning (browning) is caused by UV_A radiation, and tanning, either outdoors or indoors, produces cumulative damaging effect over time, resulting in photoaging. UV_A attacks keratinocytes in the basal cell layer, which is the site at which a lot of skin cancers develop. As a result, in the long run, it may contribute to or possibly cause the development of skin cancer [9]. In addition, UV_A damages DNA through an oxidative process that produces reactive oxygen species (ROS), causing cutaneous inflammation [23]. To protect humans against all these negative effects of UV rays, sunscreens have been developed and improved continuously.

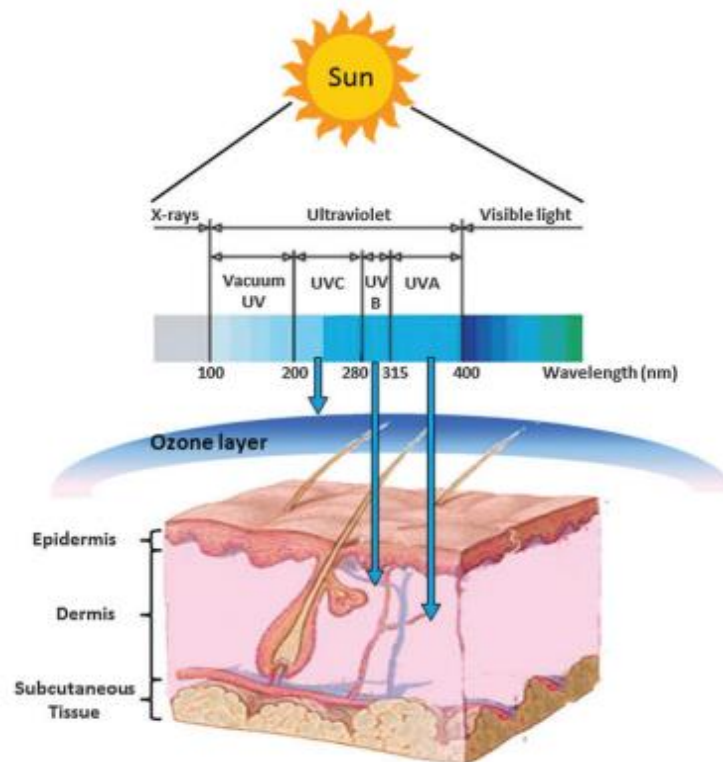


Figure 2.5. *UV-Rays wavelength-dependent penetration into the skin* [24]

2.2. Sunscreens

Sunscreens are developed systems meant to offer protection to the human skin against UV_A and UV_B rays [3]. In addition to the use of clothing, hats, and sunglasses,

sunscreens, which contain ultraviolet ray filters, have been recommended to modulate the life-threatening effects of UV-rays.

2.2.1. The history of sunscreen development and usage

Sun protection practice has started since antiquity. Ever since the discovery of weaving in 5000 BC, wool, flax, and cotton have been used to make clothes in Egypt. Cotton was the most common fabric used in the production of clothing in countries such as India. Painting's evidence demonstrates that in tropical countries, clothes covered not only parts of the body but also more extensive coverings, notably for women. In most cultures, the most common head coverings were turbans, broad-brimmed straw hats, wigs, and tarboosh. In countries like Egypt, China, Mesopotamia, and India, the use of umbrellas and clothes canopies was a common practice for protection against the sun [25]. Even though ancient Egyptians worshipped the sun, its perils were well known to them [26]. Skin fairness was more appealing to ancient Egyptians, so they avoided sun exposure, which was difficult given Egypt's sun-drenched land [27]. This perception that fair skin is more attractive than dark skin by the ancient Egyptians led to the development of sunscreen which began in 4000 BC [28]. Ingredients such as lupin extract, almond oil, Jasmin, olive oil, aquatic lotus oil, calcite powder and clay, rice bran extracts, kohl, and henna oil were used as sun-protecting agents for the skin, hair, eyes, lips, and nails [26]. This has positioned the ancient Egyptians as the first to provide a solution to the damaging effect of sunlight. Athletes in ancient Greece applied a mixture of oil and sand to their bodies while practicing for the Olympic games in the sun in 500 BC, and during the same period, an ancient Indian medical literature documented a substance called *Pushpanjan*, suspected to be zinc oxide, which was used as an ointment for burns, eyes, and open wounds. Since then, it has primarily been utilized for cosmetic purposes due to its whitening characteristics, particularly in the 1900s when mixed with magnesium salts and bismuth [28]. Johann Ritter discovered ultraviolet light in 1801 following William Herschel's discovery of light beyond visible light in 1800, but their earlier discoveries received considerable attention in the later part of the century. In 1820, Sir Everard Homes identified the sun's harmful effects, attributing skin burn to sun exposure; however, Widmark's experiment established that UV-rays are the cause of skin erythema, and he utilized *acidified quinine sulfate* solution to absorb the UV-rays [25]. This was the first solution used to reduce the skin burn caused by UV_B – rays and in 1891, Friedrich Hammer of Germany developed the world's first chemical sunscreen by incorporating

this substance into lotions and ointments [28]. Paul Unna and Dubreuilh were the two sources that reported in 1894 that skin cancer may be caused by lengthy and frequent exposure to sunlight. While Paul Unna's work attributed the development of skin cancer in sailors to acute degenerative changes in exposed parts of their skin, Dubreuilh noticed a high prevalence of actinic keratoses and skin cancer in vineyard workers but rather infrequently in surrounding city people. In 1928, two German scientists, Hausser and Vahle, pioneered the use of *benzyl salicylate* and *benzyl cinnamate* in commercial sunscreens which had a good absorption in the UV_B region. Even though the first commercial sunscreens were made accessible to the public in 1933 [28]. In another report, commercial sunscreens were first used in the globe in 1928 in the United States of America, when an emulsion containing two sunscreen compounds, benzyl salicylate and benzyl cinnamate, was introduced [26]. Milton Blake, an Australian chemist, was recognized for the first to experiment the protection from the sun, developing a sunscreen that was manufactured and distributed by Hamilton Laboratories in the 1930s ([http-19](#)). Eugene Shueller, founder of L'Oreal, sold the enormously successful Ambre Solaire utilizing para-aminobenzoic acid (PABA) in 1936 [28]. In 1943, para-aminobenzoic acid (PABA) was first patented [26], and after the patent, more potent PABA esters became available in 1948. With the growing popularity of PABA-based sunscreens, it was necessary to develop testing procedures for determining the sunscreen's protective factor. This was in 1956, when Rudolf Schulze, a German radiation physicist, proposed it. Franz Greiter, an Austrian chemist, and owner of the Piz Buin company, expanded on Schulze's proposal in 1974. Greiter came up with the term SPF, which was accepted by the Food and Drug Administration in 1978. Dermatologists began to see people allergic to PABA in 1956, after it was shown to be photolabile. Mayer and Baer discovered that PABA decomposed to form antigens when interacted with tissue, resulting in its gradual withdrawal in 1965 and the eventual designation of several sunscreens as "PABA free" [28]. For the US military in the 1940s, Benjamin Green, a pharmacist and member of the US Air Force from Florida, produced Red Vet Pet (red veterinary petroleum). Red Vet Pet, a red petroleum-based jelly-like substance, provided an effective barrier against UV radiation for World War II veterans, but its sticky and uncomfortable feel, as well as its proclivity for staining garments ([http-19](#)). This resulted in the widespread usage of both inorganic and organic UV absorbers following the war [26]. In 1944, Benjamin Green patented his formulation and developed it by combining it with coconut oil and cocoa

butter to create Coppertone suntan cream, the first mass-produced sunscreen in the United States ([http-19](#)). The discovery of UV_A's effects occurred in 1969, when Albert Kligman, an American dermatologist, demonstrated how sun exposure produces structural damage to the skin that is distinct from the intrinsic aging process. Kligman came up with the concept "photoaging" and emphasized the significance of sunscreens with increased protection, but it was not until a decade later that effective UV_A filters became accessible [28]. UV radiation research accelerated in the 1980s, as the implications of UV_A radiation, as well as UV_B radiation, on skin cancer gained prominence. Coppertone commercialized the first UV_A/UV_B sunscreen in 1985, along with the first sweat-proof sunblock for athletes ([http-19](#)). The first broad UV_A filters were dibenzoylmethane derivatives (avobenzone), which were present in less than 1 percent of sunscreens in 1980 but increased nearly up to 35 percent by 1990 [28]. Avobenzone, the only UV_A-specific chemical filter available in the 1980s, gained popularity in sunscreen formulations and was authorized by the U.S. FDA in 1988. Also in the 1980s, there were demands for zinc oxide for use in sunscreens due to its colours ([http-19](#)), and in 1986, Zinka, a Southern California-based sunscreen brand, began producing its own ZnO-based "nosecoat" in sixteen different hot colours ([http-20](#)). Micronized zinc oxide was added to photostable sunblock ingredients in 1992. Unlike UV_B filters, there are only two UV_A filters approved by the FDA; avobenzone and zinc oxide [28]. In 1983, Kollias and Baqer [29] demonstrated that irradiation with visible and near-IR light alone can induce pigmentation alterations in human skin in vivo. They were credited with the first publication on the effect of visible and infrared light on skin [28]. Iron oxide is the most extensively studied visible light filter. According to research conducted by Kaye and colleagues [30], the addition of iron oxide to sunscreen containing zinc oxide considerably lowers visible light transmission through it. Sunscreen technologies continued to advance throughout the 1990s, with the development of new formulations in the form of sprays and gels. While avobenzone is a good UV_A filter, its photostability was limited, necessitating its combination with other compounds. Since 1997, sunscreen manufacturers in the United States have been permitted to advertise their products as delivering UV_A protection due to the presence of avobenzone. In the 1990s, research concentrated on developing new UV_A filters, such as micron sized zinc oxide (ZnO) and titanium dioxide (TiO₂). At the turn of 21st century, sunscreens with a low-SPF were phased out and replaced with those with a higher protection factor. By 2009, barely 6% of sunscreens had an SPF of less than

5. SPF began to be introduced into common skincare and makeup products such as moisturizing creams, lip balms, and foundations (http-19). It is now widely acknowledged that the longer wavelengths and thus more penetrating UV_A radiation from the sun are the most dangerous UV rays and the major cause of skin cancer. As a result, more emphasis has been placed on developing broad-spectrum sunscreens that offer good protection against both skin cancer-causing UV_A radiation and sunburn-causing and age-causing UV_B rays (http-19). Numerous conventional UV filters have also come under careful and detailed investigation by the regulatory bodies in recent years. UV filters have historically been largely chemical filters that absorb and dissipate UV radiation (http-19). The scientific findings of Danovaro et al. imply that if sunscreens with the derivatives of cinnamates, benzophenones, parabens, and camphor are introduced into natural systems, they may lead to hard-coral bleaching [31]. In the same vein, a study conducted by Down et al. demonstrated the effect of a chemical UV filter (oxybenzone) on seven coral species from the marine environment of Hawaii and the U.S. Virgin Islands [32]. The study shows oxybenzone exhibited photo-toxicity and genotoxicity, resulting in the bleaching of coral at increasing concentrations and thus causing genetic harm to coral reefs. Considering these harmful effects of oxybenzone and octinoxate (ethylhexyl methoxycinnamate) on coral reefs, which could probably lead to their declination, Hawaii, in 2018, became the first state to prohibit the sale of sunscreen products containing the ingredients oxybenzone and octinoxate, or both, using regulatory actions, although the law was intended to take effect on January 1, 2021 [33]. In addition to Hawaii, the other five locations that have prohibited some organic filters are listed in Table 2.1. ZnO and TiO₂ are mineral UV filters that provide a protective shield on the skin that reflects and scatters UV rays. Mineral sunscreens are gaining popularity because they provide more effective broad-spectrum protection, higher photostability, and fewer allergic skin reactions than chemical (organic) sunscreens (http-19). Perhaps, another reason why cosmetic industries are focusing more attention on ZnO and TiO₂ is that they are both currently placed on the FDA list of Generally Recognized as Safe and Effective (GRASE) filters.

Table 2.1. Six locations that have enacted regulations prohibiting the use of organic UV filters

Location	Prohibited UV Filter	Commencement Date
Hawaii	benzophenone-3 (oxybenzone)	January 2021
	ethylhexyl methoxycinnamate (octinoxate)	
Palau	benzophenone-3 (oxybenzone)	January 2020
	ethylhexyl methoxycinnamate (octinoxate)	
	Octocrylene	
	4-methylbenzylcathinone	
U.S. Virgin Islands	benzophenone-3 (oxybenzone)	March 2020
	ethylhexyl methoxycinnamate (octinoxate)	
	Octocrylene	
Aruba	benzophenone-3 (oxybenzone)	July 2020
Bonaire	benzophenone-3 (oxybenzone)	January 2021
	ethylhexyl methoxycinnamate (octinoxate)	
Key West Florida	benzophenone-3 (oxybenzone)	January 2021
	ethylhexyl methoxycinnamate (octinoxate)	

The City of Key West's vote was later overturned by Florida Senate Bill SB 172, which preempts such rulings to the state government [33]

2.2.2. General features of a good sunscreen

Apart from the primary protective function of a sunscreen, which involves broad spectrum protection (i.e., protection in the UV_A and UV_B regions), a good sunscreen should also have the following features and characteristics:

1. Transparency: sunscreens that are meant for consumer use should exhibit transparency characteristics. This is because people usually find it uncomfortable to wear sunscreens with whitening effects on their skin.
2. Skin penetration: sunscreen ingredients should be safe to use and not penetrate the skin layer, causing other side effects.
3. Photostability: a good sunscreen should not breakdown under sunlight exposure. Sunscreens containing UV filters with low photostability should be stabilized during formulation processes.

4. Spreadability: a good sunscreen that will be widely accepted by the masses should cover the skin smoothly and stay on for an extended period of time (i.e., the skin coverage area per person should be high).
5. Irritation and skin allergies: sunscreen should be designed in a way that prevents skin irritation and allergies, especially for people with highly sensitive skin and children.
6. Environmentally friendly: sunscreens should be designed in such a way that their constituents will not cause environmental pollution. As much as people want to be safe from the adverse effects of sunlight, using a product that causes damage to their environment is something people might want to avoid.

Another feature that is sometimes found on some commercial sunscreens is water and sweat resistance. According to the US Food and Drug Administration (U.S. FDA), no sunscreen is genuinely "waterproof" as it inevitably washes off over a period of time. The FDA has stated that sunscreens branded "water resistant" must meet a minimum SPF requirement, and sunscreen's labelling must state whether it is effective for 40 or 80 minutes while swimming or sweating.

2.2.3. Organic (chemical) sunscreens

Organic sunscreen filters are usually aromatic compounds bonded with a carbonyl group [20]. These filters are classed as UV_A (dibenzoylmethanes, anthranilates, and benzophenones) or UV_B (cinnamates derivatives PABA derivatives, camphor, and salicylates derivatives). Organic UV filters are usually employed in combination, as no single active ingredient provides sufficient Sun Protection Factor (SPF) or broad-spectrum protection when used at the concentrations currently permitted by the FDA [34]. These combinations allow improved SPF values and broad-spectrum protection [20].

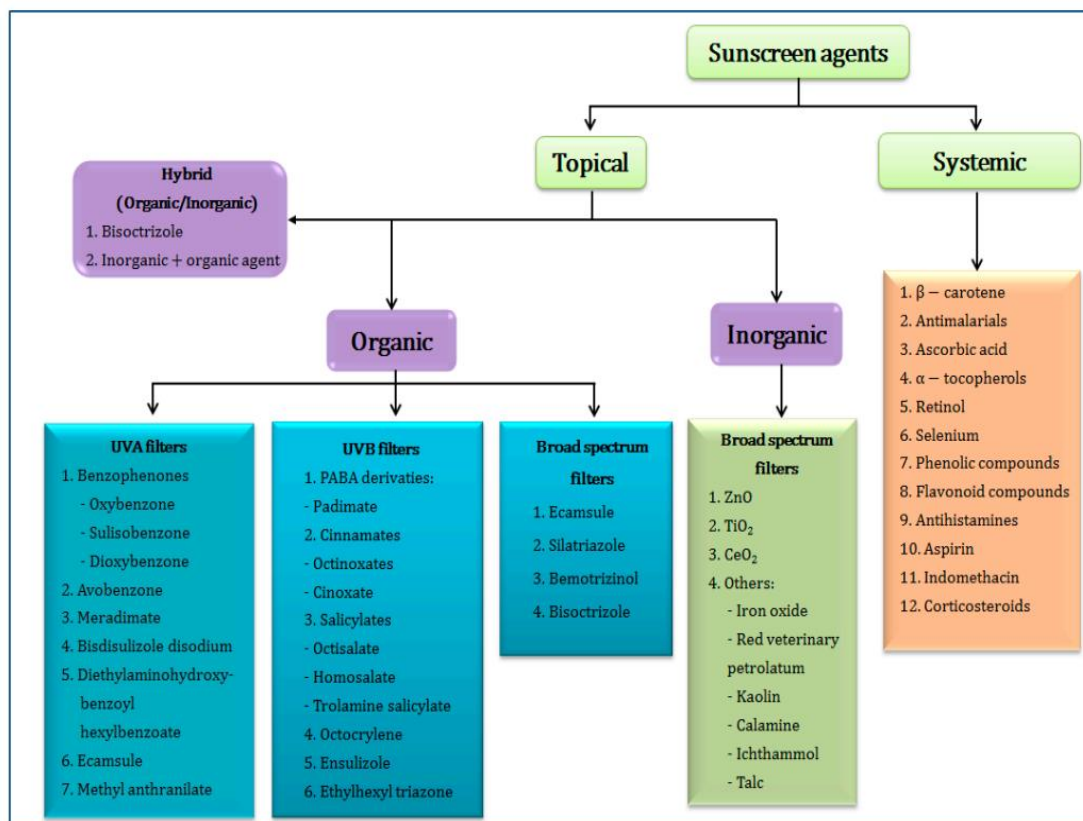


Figure 2.6. Classification of Sunscreens [35]

The current active UV filters (organic and inorganic) permitted in commercial sunscreens by the FDA and their maximum concentrations are stated in Table 2.2. In combining two or more ingredients listed in (1), (3), (4), (5), (6) and (7) through (16) in a sunscreen product, each active constituent must be present at a concentration that results in a final product with a minimum SPF of not smaller than 2. The completed final product should have a minimum SPF equal to the sum of the active constituents in the sunscreen combination multiplied by two. Also, in combining the active filters in (2), (3), (4), (6), (8) through (11), (13) and (16) to produce a sunscreen, each active constituent must be present at a concentration that results in a final product with a minimum SPF of not smaller than 2. The completed final product should have a minimum SPF equal to the sum of the active constituents in the sunscreen combination multiplied by two (<http://21>).

Table 2.2. FDA's UV filters and their concentrations ([http-21](#))

S/N	Active Ingredients/Concentration			
	Organic	Maximum Concentration (%)	Inorganic	Maximum Concentration (%)
1	Aminobenzoic acid (PABA)	15		
2	Avobenzone	3		
3	Cinoxate	3		
4	Dioxybenzone	3		
5	Ensulizole	4		
6	Homosalate	15		
7	Meradimate	5		
8	Octinoxate	7.5		
9	Octisalate	5		
10	Octocrylene	10		
11	Oxybenzone	6		
12	Padimate	8		
13	Sulisobenzene	10		
14	Trolamine salicylate	12		
15			Titanium dioxide	25
16			Zinc oxide	25

2.2.3.1. Mechanism of absorption of organic UV filters

Organic UV filters are generally linked carbon compounds that occur as discrete molecules. Molecules are composed of several atoms that can vibrate and rotate with respect to one another ([http-10](#)). The mode of action of organic filters is based on their chemical structures, which allow high-energy UV radiation to be absorbed [36]. The absorbed energy from sunlight gives the molecule thermal motion, making the molecule vibrate and rotate ([http-10](#)), allowing the molecule to achieve an excited state [36]. As the molecule goes back to its ground state, the lower energy associated with longer wavelengths is released [36]. According to ([http-10](#)), the energy released is a harmless long infrared wave (Figure 2.7).

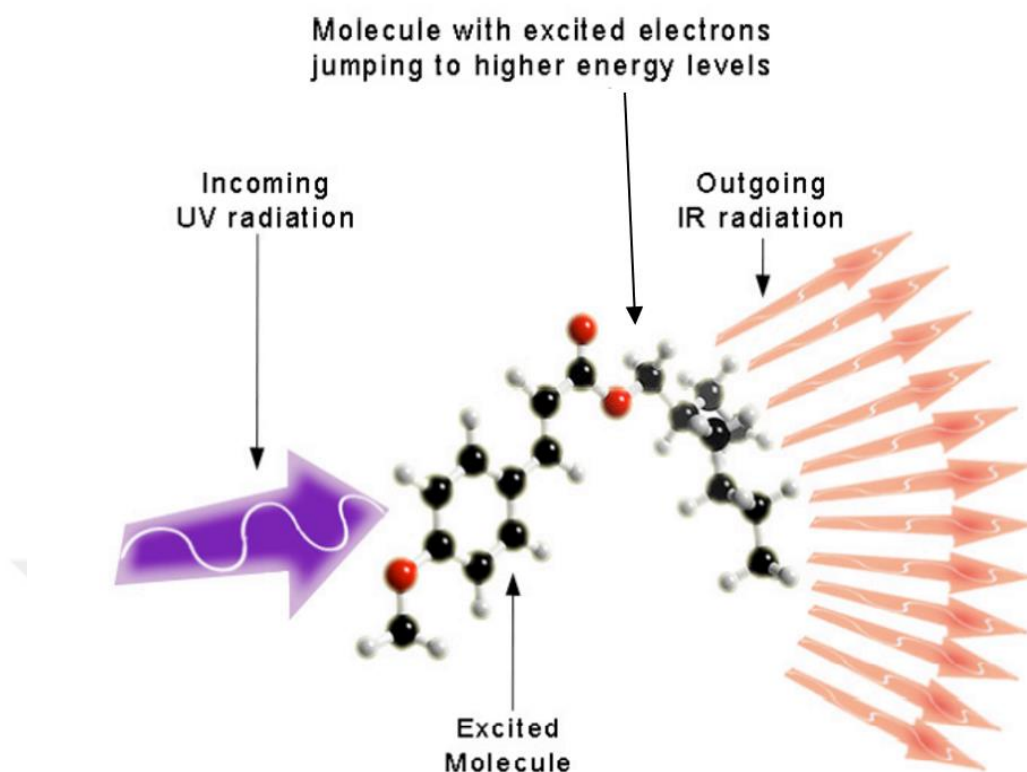


Figure 2.7. Absorption mechanism of organic UV filters (<http-10>)

Organic molecules absorb only UV radiation with an energy equal to the difference between their energy levels. Because molecules comprise groups of energy levels, they absorb a range of closely packed frequencies, and hence wavelengths, rather than a single frequency of light. While this results in a curve known as the absorption range, it is a collection of discrete energy transitions that absorb similar light frequencies. The highest absorption occurs in the center of the range, as this is the wavelength associated with the most prevalent energy transition (Figure 2.8). The combination of several closely spaced absorption lines results in the formation of an absorption band (Figure 2.9) (<http-10>). The absorption peak and range of absorption differ according to the chemical (organic UV filter). Different UV filters are effective at blocking various wavelengths of the UV rays. Combining various types of organic UV filters provides a broader range of UV rays protection (Figure 2.10 (a)-(c)) (<http-10>).

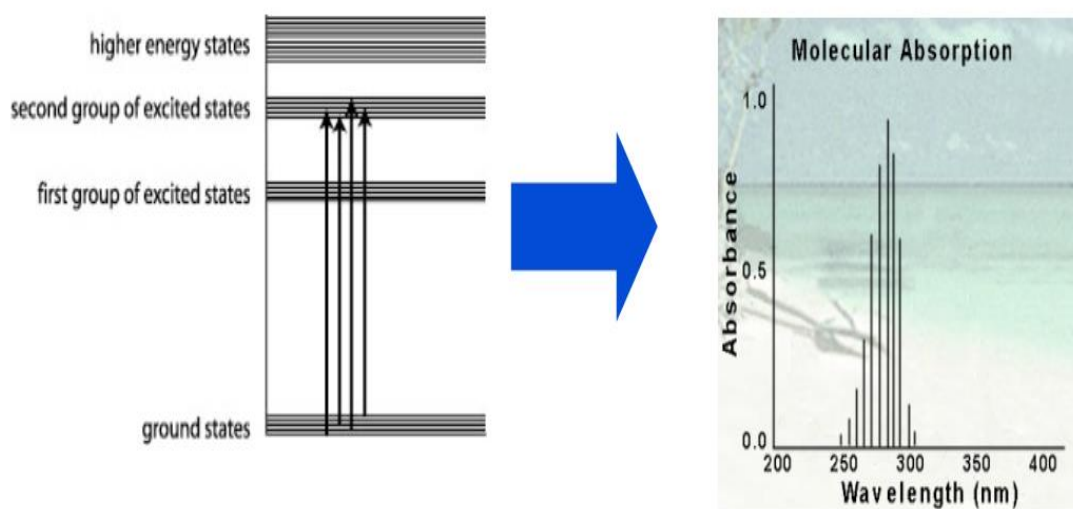


Figure 2.8. Molecule absorption of organic UV-filters (<http-10>).

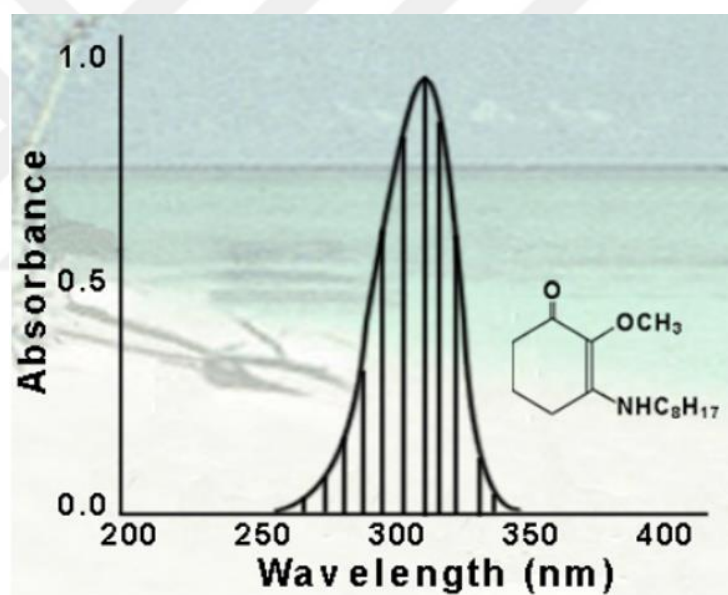


Figure 2.9. Absorption band of an organic UV filter (<http-10>)

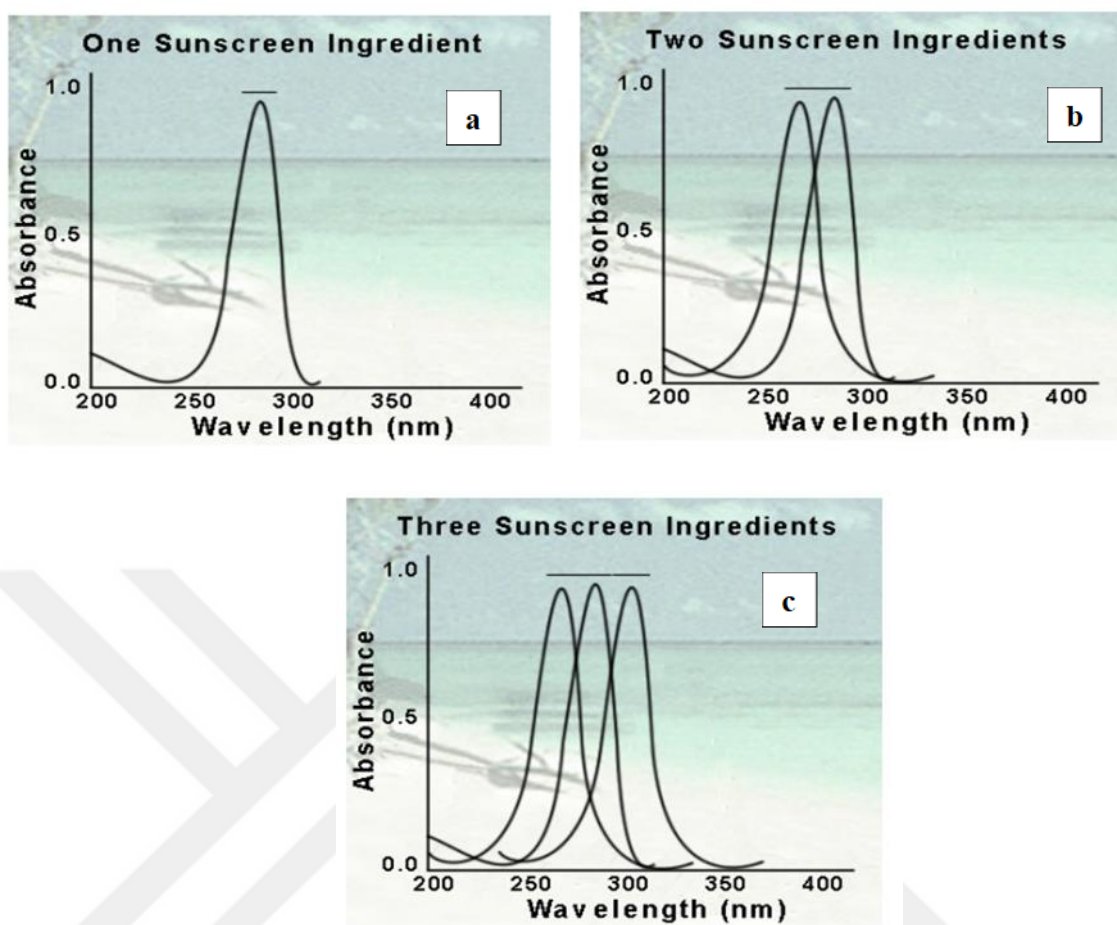


Figure 2.10. Absorption range of organic UV filters (<http-10>)

A molecule's ability to absorb light is related to a portion of its structure termed a *chromophore*, that may or may not comprise the entire molecule. In conjugated systems, the chromophores that absorb UV-rays are frequently associated with *delocalized π electrons*. Usually, whenever a molecule absorbs a photon with sufficient energy, an electron is raised from a lower to a higher energy state. This means the molecule has transited from the ground state to the excited state. While in the excited state, the molecule can take advantage of various possible routes such as:

- undergoing a fluorescence process through which it emits a photon and then returns to its ground state.
- reverting to its ground state, emitting its energy thermally through a sequence of vibrational transitions known as vibrational relaxation.
- undergoing some form of photochemistry reaction.

- undergoing a transition to a lower energy excited state, the triplet state, in which the electrons lose their spin pairing.

The lower energy excited state can then decay either radiatively (phosphorescence) or non-radiatively (vibrationally), or it can undergo a photochemistry reaction (Figure 2.11) [37]. The wavy lines in Figure 2.11 show vibrational relaxation, which is frequently observed in organic UV filters. DNA damage occurs because of photochemical reactions occurring in the lower energy excited state [37]. As a result of these photochemical reactions that induce skin damage, organic (chemical) UV filters suffer a major drawback.

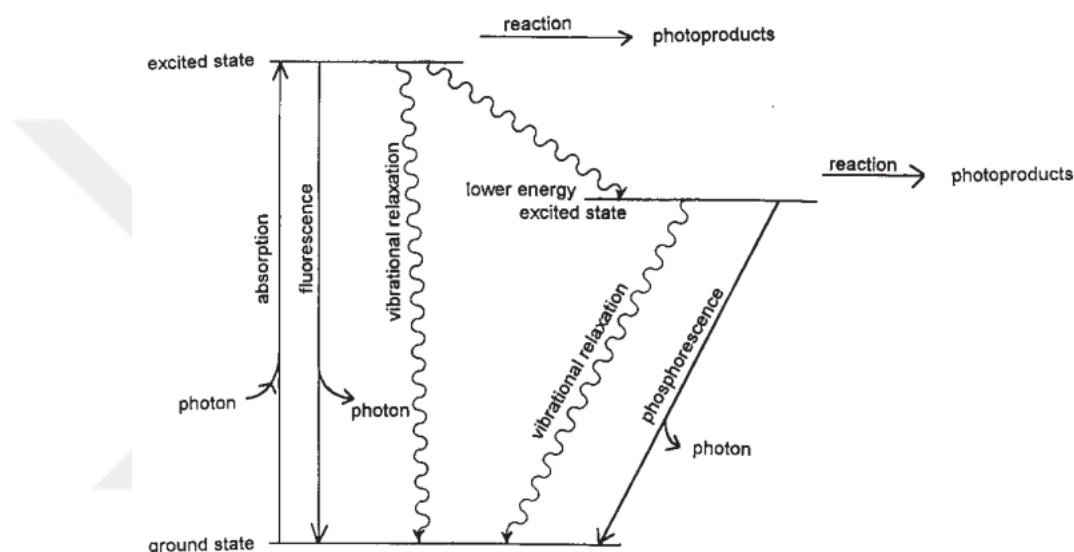


Figure 2.11. A Jablonski diagram simplified to depict the energies associated with ground state and photochemically excited state of organic sunscreens [37]

2.2.3.2. Disadvantages of organic UV filters

Although organic UV filters offer protection against the UV-rays, they incur significant disadvantages. Organic UV filters often provide narrow wavelength range protection against the deadly UV rays [3]. Since single UV filters have a rather narrow absorption band, more chemicals are combined to provide a broader protection in the UV regions [38]. The problem with sunscreen products combining many UV-filters is that mixtures of chemicals, including UV-filters, may work additively and demonstrate toxic activity, even at the threshold of no observed harmful effect for the individual chemicals [39]. Some combinations of organic UV filters have been proven to be undesirable since they are believed to accelerate the competitive photodegradation process [40]. In a study conducted by [41] for instance, the photodegradation of a sunscreen product including

octyl methoxycinnamate and avobenzone is increased due to their competitive degradation process [40]. Additionally, UV filters' function can be altered not just through interaction with UV rays, but also through the interaction of individual ingredients in sunscreen products and through the improper combination of UV filters [42]. Organic filters are photo-unstable, as they cannot withstand the long-term effects of UV rays on their function and structure [40]. The photochemical reaction caused by the UV filters' instability influences both their physical and chemical properties [43]. These filters undergo molecular changes due to UV rays' absorption, resulting in the generation of chemically reactive species. The reactive species formed eventually enable photo-oxidation, which results in the formation of free radicals. Lack of photostability also contributes to its lower efficacy as a UV filter, since it undergoes transformations that reduce its ability to absorb UV rays, hence reducing the filter's UV protection [40]. These Free radicals, referred to as reactive oxygen species, which may also be produced without UV rays' triggering [44], may react with not just other sunscreen agents, but with skin constituents such as proteins, nucleic acids, and lipids [42]. Organic UV filters are reported to be allergenic, causing photoallergic contact dermatitis, a kind of skin allergy triggered by skin exposure to certain chemical compounds [44]. A study conducted in 2006 across 17 medical centers in the United Kingdom, Netherlands, and Ireland concluded that photoallergens were attributed to chemical sunscreen filters, the most common being benzophenone-3 [45]. In another study conducted at the School of Medicine at New York University, it was reported that the most frequently observed allergens triggering photoallergic contact dermatitis were sunscreens and antimicrobial agents [46]. Organic UV filters such as cinnamate, camphor and benzophenone derivatives are reported to have endocrine disrupting effects. These filters induce androgenic and estrogenic-disrupting effects. They also show disrupting effects on the progesterone receptor and thyroid hormone receptor [47]. Another review report on organic UV filters concluded that numerous in vitro and in vivo animal investigations have demonstrated that the organic UV-filters found in some commercial organic sunscreens have hormone disruptive properties [39]. A follow-up study conducted on 521 adolescents in Shanghai reveals that organic UV filters alter adolescent endocrine function. Ethylhexyl methoxycinnamate and benzophenone derivative exposure were substantially linked with late pubertal growth in males, while Ethylhexyl dimethyl PABA exposure was attributed to early pubertal development in females [48]. Another concern

of organic UV filters is their dermal absorption potential. This absorption involves penetration; the entering of the UV filters into the topmost layer of the skin; permeation; the further entering of the UV filters into other layers of the skin completely different from the topmost layer; and resorption, the process by which UV filters are taken into the vascular system (blood artery and lymphatic or both) [42]. A study conducted by exposing human skin to organic sunscreens containing UV filters such as octocrylene, avobenzone, padimate O, octinoxate, and oxybenzone for a day revealed that measurable quantities of all UV filters were found in the stratum corneum and functional epidermis, with oxybenzone having the greatest epidermal penetration [49]. Another experiment which supported the skin absorption of organic UV filters demonstrated that oxybenzone, 2-ethylhexylsalicylate and 2-ethylhexyl 4-methoxycinnamate permeate the skin [50]. Apart from the negative impacts of organic UV filters on human health, scientific discoveries have also shown their effects on the environment. These filters have found their way to not only water bodies but also soil, sediment, and indoor dust. Also, certain organic UV filters have been shown to bioaccumulate in a variety of aquatic creatures (see Figure 2.12) [51].

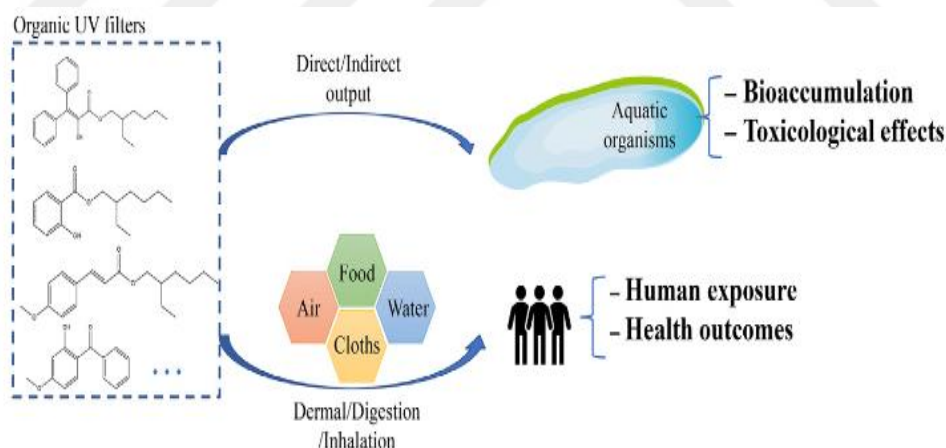


Figure 2.12. Impacts of organic UV filters on health and environment [51]

As pointed out earlier in this chapter, scientific findings by Danovaro et al. and Down et al. have shown that when sunscreens with the derivatives of cinnamates, benzophenones, parabens, and camphor are introduced into marine systems, they will lead to hard-coral bleaching [31], [32]. As a result, a ban was imposed on some organic UV filters at six different geographical locations (see Table 2.1) [33].

2.2.4. Inorganic (mineral) sunscreens

Inorganic UV filters are referred to as physical filters because their mechanism of action is related to physical processes which including ultraviolet rays scattering and reflection besides absorption [52]. In adequate amounts, they will act as physical barriers to incident ultraviolet and visible rays from the sun. Their popularity has increased in recent years, owing largely to their low toxicity. Additionally, they provide excellent protection against both UV_A and UV_B rays [53]. Physical sun blockers have undergone an intriguing evolution. Iron oxide, red veterinary petrolatum, kaolin, ichthammol, calamine, talc, titanium dioxide, and zinc oxide are just a few of these UV filters [54]. Titanium dioxide (TiO₂) and zinc oxide (ZnO) are the most used particle sunscreen ingredients [53], and currently, they are also the only two approved inorganic sunscreen filters by the US FDA ([http-21](#)). Independent of the sunblock base as well as other constituents, inorganic filters are photostable. They offer broader protection by reflecting and scattering both UV_A and UV_B rays (TiO₂ filters block UV_B and UV_A II rays, whereas ZnO filters block UV_B, UV_A II, and UV_A I rays) [9]. Because TiO₂ fails to offer protection against UV_A I rays, ZnO is regarded as the only broad-spectrum inorganic UV filter ([http-22](#)). currently on the FDA list of Generally Recognized as Safe and Effective (GRASE) filters and also approved as a UV-filter in the rest of the world.

2.3. Zinc Oxide (ZnO)

Zinc oxide (ZnO) is a multifunctional material that is utilised in a wide variety of productive sectors. It is most employed in rubber, then ceramics, chemicals, medicines, cosmetics, care products, and agriproducts. ZnO is widely used in a variety of applications, including piezoelectric transducers, catalysts, conductors, sensors, and surface acoustic wave devices [55]. At the nano scale, ZnO is utilized in surface coatings for various applications [56], and it is used in oil-based paintings [57], as well as an antimicrobial with a long-lasting UV blocking effect [55]. Due to its antibacterial, disinfecting, antimicrobial, and drying qualities, ZnO is appropriate for pharmaceutical products, ointments, and lotions. ZnO is added into polymeric matrices in the food industry to impart antibacterial activity and enhance the packaging material's properties [55]. Moreso, ZnO is used in the cosmetics industry as a colorant or bulking agent, as a UV ray blocker in sunblock creams, and as a soothing and barrier layer against skin irritation and abrasion. Zinc oxide is a semiconductor material that exhibits a wide variety of morphologies. Its morphology, size, and properties are determined by the type of

precursor, the solvent, and its concentration, as well as the temperature used during the synthesis process [58]. Zinc oxide can be synthesized using a variety of techniques, including hydrothermal synthesis [59]–[63], sol-gel technique [64]–[67], solvothermal process [68]–[70], microwave-assisted process [71], emulsion precipitation process [72], [73], microemulsion [74]–[76], precipitation process [77], [78], surfactant-mediated precipitation process [79], [80], mechanochemical technique [81]–[84] and other methods such as chemical vapor synthesis [85], spray pyrolysis [86], etc.

2.3.1. Crystal structure of zinc oxide (ZnO)

Zinc oxide is a non-toxic metal oxide n-type II–VI semiconductor having a direct and wide band gap of 3.37eV due to the tetrahedral coordination, which results in the formation of sp^3 covalent bonds, and the structure's ionic character [87]. Wurtzite, zinc blende, and rocksalt are crystallized forms of ZnO, as shown schematically in Figure 2.13-2.14. At room temperature, the wurtzite structure is the most thermodynamically stable phase of the three forms of ZnO [88]. Utilizing cubic substrates stabilizes the growth of the zinc blende structure and, at fairly high pressure, the rock-salt structure can be obtained [89], [90].

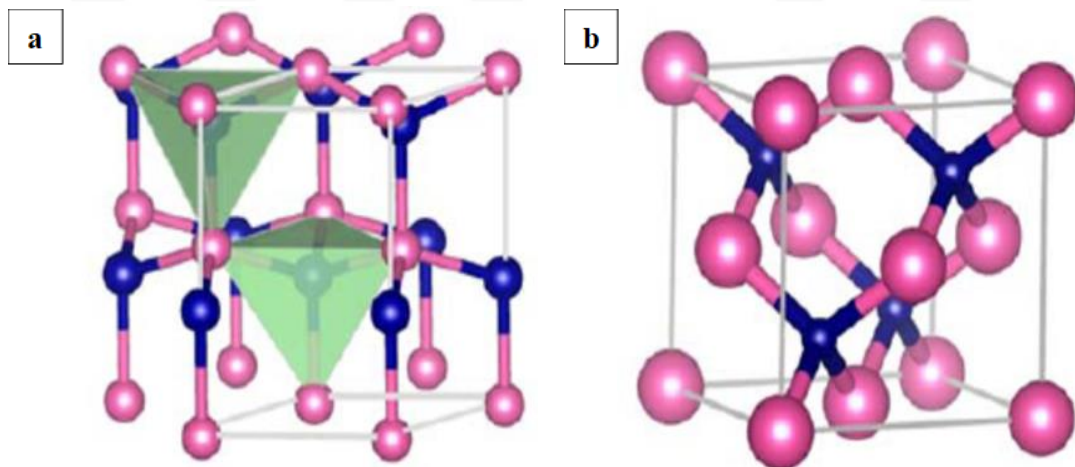


Figure 2.13. ZnO crystal structures (a) wurtzite hexagonal (b) cubic zinc blend structures [58]

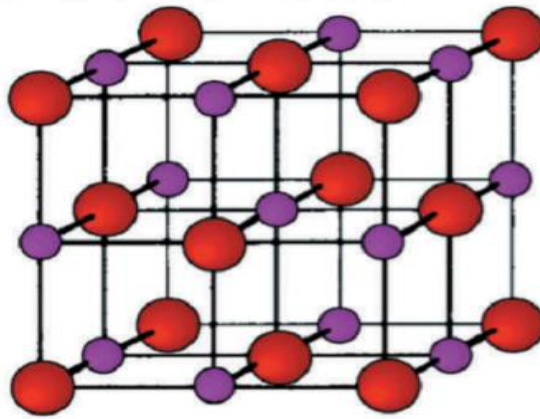


Figure 2.14. *Rocksalt ZnO crystal structure [87]*

In wurtzite, cations are connected to four anions at the tetrahedron's corners, whereas in zinc blende, anions are linked to four cations at the tetrahedron's corners [87]. Wurtzite ZnO is a hexagonal structure with lattice parameters a (usually from 0.32475-0.32501 nm) and c (usually from 0.520642-0.52075 nm) and belongs to the space group $P6_3mc$ [89]. ZnO lattice constants deviate from their ideal values due to the existence of point defects like oxygen vacancies and zinc antisites as well as dislocations [89], [90]. The ratio of the lattice constants of the hexagonal unit cell of wurtzite is $c/a = \sqrt{8/3} = 1.63$. The wurtzite structure comprised of two interpenetrating hexagonal close packed sublattices, each containing a single atom type displaced by $u = 3/8 = 0.375$ (ideal value) along the threefold c -axis (see Figure 2.15). The lattice constants of the hexagonal wurtzite structure a and c are in the basal plane and direction, respectively, and the u parameter is the bond length along the c -axis. The bond angles are represented by α and β (ideal value of 109.47°). Changes in the c/a ratio or the u value cause a deviation from the ideal arrangement in a real ZnO crystal. At modest external hydrostatic pressures, wurtzite ZnO can be converted into the rocksalt structure. This is because a decrease in the lattice dimensions can lead to interionic Coulomb interaction, favoring ionicity over covalent nature [90].

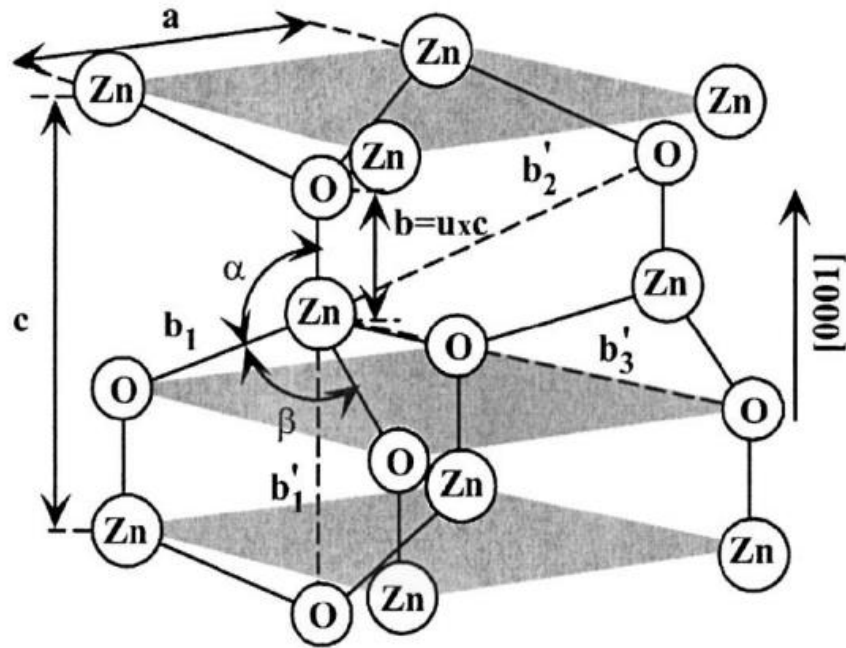


Figure 2.15. Wurtzite hexagonal structure [90]

2.4. Optical Properties of Particle Materials

2.4.1. Light-material interaction processes

There are various ways in which light interacts with matter. The diverse optical properties of solid materials resulting from their interaction with light can be categorized into a few fundamental phenomena. The most fundamental groups consist of reflection, propagation, and transmission. When incident light strikes an optical material medium, as shown in Figure 2.16, some of the light is reflected at the front surface, while the remaining enters and propagates through the medium. If some of this light strikes the rear surface, it could be reflected or transmitted to the opposite side. This means that how reflective the front and back sides are, as well as how light moves through the material, affects how much light is transmitted [91]. Figure 2.17 shows the optical processes that can occur as light propagates across an optical medium.

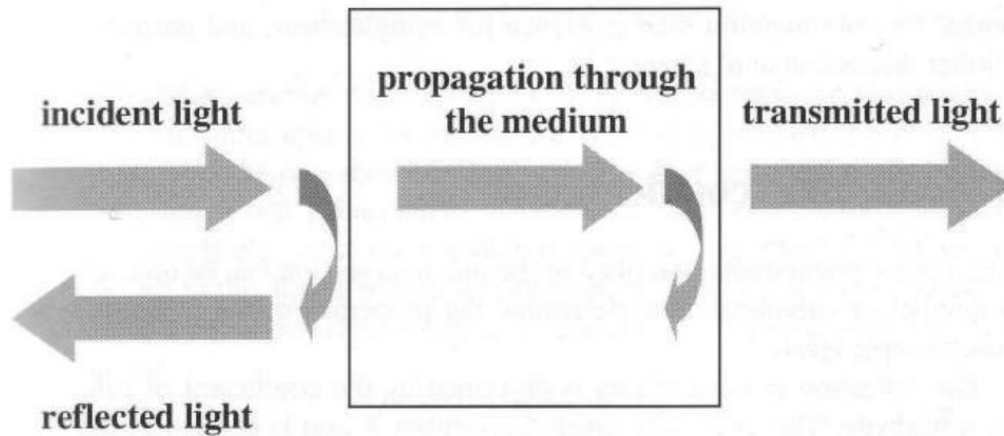


Figure 2.16. Reflected, propagated, and transmitted light through a medium [91]

Refraction, absorption, luminescence, and scattering are the optical phenomena which can occur as light propagates across an optical medium. Refraction causes light rays to propagate at a lesser speed than they do in open space. This decrease in speed results in the bending of beams of light at Snell's law of refraction-defined boundaries. Refraction alone has no effect on light rays' intensity during their propagation. Absorption occurs during the propagation of light when the light frequency is in resonance with the transition frequencies of the atoms of the material medium. In this instance, As the beam travels, it will become attenuated. Transmission of light through the medium is inextricably linked to absorption, as only unabsorbed light transmits [91].

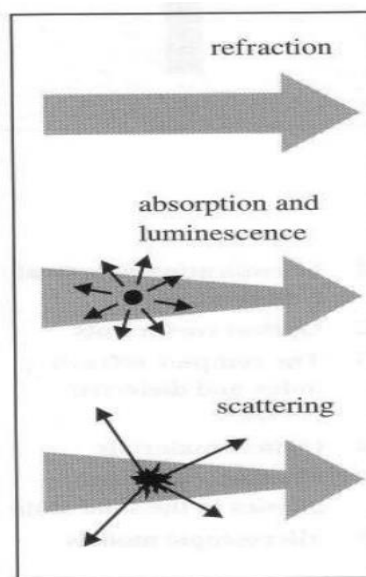


Figure 2.17. Optical processes that can occur as light propagates across an optical medium [91]

The term "luminescence" refers to the spontaneous light emitted by excited atoms in a material (solid state). Light absorption is one of the ways in which atoms can be raised into excited states preceding spontaneous emission. Thus, luminescence can occur in conjunction with light propagation through an absorbing material. The light that is emitted in all directions has a frequency different from the incoming beam. Luminescence is not frequently associated with absorption. Typically, excited atoms re-emit by spontaneous emission after a certain period of time. This implies that the excited atoms may dissipate their excitation energy in the form of heat prior to the process of radiative re-emission. Thus, luminescence efficiency is highly dependent on the dynamics of the atom's de-excitation mechanisms [91]. Scattering is the process by which light rays change direction and, perhaps, frequency as a result of interaction with the material medium. The overall number of photons remains constant, but the amount traveling forward diminishes as light rays are redirected in various directions. As a result, the attenuating effect of scattering is the same as absorption [91]. Scattering gives materials their translucency and opacity [92]. Transparency is described as a substance's capacity to transmit light rays without scattering it (i.e., no internal scattering), which enables small details of an item located behind the material (for example, behind a film) to be clearly discernible. The refractive index of a material is the parameter that specifies its absorption-scattering characteristics. Scattering and absorption are not limited to the optical region of the electromagnetic spectrum; every radiation, regardless of wavelength, is scattered and/or absorbed [92]. When the frequency of the scattered rays of light remains constant, the scattering is referred to as elastic; if there is a frequency change during the process, the scattering is referred to as inelastic. In inelastic scattering, the difference in the energy of the photon must be removed from or provided to the medium depending on whether the frequency increases or decreases. Other phenomena that can result from light propagation through the material when the light intensity is really high are explained by nonlinear optics [91]. Apart from the refractive index, particle size is crucial parameter which determines the scattering characteristics of particulate materials. Although the refractive index of a substance is a fixed property, the particle size can be deliberately selected. As a general rule, a material's scattering power is greatest when its particle size is nearly half the wavelength of the light rays to be scattered. The Lorenz-Mie theory is used to estimate the effect of particle size on a material's scattering

characteristics. However, it has four limiting scenarios based on the particle size, wavelength, and refractive index (see Table 2.3) [92].

Table 2.3. Limiting scenarios of Lorenz-Mie Theory [92]

$d \ll \lambda$	Rayleigh	$p \ll 1$
$d < \lambda$	Rayleigh-Gans-Debye	$p < 1$
$d > \lambda$	Anomalous diffraction	$p > 1$
$d \gg \lambda$	Fraunhofer diffraction	$p \gg 1$

d is diameter, λ is wavelength, $p = 2\pi d(m-1)/\lambda$, $m = n_p/n_o$ = relative refractive index

2.4.2. Light-ZnO powder interaction

Light can be reflected, scattered, or absorbed when it strikes a particle. Equation 2.1 is a basic equation describing light-particle interaction [93].

$$I_{trans} = I_{inc} - (I_{ref} + I_{abs} + I_{sca}) \quad (2.1)$$

In Equation 2.1, I_{trans} is transmitted light intensity, I_{inc} is incident light intensity, I_{ref} is reflected light intensity, I_{abs} is absorbed light intensity, and I_{sca} is scattered light intensity.

The specular reflection of submicron particles is frequently quite low. Scattering and absorption are the primary mechanisms of attenuation, and their relative importance is dependent on the particle size as well as chemical composition [93].

2.4.2.1. Scattering

Rayleigh scattering dominates the scattering of extremely small particles ($< 0.1\lambda$). Mie scattering predominates whenever the particle size is equal to the wavelength of the incident light. This scattering generates an antenna-lobe-like pattern, with much more pointed and intensely forward lobes for bigger particles (see Figure 2.18) [93]. The Mie theory establishes the connection between the particle size of spheres, their refractive index, light wavelength, and the scattering light intensities, together with the scattering efficiency for each size [94]. The Mie-scattering equation is given in Equation 2.2. According to Mie's equation, the scattering intensity is proportional to (d^6) , implying that a large particle scatters more efficiently. Nd^3 is a constant at any given weight. As a result, scattering has a proportionate relationship with (d^3) . For the visible light scattering causing the whitening effect to be minimized, it is more critical to reduce the top size of a distribution than to decrease the mean particle size. On the other hand, when the size is

lowered excessively to avoid a whitening effect, the dominance of UV light scattering is given to absorption. The relative refractive index is another significant parameter in Mie's equation. The media (such as oils) used in the majority of sunscreen formulations have a refractive index in the range of 1.33–1.6. The refractive index of ZnO and rutile TiO₂ are given by 1.99 and 2.76 respectively [93]. TiO₂ pigments exhibit a white appearance, partly because of their high refractive indices [95].

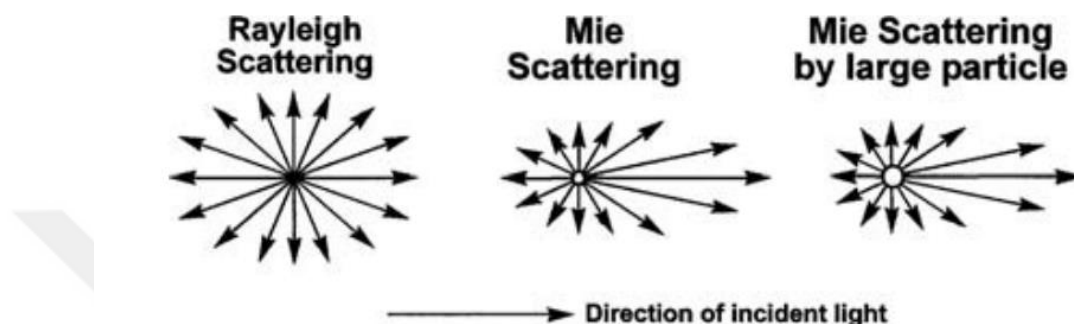


Figure 2.18. Rayleigh and Mie scattering patterns [93]

$$I_s \propto \frac{Nd^6}{\lambda^4} * \left[\frac{m^2-1}{m^2+1} \right]^2 * I_0 \quad (2.2)$$

In Equation 2.2, I_s = scattering intensity, I_0 = incident light intensity, N = number of the particles, d = particle diameter, λ = incident light wavelength, and m = relative refractive index (ratio of the refractive index of particle to the medium).

Using a refractive index of the cosmetic oil (n_{oil} around 1.5) [92], the relative refractive index of ZnO ($n_{ZnO} / n_{oil} = 1.99/1.5 = 1.3$) and that of TiO₂ ($n_{TiO_2} / n_{oil} = 2.76/1.5 = 1.8$). Thus, according to Mie's theory, TiO₂ will scatter light roughly three times as effectively as ZnO [93]. The fact that TiO₂ in sunscreens gets whiter upon rewetting is due to both increased effective particle size due to agglomeration and the removal of the outer oil layers, which raises the refractive index difference. A graphical illustration in Figure 2.19 demonstrates that TiO₂ scatters more than zinc oxide.

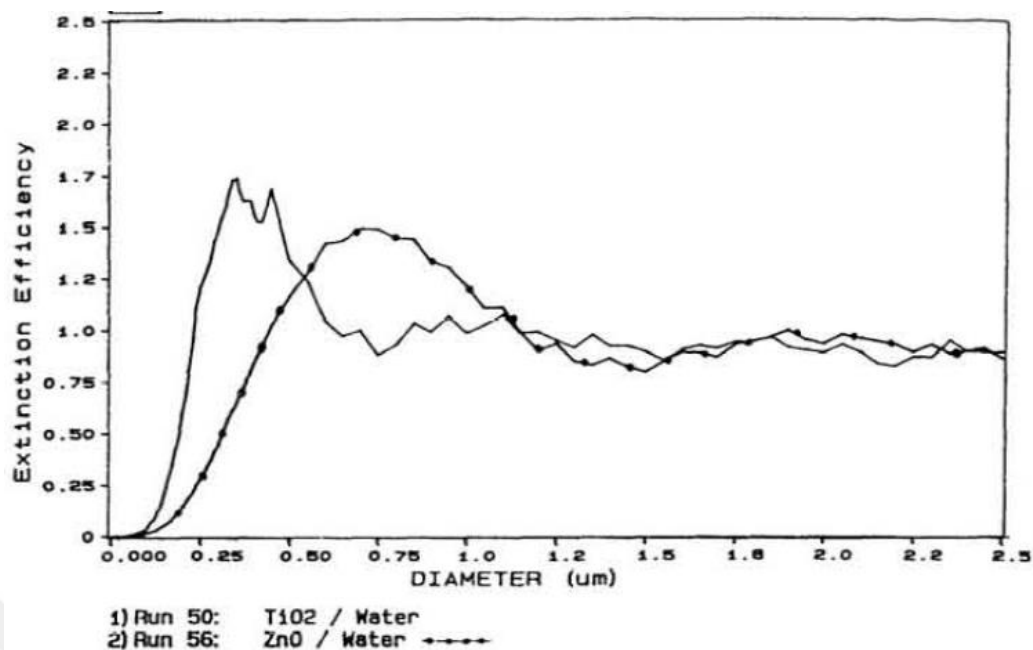


Figure 2.19. Comparison of the scattering efficiencies of ZnO and TiO₂ [92]

ZnO and TiO₂ scattering efficiencies were computed with an integrated value of the white light wavelength (400-700nm). The theory suggests that for every particle size in the colloidal size range ($< 1\mu\text{m}$), TiO₂ is a significantly more efficient light scatterer than ZnO. However, the ZnO function is smoother than the TiO₂ function, indicating that ZnO absorbs more efficiently than TiO₂ in the visible region [92]. Thus, in comparison to TiO₂, ZnO has a reduced whitening effect [95], which is cosmetically unappealing.

2.4.2.2. Absorption

Along with scattering, ZnO particles absorb harmful UV rays. At wavelengths smaller than those in the visible light spectrum, the optical behavior of material, particularly particulate material such as ZnO and TiO₂, becomes more complicated. Apart from particle size, the energy band gap and the crystal structure must now be considered. Each crystal has a characteristic wavelength which excites electron from the valence band into the conduction band. This is how metal oxides like ZnO and TiO₂ obtain their semiconductor characteristics [92]. ZnO and TiO₂ semiconductors have an electronic structure characterized by bands which comprised of orbitals. These Bands are separated by energy gaps where no orbitals exist. When an incident photon of equal or greater energy bandgap interacts with the semiconductor, an electron is excited from the valence to the conduction band and a hole is left in the valence band, as illustrated in Figure 2.20

[95]. This indicates that the wavelength of the light absorbed must be equal to or less than the wavelength that corresponds to the energy band gap (http-10).

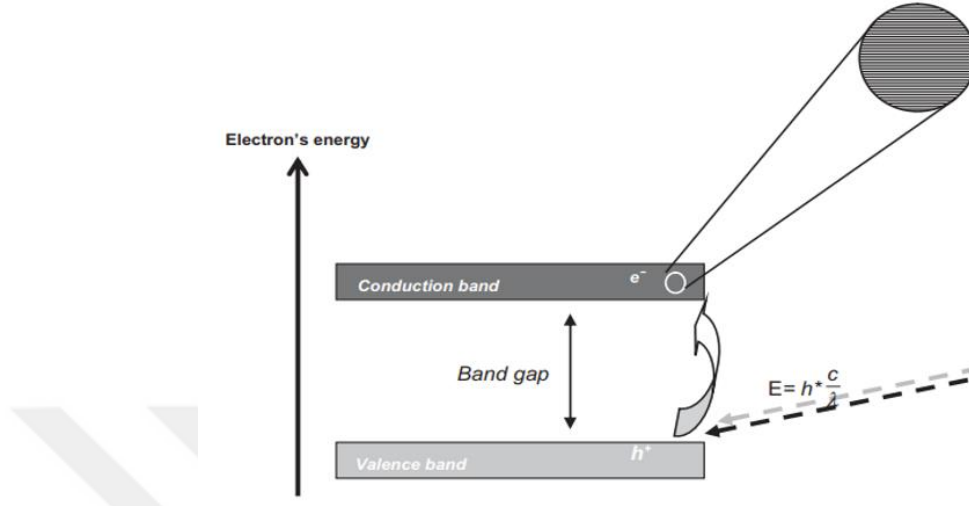


Figure 2.20. ZnO and TiO₂ band gap energy representation [95]

At 77K, ZnO is a broad bandgap semiconductor in which 3.22 eV and 3.32 eV band gap energies were reported for wurtzite and zinc-blende ZnO, respectively. These band gaps can be changed to the wavelength of light required for absorption by using Equation 2.3.

$$E = \frac{h \cdot c}{\lambda} \quad (2.3)$$

In Equation 2.3, λ = wavelength, h = Planck's constant and c = speed of light [95].

Absorption is dependent on the number of particles that interact with the light along its path. When particle size decreases, more particles become available for interaction and hence absorb UV radiation. Owing to an increase in interactions, while the weight of semiconductor (ZnO or TiO₂) is fixed, a smaller particle size will lead to a greater UV absorption. However, the particle size constraint is due to quantum behavior, which happens when the particle is about exciton Bohr's diameter (5nm), none of the commercially available UV filters (TiO₂ or ZnO particles) come close to this size, which implies that the smaller the size of the particle, ideally, the greater the UV absorption [93]. The ZnO crystal structure efficiently absorbs radiation over almost the whole UV spectrum, and TiO₂ is primarily a highly effective UV_B absorber. At 360 nm, approximately 90% of ZnO attenuation is due to absorption, whereas approximately 90% of TiO₂ attenuation is due to scattering. Zinc oxide remains an effective sun blocker

because of its stronger absorption of UV_A radiation. Due to its reliance on scattering for attenuation, microfine particle size TiO₂ is a somewhat weak UV_A sunscreen filter. Larger TiO₂ particles, on the other hand, provide better UV_A protection, but cause skin whitening, which is unappealing to the consumers (see Figure 2.21) [93].

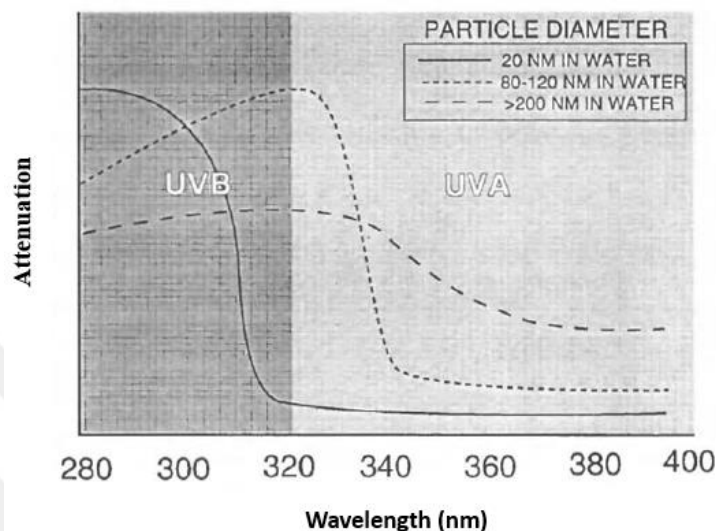


Figure 2.21. Particle size dependent UV characteristics of TiO₂ [93]

2.5. UV Filters Available in the Market

The ZnO UV filters in sunscreens currently available on the market can be classified into conventional ZnO, micron-sized and nano-sized ZnO, and a more recent development in cosmetic powder technology, MicNo-ZnO[®].

2.5.1. Micron-sized ZnO

Micron-sized ZnO formulations comprise of particle size > 100 nm. Due to the large particle size of the micron-sized ZnO, it is considered safe since it does not penetrate the skin (http-23). While micron-ZnO particles are more environmentally friendly than nano-sized ZnO particles, their UV ray's protection per mass is lesser, and an undesired whitening effect upon application is usually unavoidable [96]. This is due to the fact that micron-sized ZnO particles are known for scattering visible light. The interaction of the micron-sized ZnO with the visible light wavelength range is the main reason for exhibiting this phenomenon (http-10). This phenomenon is described below.

2.5.1.1. Mechanism of scattering of visible light by micron-sized ZnO

When light rays strike micron-sized ZnO particles suspended in a medium, they can be redirected in a variety of directions without chemical interaction with the ZnO particles. This effect, referred to as scattering, is dependent on the particle size of ZnO as well as the refractive indices of both the ZnO particles and the suspended medium. It does not require energy conversion; rather, the light rays' energies are scattered in multiple directions. Multiple scattering occurs when light ray which has already been redirected after striking ZnO particle strikes another particle and then redirected in another direction (see Figure 2.22). When light is scattered, it travels in a variety of directions. It can also either go back in the direction of its origin or move forward in the direction it was traveling. These are called back and front scattering, respectively, and they have a contribution to reflection (back scattering) and transmission (front scattering). The visible light scattering by micron-sized ZnO is what gives sunscreens their thick whitish appearance. When the sunscreen scatters the visible light back and away from the sunscreen to our eyes, the back scattered visible light will appear white because the visible spectrum when combined appears white to human eyes, as illustrated in Figure 2.23 (<http-10>).

As earlier pointed out in this chapter, the scattering of micron-sized ZnO particles is greatest at wavelengths twice the size of the ZnO particle. As the conventional micron-sized ZnO particles have a particle size greater than 200 nm, they scatter light rays of wavelength ($\lambda = 400$ nm), including visible light which causes unappealing whiteness on the skin, as illustrated in Figure 2.24 (<http-10>). This serves as a major drawback to the use of conventional micron-sized ZnO in are commercial sunscreens.

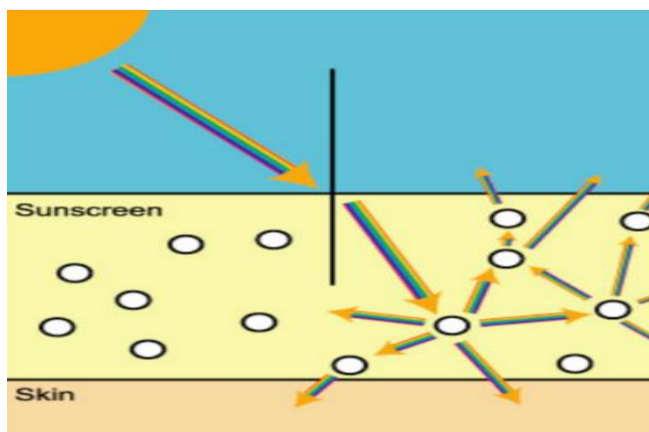


Figure 2.22. Multiple scattering of micron-sized ZnO particles (<http-10>)

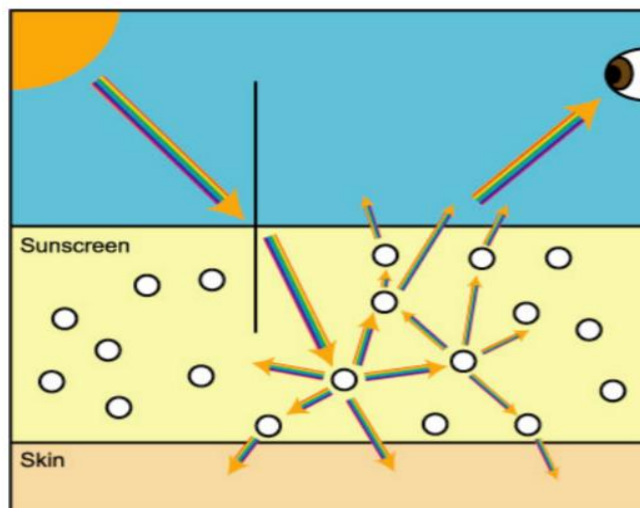


Figure 2.23. Back scattered light rays appearing white in the eyes (<http-10>)

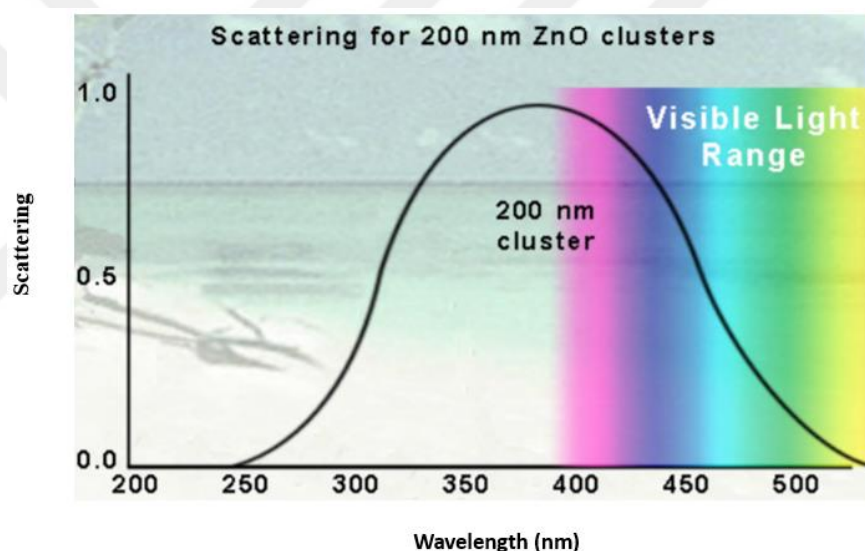


Figure 2.24. Scattering of convectional micron-sized ZnO (<http-10>)

2.5.2. Nano-sized ZnO

Nano- sized ZnO formulations comprise of particle size $< 100\text{nm}$. Despite the fact that micron-sized ZnO is regarded as the safer alternative, sunscreen formulators choose nano-sized ZnO. This is because nano-sized ZnO is a great UV filter ingredient. Compared to micron-sized ZnO, nano-sized ZnO offers greater protection from UV radiation per mass percentage and may cover a larger surface area per mass percentage. Additionally, its high level of transparency (resulting from its small size) makes it look and feel better on the skin (<http-23>). Along with the challenge of synthesizing nano-sized ZnO particles, there is an additional challenge of dispersing the particles, which frequently clump together. This poses two issues: first, when particles clump, UV light

absorption might be spotty; and second, the effective particle size increases, thereby increasing the likelihood that the particles scatter visible light and look white when applied to skin (http-10). Moreover, it has been reported in the literature that nano-sized ZnO UV filters can penetrate through the skin due to their size and can possibly be harmful to humans [97] and the environment (http-23), [98]. The safety of the nano-sized ZnO is a major drawback to its usage in commercial sunscreens.

2.5.3. MicNo-ZnO[®] particle

MicNo-ZnO[®] is a patent-protected commercial product that allows for the incorporation of nano-sized ZnO advantages into micron-sized ZnO in the research areas of cosmetic and semiconductor technology [99]. The name "MicNo" is coined from the micron and nanoparticle sizes of ZnO. MicNo is made up of micron-sized ZnO hexagonal platelets and nano-sized spherical primary particles (see Figure 2.25). The first three letters of "MicNo" are based on the first three letters of micron, and the last two letters are based on the last two letters of nano. This novel powder was designed to maximize the benefits of both micron-sized and nano-sized ZnO while minimizing their drawbacks. A comprehensive in vitro toxicity test demonstrates that MicNo-ZnO[®] particles are significantly more biocompatible than ZnO nanoparticles [3]. A study conducted by Demirel et al. demonstrates MicNo-ZnO[®] particles exhibit excellent antimicrobial activity, especially when doped with Ag, compared to nano-sized ZnO particles. This has positioned this novel MicNo-ZnO[®] particle as excellent choice for various industrial applications [100].

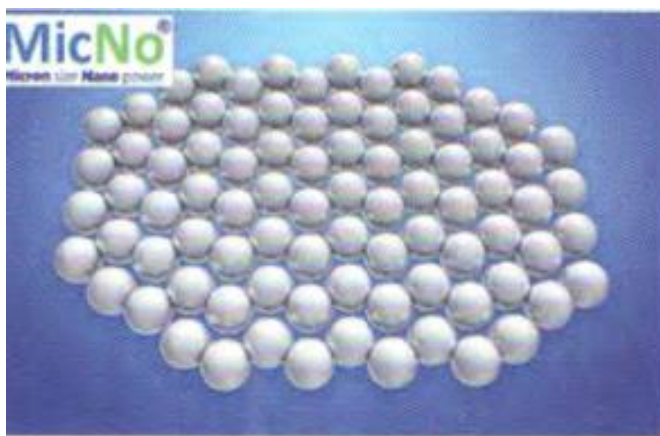


Figure 2.25. MicNo-ZnO[®] hexagonal platelet with spherical fine primary particles [98]

In another study where the phytotoxicity activities of MicNo-ZnO[®] and nano-sized ZnO available on the market were carried out using green beans, MicNo-ZnO[®] was not found in the root tips of the plant, but a significant amount of commercial nano-sized ZnO was observed in the root tips. This has clearly demonstrated that MicNo-ZnO[®] is environmentally friendly [96]. The MicNo-ZnO[®], which is composed of spherical primary fine ZnO particles that have been firmly bonded to produce hexagonal platelets, offers broad spectrum UV-rays protection, and guarantees greater surface coverage during usage, consequently increasing UV efficacy and minimizing the volume of active ingredients used in sunscreen formulations. The MicNo-ZnO[®] morphology and the particle size are shown in Figure 2.26.

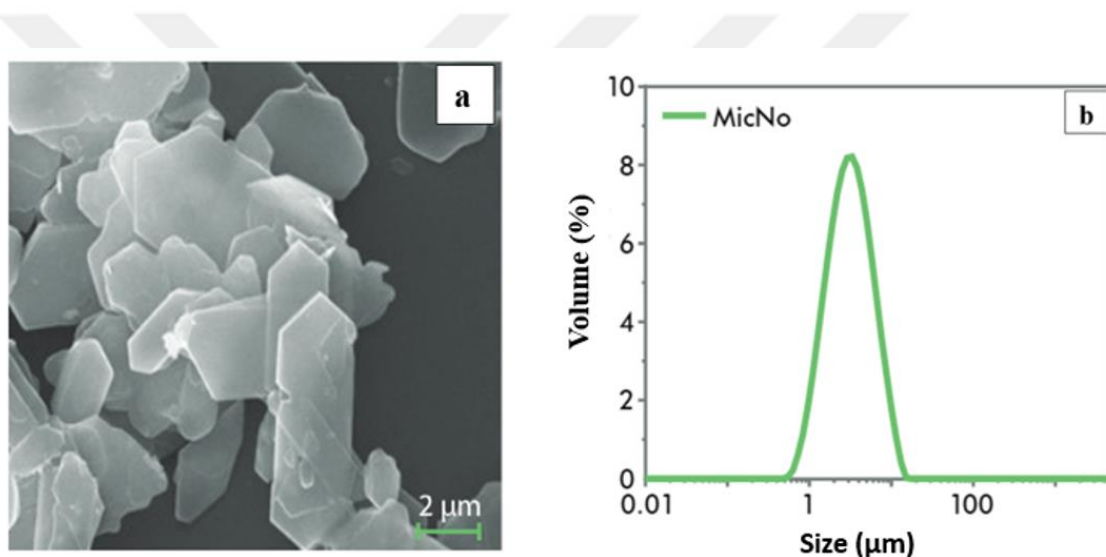


Figure 2.26. Morphology and particle size distribution [96]

The primary fine particles give a high SPF (see Figure 2.27) and visible light transparency, while the micron-sized platelet structure (see Figure 2.26a) gives a great skin feel as well as prevents skin penetration, as demonstrated in the graph in Figure 2.26b [98]. The comparison of MicNo-ZnO[®] characteristics to convectional micron-sized and nano-sized ZnO particles available on the market as well as its excellent broad-spectrum protection in the UV ranges with good light protection are shown in Table 2.4 and Figure 2.28, respectively.

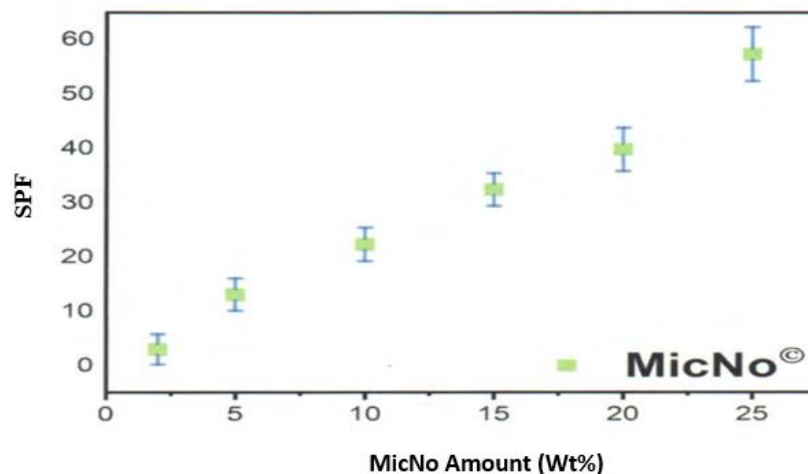


Figure 2.27. Correlation of MicNo-ZnO[®] amount in formulations and SPF [98]

Table 2.4. MicNo-ZnO[®] characteristics [98]

Attribute	Micron	Nano	MicNo [®]
UV protection per mass (Unless they are agglomerated)	Low	High	V. High
Transparency	No	V. High	High
Surface cover per mass (Unless they are agglomerated)	Low	High	V. High
High Energy Visible Light/ Blue Light protection	High	Low	High
Level of toxicity	Low	V. High	Low
Uncontrolled agglomeration	High	V. High	Low
Level of phytotoxicity	Low	V. High	Low

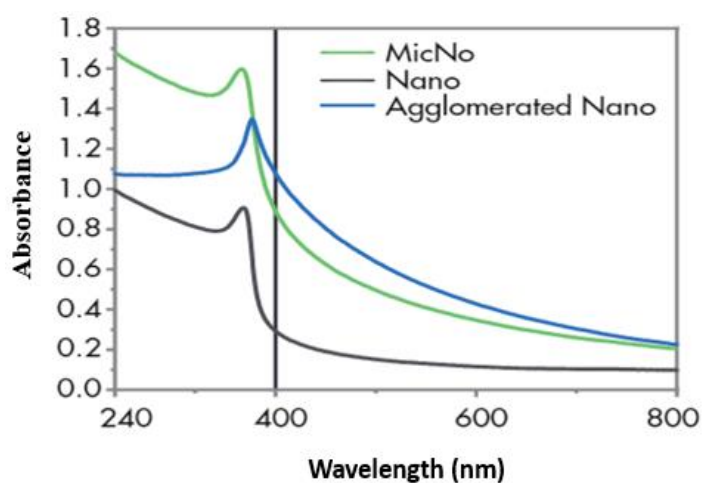


Figure 2.28. Excellent broad-spectrum protection of MicNo-ZnO[®] [96]

2.6. Previous Studies and Research Objectives

As pointed out briefly at the introductory part of this thesis, the optical properties of ZnO are dependent on its shape and particle size. In a study conducted by Kiomarsipour et al. using five hydrothermally synthesized ZnO of different morphologies and sizes to investigate ZnO pigment with high scattering efficiency in aerospace coating applications, it was demonstrated that the particle size and shape of ZnO powders had a significant effect on their optical characteristics. The nanoparticle surface-decorated ZnO pigment exhibits the highest UV/VIS/NIR specular reflectance, which is a function of its multiple scattering characteristics [101]. The study by Johnson et al. used a Mie scattering based model to investigate the scattering efficiency of ZnO pigment in a potassium silicate matrix and demonstrated that a narrow particle distribution size with its center positioned at $0.35\mu\text{m}$ exhibits the largest overall scattering coefficient. The study concluded that ZnO pigment with an optimized particle distribution size will have a scattering efficiency of about 2–10 times greater than its unoptimized counterparts [102]. Egerton and Tooley examined scattering coefficients of ZnO nanoparticles of 50-200 nm size range within 300 -540 nm wavelength range and reported nanoparticle size of ZnO and radiation wavelength relation in terms of the scattering's properties. From this study, it can be concluded that the scattering coefficient is strongly dependent on the particle size and shape of the ZnO nanoparticles. Egerton and Tooley stated that it is critical to determine the optimal particle size of the mineral sunscreen filters and maintain that size throughout the sunscreen formulation as well as the film on the skin to assure sunscreens' UV efficacy [7]. Penttilä and Lumme examined the scattering efficiency of nanoparticles based on their shape (see Figure 2.29) in the visible range ($\lambda = 545\text{ nm}$) and estimated scattering coefficients for various nanoparticle sizes and shapes. The results indicate that the scattering coefficient (and consequently the scattering efficiency) is greatly dependent on the size and shape of the nanoparticles and decreases after attaining the maximum value [8].

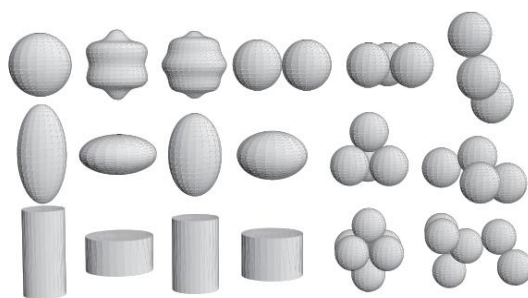


Figure 2.29. Particle geometries studied by Penttilä and Lumme [8]

As demonstrated in the literature and briefly discussed above, the size and shape of nanoparticles have a significant effect on their optical properties. It is therefore critical to research the scattering, reflection, and absorption properties of ZnO particles in detail based on their shapes and sizes in order to determine their utility in sunscreen products. With the excellent properties of MicNo-ZnO[®] described earlier, it is of uttermost importance to investigate its optimum particle size and shape along with other commercially available micron-sized and nano-sized ZnO powders of various shapes and sizes that can offer maximum sun protection both in the UV and blue light wavelengths. Therefore, the research objective of this study was first to develop an understanding about the relationship between particle characteristics and their attenuation (absorption+scattering) capabilities of harmful UV rays and then by using this understanding contribute to the optimization of sunscreen products in terms of ZnO particle size ranges and shapes.

3. SUNSCREEN FORMULATION

3.1. Sunscreens Available in the Market

Sunscreen products found on the market can be divided into two broad categories based on their intended use, namely, primary and secondary sunscreens. Primary sunscreens are designed mainly to offer protection against the damaging effects of UV rays, whereas secondary sunscreens are designed primarily for other cosmetic purposes but contain sunscreen filters that provide these products with UV radiation protection benefits. Secondary sunscreens include daily moisturizing creams, facial foundations, anti-aging creams, etc. [9]. Primary sunscreens, which serve primarily as a substance that can help protect the skin from damaging UV rays, are available in emulsion (cream and lotion), oil, ointment, spray, gel, stick, butter, paste, mousse, shake-well and powder dosage forms (formats) on the global market [103], [104]. A dosage form (sunscreens format) is the final physical product that comes from combining active and inactive ingredients in a specific ratio that people can hold, buy, and utilize [9]. Sunscreen dosage forms come under the general cosmetic dosage forms as shown in Figure 3.1. While each of these dosage forms has distinct advantages, they can all provide protection from the sun when utilized properly (http-24). For dry skin as well as the face, creams seem to be best suited. Gels are beneficial for areas with excessive hair, like the chest or the scalp. Sticks are excellent for use in the vicinity of the eyes, and parents occasionally choose sprays because they are simple to apply to children (http-25).

3.1.1 Emulsions

An emulsion is composed of a minimum of two immiscible liquids in which one is dispersed in the other as droplets. The droplets form the internal phase while the other liquid forms the external phase. Emulsions are the most common type of sunscreen dosage form because they provide a range of textures (creams and lotions, sprayable lotions, and thicker lotions). Perhaps another benefit of emulsions is that water-soluble and oil-soluble cosmetic ingredients can be added to them. Emulsions are categorized into two: oil-in-water (O/W) and water-in-oil (W/O). In an oil-in-water emulsion (O/W), the oil phase is dispersed in water in the form of droplets (internal phase), while water forms the external phase [9]. Stabilization is really the primary objective when formulating sunscreen emulsions, as all emulsions tend to separate. Emulsifiers are usually combined surfactants or one surfactant that bind and maintain the phases in the emulsified condition [105]. In O/W emulsion type, an emulsifier coats the oil droplets'

surfaces, increasing their miscibility with water. As shown in Figure 3.2, this helps to prevent the oil phase from rising to the surface [9].

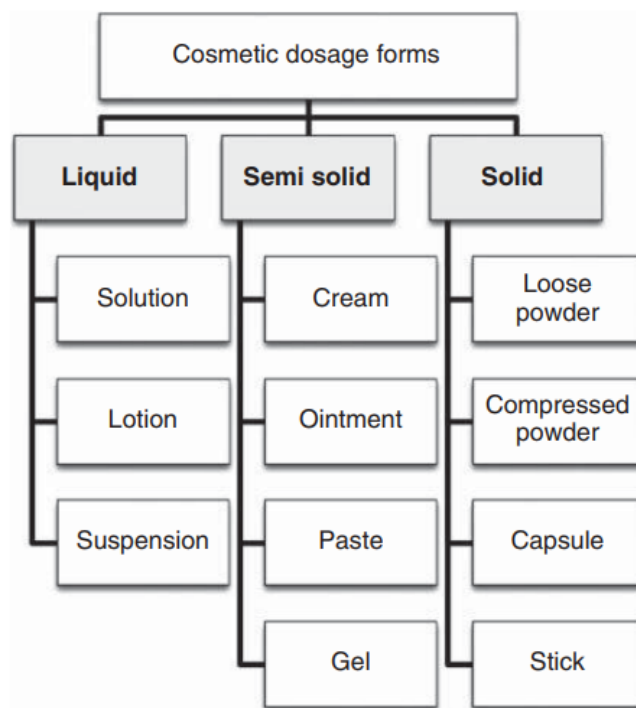


Figure 3.1. General cosmetic dosage forms [9]

Oil-in-water (O/W) emulsions are widely known because they provide a more appealing skin feel as well as a relatively low cost of production. On the other hand, water-in-oil emulsion (W/O) has water as the internal phase and an oily external phase and is therefore sticky and greasy, making it more water-resistant. The stability of an emulsion can be affected by the droplet (internal phase) size, density difference of the phases present, viscosity of the external phase (continuous phase), types and amounts of emulsifiers used, and the final temperature at which the product is kept. Typically, two types of emulsions are used in sunscreens: lotions and creams, which can be distinguished based on their viscosity [9]. Lotion is a low-viscosity (< 50,000 centipoise) liquid emulsion that is made to be applied to the skin without rubbing vigorously. Lotions typically contain a greater proportion of water phase, making them less greasy and thus easy to wash off the skin. On the other hand, creams are semisolid emulsions with a high viscosity (often in the range of 150,000–500,000 centipoise). They contain a greater oil phase, making them greasier, including the O/W types [9], [106]

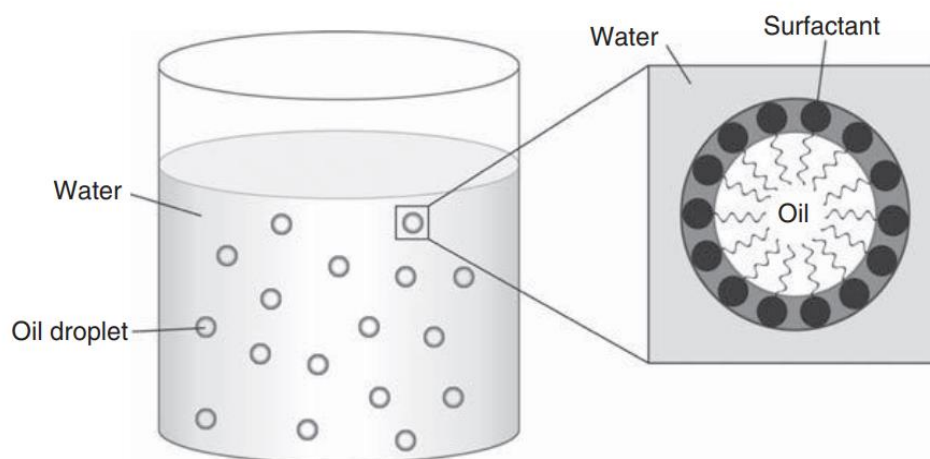


Figure 3.2. *Oil-in-water emulsion* [9]

3.1.2. Sticks

Sticks are made available in the form of lip balms, lipsticks, and baby sticks. They are intended for use on smaller skin areas, like the nose and lips, as well as for infants. However, utilizing sticks on a larger skin area, such as an adult's legs and back, could be time-consuming [9]. The large proportion of sticks is made up of oils or oil-soluble sunscreens thickened with petrolatum and waxes. Sticks have a greasy or oily texture and are probably the most water-resistant sunscreen dosage form available [106]. They offer water-resistance properties and increased efficacy because of their anhydrous nature but are expensive to produce [9].

3.1.3. Mousses

Generally, this is an emulsion lotion that has been loaded with propellant. When the sunscreen product is released into the atmosphere's lower pressure (as opposed to the pressure within the sunscreen container), foam is produced as the propellant flares. These foams are more similar to shaving creams than other product categories. Most mousses employ anionic emulsifiers (e.g., triethanolamine stearate), which are frequently combined with a small proportion of nonionic (e.g., ethoxylates). Also, active UV filters are simple to introduce into the droplet (internal phase) of their O/W emulsions. Non-aerosol mousses available on the market utilize foaming surfactant and apply high mechanical pressure in order to force the emulsion through a mesh, thereby producing the foam. Due to the surfactant's high hydrophilicity, preventing such a sunscreen from washing away will be extremely difficult [106].

3.1.4. Aerosols

They can be propellant or mechanical (pump spray) based, and are often oil-based, which increases their cost and often diminishes their effectiveness [106]. Aerosol sprays are a very common type of sunscreen. The multiposition spraying nozzles enable easy and fast application, covering a reasonably large area of the body and allowing for coverage of even difficult-to-reach regions. However, a typical issue is improper application and the amount of sunscreen applied is considerably less than what the U.S. FDA recommends. Aerosol sprays are often alcohol-based sunscreen products that incorporate organic UV filters that are soluble in alcohol. Due to the fact that physical sunscreens are insoluble in alcohol, they are generally not made as aerosol sprays [9].

3.1.5. Ointments

These products are chemically and functionally identical to the stick products. Generally, they are composed of esters and mineral oil thickened with petrolatum and various waxes. Their primary advantage is that they are difficult to wash off with water; hence, they are utilized by individuals who require a sunscreen that will remain on the skin during swimming or any other sport. They are unattractive to use due to their oily and greasy nature [106].

3.1.6. Oils

Oils are among the earliest and easiest sunscreen vehicles to manufacture. Due to the fact that there is just one phase, great product stability is easily achieved. Because the majority of sunscreen active ingredients are lipophilic, they dissolve in sunscreen oils, simplifying the process of production, especially when compared to emulsion synthesis. Oils are simple to apply to the skin and quickly distribute to cover a large surface area. One disadvantage of sunscreen oils is that their superior spreadability results in an extremely thin and transparent film, which reduces their SPF. Another impediment to their widespread use is the high cost of production. Because of the anhydrous nature of this system, with no water to offset the high raw material cost, sunscreen oils are among the most costly types of sunscreens available [106].

3.1.7. Gels

Gels have a pleasant skin feel and are rapidly absorbed; nevertheless, ensuring water resistance for these kind of sunscreen formulations is rather difficult. Furthermore, the active substances that may be employed in this dose form are extremely limited. Another downside may be irritation if the sunscreen formulation contains alcohol [9].

Sunscreen gels are classified into four main formulation groups: namely, aqueous gel, microemulsion gel, gelled oleaginous (i.e., oily anhydrous) and hydro-alcoholic gel. Each of these groups presents a plethora of formulation challenges to sunscreen formulators [106].

3.1.7.1. Aqueous gel

This gel usually contains sunscreens soluble in water or utilizes solubilizers (typically nonionic surfactants) in high concentrations to enable the gel to remain clear at any extreme temperature. Neither of these techniques yields satisfactory results, as the resulting sunscreen product is highly susceptible to washing away when exposed to either water or excessive sweating. The higher amount of surfactant in the final formulation can make it both pricey and, more significantly, irritating. Topping it off, these gels have a lot of batch-to-batch variability due to the extremely precise raw material balance necessary to produce clarity. The addition of a suitable gum is frequently used to achieve gel formation. Cellulose-based materials, which are also employed for this purpose, are used in very significant amounts (2–3 percent) to get the desirable structure of the gel. However, the final product can be very sticky with this amount of use. Carbomers seem to be the most commonly used thickeners enabling the sunscreen formulators to obtain crystal clarity at decent levels (0.5–1.0 percent). However, the carbomers have issues with compatibility, appearance, and efficacy. Owing to their anionic nature when neutralized, any cationic additives must be avoided in the formulation, otherwise gel disintegration will occur. The carbomers can cause a temporary tackiness, which is particularly noticeable during skin application. This is especially noticeable in gels, and the use of emollient esters has to be restricted or avoided to guarantee maximum clarity. Carbomers are also highly sensitive to electrolytes present on the skin. As a result, its gel breaks when it is put on the skin, resulting in a product with poor application properties. Swimming in saline water or excessive sweating worsens this effect [106].

3.1.7.2. Microemulsion gel

Because the particle size of microemulsion gels is small (i.e., $< 0.25\ \mu\text{m}$), light appears to pass directly through the emulsion, resulting in a clear gel. The microemulsion gel can have an appealing skin feel and can leave a thick, smooth, and uniform layer on the skin, effectively increasing the SPF. Producing clear microemulsion gels typically requires 15–25 percent emulsifier, which results in a more expensive final product. Consequently, the high percentage of emulsifiers employed in these gels can result in low

water resistance as well as increased skin irritation. Producing microemulsion gels also comes with a lot of challenges. For example, small changes in raw ingredients can and often do make products that are cloudy or murky [106].

3.1.7.3. Oleaginous gel

Oleaginous gels are similar to ointments in many ways, except that they are clear, while ointments have a translucent or opaque appearance. These products are not common in the market owing to their difficulty of manufacture and high cost. They are usually made by gelling sunscreen and mineral oil mixtures using gellants such as fumed silica, etc. [106].

3.1.7.4. Hydro-alcoholic gel

As its name suggests, the major carrier constituents of this gel are alcohol (typically ethanol) and water (which often comes from the alcohol). A great advantage offered by this vehicle is a desired cooling effect on the skin, which is really refreshing, especially during summer. Because the majority of lipophilic sunscreens appear to be miscible with ethanol, using alcohol reduces the need for special solubilizers to a large extent. The common problems of hydro-alcoholic gel include low water resistance, eye or facial sting, low efficacy, and increased cost of product packaging due to coating. Although its water resistance property can be enhanced through the addition of resins and some other film formers, humectants are employed to mitigate the facial stinging problem, and film formers are used to reduce the vaporization of alcohol when exposed to heat and sunlight, which results in low SPF. However, these problems are never completely solved [106].

3.1.8. Wipes

The most recent formulations are presumably wipes, which resemble wet facial wipes. These sunscreen formulations are pre-moistened and emollients as well as other moisturizers are added to the cloth wipes, which could offer extra benefits [9].

3.2. Sunscreen Compositional Ingredients

The three primary components of sunscreen formulations are UV filters, emollients, and emulsifiers. Photostabilizers, boosters, sensory enhancers, and film formers are other components typically included in the formulation (see Figure 3.3) [104]. Other important ingredients include thickeners, antioxidants, water, waterproofing agents, preservatives, humectants, chelating agents, propellants (applicable to aerosol sunscreens), pH modifiers (neutralizers), colorants, fragrances, natural ingredients (e.g., aloe vera, etc.) are also included in sunscreen formulations. While UV filters are known as the active

components of sunscreen, other ingredients different from the UV filters are termed inactive components [9].

3.2.1. UV filters

UV filters (organic, inorganic, and hybrid) are undeniably the primary active components required for UV radiation protection [104]. Additionally, botanical substances rich in antioxidants can be employed as inactive components to protect the skin from the life-threatening effects of sun exposure (for instance, photoaging, wrinkling, and pigmentation) [35].

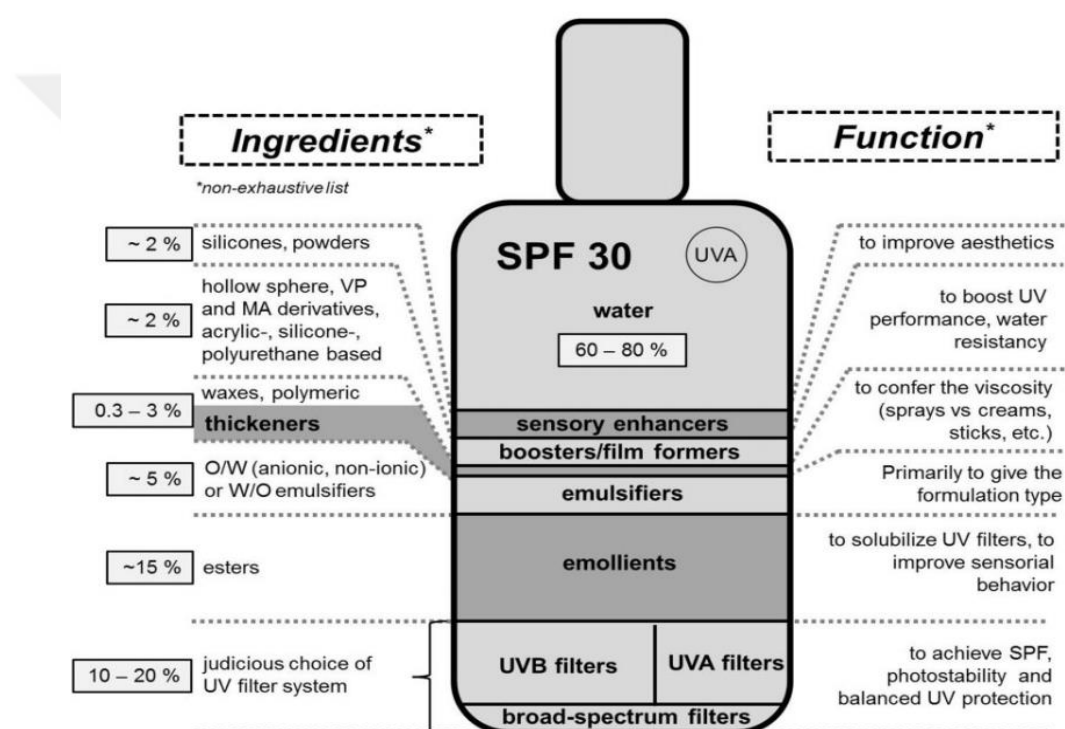


Figure 3.3. Sunscreen ingredients and their functions [104]

3.2.2. Emollients

Emollients, in addition to UV filters, are critical components of sunscreens, and their functions include solubilizing, sensorial enhancing, and photostabilizing properties [104]. While both oil- and water-soluble emollients exist, oil-based significantly outnumber water-soluble emollients. They impart a velvety skin texture upon application and serve as a medium for the delivery of the oil-soluble formulation. Esters (solid or liquid), mineral oils, waxes, silicone compounds, and fatty alcohols are all examples of fatty emollients [106]. Emollients (such as benzoate esters and phenethyl benzoate)

facilitate the solubility of active UV filters as well as the uniform distribution of active UV filters within the sunscreen formulation. Certain emollients have been reported to exhibit photostabilizing characteristics, especially for organic UV filters. These emollients include but are not limited to polyester-8, ethylhexyl methoxycrylene, tridecyl salicylate, etc. Emollients have a significant effect on how the skin feels in the aspects of spreadability, greasiness, and stickiness. Emollients like propylheptyl caprylate, coco caprylate, dibutyl adipate, and dicaprylyl carbonate are specifically used for sunscreen formulations, as they effectively disperse crystalline UV filters while offering a non-greasy, light skin feel [104].

3.2.3. Emulsifier system

This system determines the type of emulsion, which is either O/W or W/O. By and large, O/W systems are chosen because they are easier to distribute and also have a lighter skin feeling. Water (external phase), which vaporizes primarily during application, may also produce a refreshing and pleasing feeling. Emulsifiers are categorised as cationic, anionic, non-ionic or amphoteric based on their major chemical charge [107]. Anionic emulsifiers like sodium cetearyl sulfate, C20–22 alkyl phosphate, and potassium cetyl phosphate are frequently employed in sunscreens in low quantities because they enable the addition and stability of mineral UV filters [104].

3.2.4. Rheology modifiers

These are thickeners that are used in sunscreen formulations. They have an effect on how the sunscreens are applied, how they spread, and how effective they are [104]. These include carbomers (e.g., hydroxypropyl cellulose), gums (e.g., xanthan gum), polymers (e.g., acrylates), and lipophilic thickeners (e.g., waxes). In W/O, thickeners like organophilic clays and fumed silica and some commonly used waxes like glycerides, fatty acids, and fatty alcohols as well as ester waxes are incorporated into the external phase (oil). In comparison to fumed silica, waxes do not thin on shear. In some cases, starch, cellulose, and hydrophilic clay-based viscous enhancers may be used in O/W systems, but in most cases, synthetic polymers based on acrylates are used for the thickening systems. When a synthetic polymer-based thickener and a mineral UV filter are included in a sunscreen formulation, care should be taken in selecting the synthetic polymer-based thickener and the mineral UV filter, as synthetic polymers have poor compatibility with mineral UV filters. Also, when natural gums like xanthan gum are utilized, they mostly provide a stabilizing effect instead of a thickening effect. [104].

3.2.5. Boosting ingredients

These ingredients are utilized in order to increase the efficacy of UV filters as well as to improve the film forming property of the sunscreen formulation on skin. Because of their light scattering properties, hollow copolymers materials made of styrene and acrylates added to the formulation can help increase the optical pathlength of UV rays. This makes it more likely that UV rays will interact with UV filters, which attenuate the UV radiation before hitting the skin surface, thereby increasing the efficacy of the UV filter. Film formers improve UV efficacy by either enhancing the film-forming characteristics of sunscreen upon application, resulting in a more homogenous distribution of the UV filters on the skin, or through enhancing the water resistance property of the sunscreen [104].

3.2.6. Sensory enhancers

To produce an aesthetically pleasing sunscreen formulation, sensory enhancers can be incorporated. These are primarily powders or silicone fluids/powder form that assist spreading, decrease greasiness and, tackiness. Powders can adsorb oil, improve spreadability, produce a matte or powdery finish, minimize tackiness, and even offer a velvety feel, based on their particle shape and size [104].

3.3. Formulating Sunscreens with ZnO

The popularity of zinc oxide inorganic UV filters in sunscreen formulations is increasing. According to Gripp et al. ([http-26](#)), between 2017 and 2018, the number of sunscreens released in the United States that contained ZnO as the sole UV active ingredient rose by 20 percent. This was based on data obtained from Mintel ([http-26](#)). Appropriate formulation procedures must be used to optimize zinc oxide's performance in sunscreens. Usually, the active UV filter, its correct dispersion and solubility in the emulsion, and the homogenous distribution of the active UV ingredient particles on the skin are all critical aspects in achieving optimal efficacy [104]. Figure 3.4 shows the ideal situation when the sunscreen is uniformly distributed on the peak and valley of the skin surface. However, it is improbable that a homogeneous film thickness will be achieved as depicted in Figure 3.4.

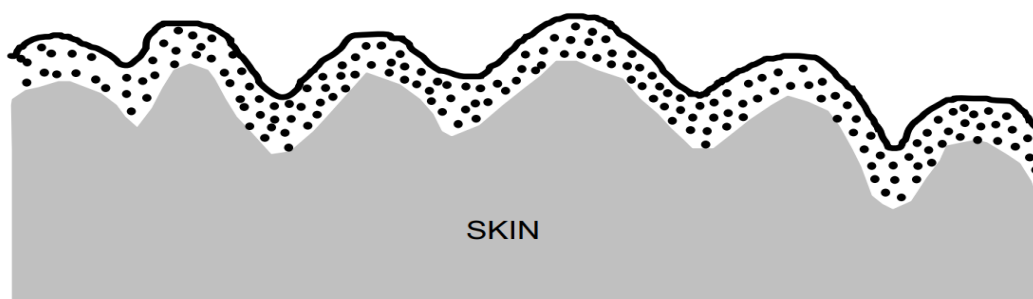


Figure 3.4. *Homogeneous distribution of sunscreen on skin surface under ideal situation* [108]

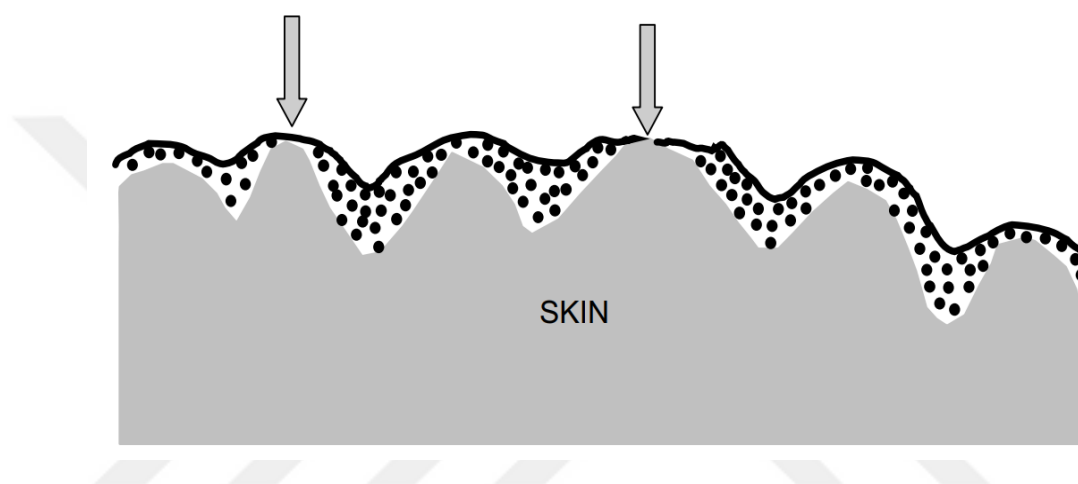


Figure 3.5. *Non-uniform sunscreen coverage on the skin's surface* [108]

The actual scenario is almost certainly more similar to that illustrated in Figure 3.5, where the sunscreen film is somewhat gathered into the skin's valley, while the peaks receive only a thin layer, if any at all. Arrows in Figure 3.5 point to areas where the sunscreen layer is thin or absent, allowing UV rays to penetrate the skin. This vast thickness variability of the sunscreen layer has a significant detrimental effect on its efficacy [104], [108]. The level of film inhomogeneity is formulation dependent, most notably on the type of emulsion used for the formulation, film viscosity and rheology, as well as the inclusion of film-forming agents [104]. Formulating sunscreen products with a high Sun Protection Factor (SPF) value is dependent on whether or not effective film-forming agents are used and how well the active UV filters are evenly distributed in the film. Incorporation of an effective film forming agent will help to improve the situation in Figure 3.5, leaving fewer peak areas uncovered and thereby increasing the SPF value of the film [108].

3.3.1 Factors affecting film-forming

The factors affecting film-forming are generalisable regardless of the type of active utilized. These factors can be described under rheological and de-emulsification behaviours.

3.3.1.1 Rheological behaviour

To obtain uniform skin coverage, the sunscreen product must first spread widely across the surface of the skin to produce a film which must possess some structure to guarantee coverage across the skin's valleys and peaks. As a result, the rheological properties of the sunscreen product have a significant impact on its SPF performance. Spreading a sunscreen product across the skin surface is a high shear rate procedure, generally in the range of 10^3 s^{-1} to 10^4 s^{-1} [108]. Thus, it is the product's behaviour under and right after the shear removal that influences film-forming and thus SPF. With respect to rheological behaviour, the primary criteria for a high SPF value include:

1. Low viscosity at high shear rates.
2. Short time for recovery following spreading on the skin surface (i.e., quick restoration of viscosity and structure following the removal of shear).
3. The value of thixotropy should be low and finite [108].

Thixotropy is a more complicated parameter since it is dependent on additional rheological parameters such as viscosity at rest, shear viscosity, and recovery time. Because measured thixotropy values are contingent on the rheological measurement conditions, they are difficult to compare, except if they are obtained at similar conditions. Sunscreen dosage forms exhibit rheological behaviour similar to Newtonian fluids and viscoelastic behaviours. For instance, sunscreen oils, which usually have low viscosity, exhibit the same behaviour as Newtonian fluids, where shear has no effect on viscosity. Although sunscreen oils are extremely effective at initial spreading on the skin surface, film-forming is typically poor due to the lack of structure, and thus, they are typically confined to lower SPFs. The majority of other sunscreen formats such as emulsions, mousses, gels, and sticks display viscoelastic behavior. That is to say, they have viscous liquid flow behaviour and elastic solid flow behaviour. Sunscreen products that have the rheology described above can be made such that they mostly behave like liquids during high shear, enabling spreading, and mostly behave like solids when there is very little shear in order to keep the structure of the film intact. The tactics for

optimizing rheology are dependent on the type of emulsion, O/W or W/O. In W/O emulsions, for instance, the water evaporation rate is very low, and waxes and rheological modifiers have been observed to increase their SPF values. This has also been linked to quicker recovery times following shearing. Another technique used to optimize the rheology of W/O emulsions is by increasing the amount of internal (water) phase, which in turn increases the viscosity. For O/W emulsions, the situation is complicated due to rapid water evaporation during the rubbing of the sunscreen products on skin, which causes a constant change in the rheology as a result of the constant change in the emulsion constituents. Some sunscreen formulation ingredients have an effect on O/W rheological behaviour. They include emulsifiers, fatty alcohols or acids, hydrocolloids, as well as liquid crystal structures often added to the O/W emulsion system [108].

3.3.1.2. De-emulsification

The disintegration of the O/W emulsion as discussed above has an effect on film-forming. Oil droplets merge to produce a film while the water phase vaporizes. To achieve maximum efficacy in sunscreen products, this film must be as homogeneous as it can be, with the UV filters spread uniformly throughout it [108].

3.3.2. Basic criteria for obtaining optimum performance

Hewitt [108] has laid out three basic criteria for obtaining optimum performance when formulating with ZnO particles. These include

1. Choose a UV filter with the optimal particle size as well as particle size distribution.
2. Ascertain UV filter particles are distributed uniformly all through the emulsion.
3. When the sunscreen is utilized, ensure that the particles are distributed evenly on the skin's surface [108].

The first point listed above is closely related to one of the objectives of this thesis. The second point is very dependent on the type of ZnO particle coating (hydrophobic or hydrophilic) and predispersion/preformulation used (in terms of the organic emollients), the type of emulsion, and the various other elements included in the sunscreen formulation. The last point has to do with film rheology. Another parameter that is crucial, especially when formulating an O/W emulsion system with ZnO, is the pH. For instance, when the pH has a value of less than 6, zinc oxide becomes more soluble and migrates from the oil phase to the water phase [108].

3.3.3. Formulation basic principles

Due to the fact that a large portion of sunscreen in the market are emulsions (lotions and creams), it is critical to grasp the complexities of designing this most difficult type of sunscreen products. It has always been challenging for sunscreen formulators to formulate an emulsion to meet the market demand in terms of efficacy, cost, and aesthetic appeal. Perhaps the most challenging part is the stabilization of the emulsion after production. However, by grasping the fundamental emulsification principles and combining them with a good blend of experience obtained via several trials, significant progress can be made in this pursuit [106]. As stated earlier in this chapter, an emulsion is composed of a minimum of two immiscible liquids in which one is dispersed in the other as small droplets. The droplets form the internal phase while the other liquid forms the external phase. These small droplets are always attempting to merge into a single bigger droplet. Emulsion formulators must have as their primary objective the prevention, or more practically, minimization, of this particle interaction. This interaction can be explained by Stokes' law shown in Equation 3.1.

$$V = \frac{[d^2 (\rho_1 - \rho_2)g]}{18\eta} \quad (3.1)$$

From Stokes' law, V denotes the sedimentation (interaction) velocity assuming spherical particles, d denotes the diameter of the dispersed phase's particles, ρ_1 and ρ_2 denote the dispersed (internal) and continuous (external) phase's specific gravities, respectively, g and η denote the acceleration due to gravity and the external phase's viscosity, respectively [106]. It is observed that the way to avoid instability of emulsion resulting from sedimentation is to reduce the rate of sedimentation of particles, which is either done by reducing the numerator or increasing the denominator values. Three parameters can be seen from the expression in the numerator, namely d , ρ , and g , where g is not manipulable. For parameter d , the first practical approach to reducing its value is placing the sunscreen emulsion under shearing forces using a homogenizer machine, which mechanically reduces the large dispersed particle diameter as well as gives a uniform particle size distribution [106]. The second approach to reducing d has been reported by [109]. This approach has the potential to significantly reduce manufacturing costs and produce a great emulsion. The approach to reducing the numerator in Stokes' law using ρ explores the possibility of making the values ρ_1 and ρ_2 closer, thus making their difference, $\rho_1 - \rho_2$, very small. For instance, in an O/W emulsion with oil and water

internal and external phases respectively, ρ_1 , the specific gravity of the oil phase is usually in the range of 0.80–0.95 while that of the water phase, ρ_2 , is 1. The approach explored to reduce the ρ_2 value a bit less than ρ_1 is by incorporating alcohol into the water phase. However, the emulsion dramatically disintegrates due to the good solvency of alcohol with numerous emulsifiers; thus, the emulsifier is extracted from the oil/water boundary and the emulsion disintegrates. Incorporating alcohol into the water phase is therefore not a viable option [106]. The second option of reducing the rate of sedimentation (V) of particles as well as obtaining a more stable sunscreen emulsion through the increment in the denominator value of the Stokes' law can be done using the viscosity parameter of the external phase (η). There are many approaches to this, which include the addition of more internal phases. This can be successfully applied to both W/O and O/W at ambient temperature and will bring about an increase in η value. However, the emulsion undergoes thinning at higher temperatures, resulting in instability [106]. Another approach is to decrease the particle size to the point that the same internal phase amount seems to fill a larger volume, which then results in an increase in viscosity. An even more important method is to incorporate a fatty moiety into the water phase (in the case of O/W, the external phase) to initiate the formation of liquid crystals, which results in a significant increase in viscosity. Moreso, a simple method of increasing the η value in Stokes' law is by the addition of a certain thickener to the continuous phase. This, at a higher temperature, enables the emulsion to maintain its viscosity [106]. As one of the basic criteria for optimum performance above said, making sure that the ZnO particles are evenly dispersed in the emulsion requires an adequate repulsive force between the ZnO particles to keep them from agglomerating when they come near each other. This is accomplished through electrostatic or steric repulsion, which must be maintained to ensure that the ZnO particles are effectively dispersed [108]. Inorganic UV filters are often surface-coated (hydrophilic coating, e.g., silica and alumina; hydrophobic coating). The electrostatic repulsion is typically utilized to maintain well dispersed inorganic oxides (silica and alumina) particles in water, either by using the particles' intrinsic surface charge or by adding a dispersant with a charge of its own. In any instance, the isoelectric point (IEP) is a critical parameter for maintaining the dispersion. Charges (positive and negative) are present on the surface of all inorganic UV filters particles. The dispersion of these particles in water can exert a significant influence on the interparticle forces [108]. While the overall charge is negative at higher pH values, it is positive at

lower pH values. Between these two points, there is a pH value where the positive charges are equal to the negative charges (i.e., no net surface charge) [108]. This value is called the point of zero charge [110]. The isoelectric point is the value of the pH when the electrokinetic potential is zero. If no other ions apart from the ones that determine potential, such as H^+ and OH^- , adsorb at the surface, the isoelectric point is equated to the point of zero charge. For pure oxides in water, this is a common occurrence [110]. Figure 3.6 is applicable when this condition occurs.

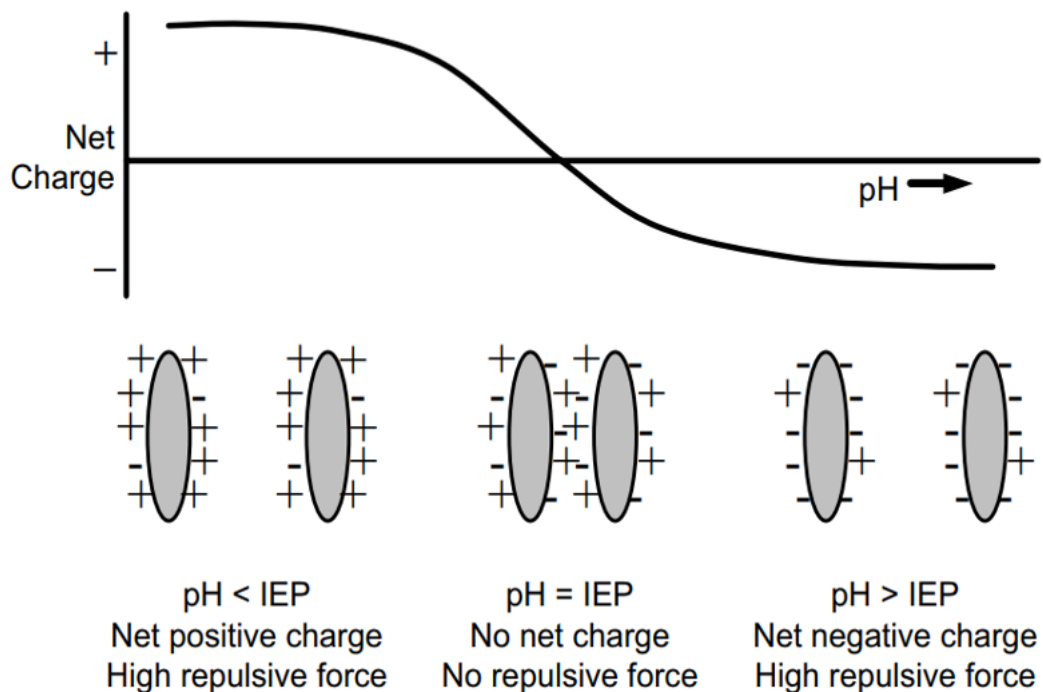


Figure 3.6. The pH effect on the overall charge on the surface of particles [108]

Because the isoelectric point is a surface characteristic of the particle, it is dependent on the surface coating as well as on the dispersant utilized. The isoelectric point is usually prevented during formulation, as the absence of electrostatic repulsion associated with this point allows particles to form agglomerates that are very difficult to disintegrate. As a result, when formulating with hydrophilic particles dispersed in the aqueous phase, pH control is crucial [108]. Inorganic filters can also be surface-coated with hydrophobic particles. In this instance, surfactants or polymers are utilized to maintain the dispersion by providing steric repulsion in between the particles. The molecular structure of these dispersing agents is crucial and must contain an anchor group that interacts with or adheres to the surface of the particle, as well as a stabilizer

component that stretches through into the carrier medium and is solvated by it. When hydrophobic particles are dispersed in water, the anchor and the stabilizer ought to be hydrophobic and hydrophilic, respectively, such that the anchor is properly solvated by water to give steric repulsion. A benefit of this kind of dispersion is that the repulsions are not pH-dependent; hence, they lack an isoelectric point and can therefore be employed across a wide pH range [108]. When mineral UV filters are applied to the oil phase, the charges on the surface of the particles are insulated, making the electrostatic repulsive forces low. Steric repulsion therefore performs a significant function in dispersing the particles. This is accomplished by either coating the particles using organic or silicone compounds or by using a dispersion agent that forms an interaction with the surface of the particles. Oftentimes, for both water and oil dispersed particles, the best performance is obtained when the mineral sunscreen is utilized in a stabilized predispersion form. This predispersion can be obtained by milling the mineral sunscreen filters in the carrier medium and adding an appropriate dispersing agent. If predispersion, which makes mineral sunscreens more effective, is optimized. Other factors that affect the SPF of mineral sunscreens depend on the phase (oil or water) in which the particles are added [108].

3.3.3.1. Formulating sunscreen with ZnO dispersed in the water phase

Formulating products containing ZnO dispersed in water phases are not uncommon. However, one problem with dispersing ZnO in the water phase is that it forms alkaline complexes that raise the pH of the formulation products to a higher value, which may not be suitable for the skin. As a result, ZnO is typically added into the formulation's oil phase. On the other hand, ZnO is extremely hydrophilic and readily migrates from oil to the water phase. This process is accelerated if the water phase has a pH value of less than 6. This is because the solubility of ZnO particles in the water phase dramatically increases below pH value 6. The migration and solubility of ZnO particles results in an increase in pH as well as contributes towards reducing its efficacy provided that inadequate measures are taken to ensure the particles are well dispersed within the aqueous phase [108]. These issues can be mitigated or solved in a number of ways, one of which involves the utilization of optimized predispersion that assists in keeping the ZnO particles in a finely dispersed state within oil phase. Such dispersion approaches are adequate to minimize migration and maintain ZnO efficacy in W/O emulsions. Additionally, ZnO can be surface-coated with hydrophobic compounds to inhibit migration. In either instance,

additional formulation strategies are required to totally remove migration from O/W emulsion systems or to limit its impacts. For hydrophilic surface coated ZnO dispersed in the water phase of the O/W emulsion, evaporation of the water phase occurs during the sunscreen emulsion application on the skin (see Figure 3.7), and after the emulsion dries on the skin, the spreading is discontinuous, thereby resulting in a low SPF value (see Figure 3.8) [108]. This problem can be addressed by incorporating liquid crystal (lamellar structure). Surfactants such as "polyglyceryl esters, glyceryl stearate, sucrose esters, and sorbitan esters" can all be used to create this structure. The lamellar structure houses the ZnO particles and helps to transfer the ZnO particles into the oil phase when de-emulsification occurs as a result of vaporization of the water phase, thereby leading to better skin coverage (see Figure 3.9). Although the particles are unlikely to be found within the lamellar in the case of a hydrophobic coated ZnO particle, the hydrophobic ZnO surface means that as evaporation of the water phase occurs, the particles will naturally move into the emulsion oil phase. As a result, lamellar structures are therefore not needed to maintain homogeneous particle dispersion in the oil phase [108].

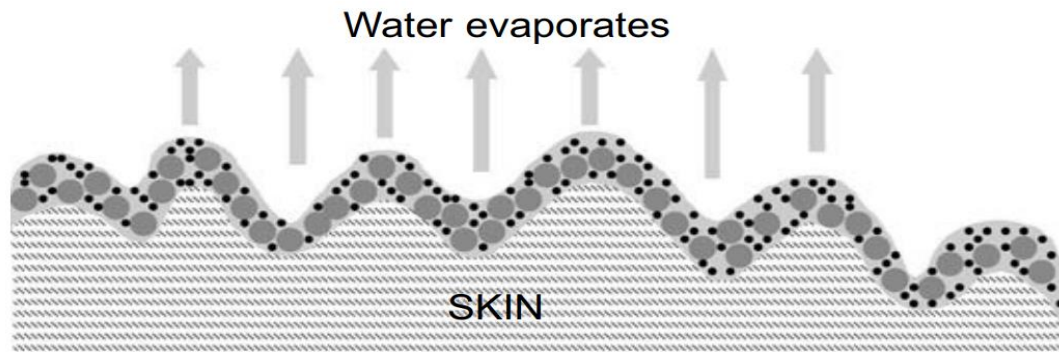


Figure 3.7. *Evaporation of the water phase in water dispersed ZnO emulsion [108]*



Figure 3.8. *Discontinuous coverage resulting water phase evaporation [108]*

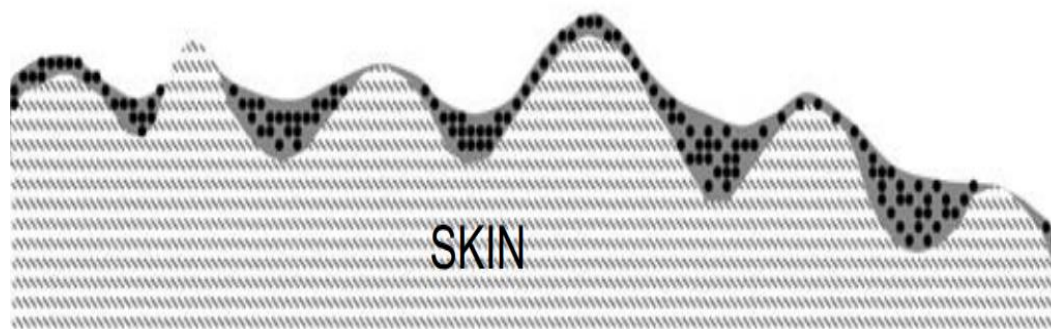


Figure 3.9. Better skin coverage achieved through the incorporation of liquid crystalline structure [108]

3.3.3.2. Formulating sunscreen with ZnO in the oil phase

Both hydrophobic and hydrophilic ZnO can be utilized to formulate a stable oil-based dispersion with the right dispersing agents. Also, they can both be employed successfully in W/O and O/W and emulsions. Other components in the sunscreen formulation have the potential to influence the SPF offered by mineral sunscreen filters in two ways:

1. Adjusting the particle's degree of dispersion
2. Adjusting the degree to which the sunscreen product covers the skin surface effectively.

Consider the utilization of ZnO that has been dispersed in the oil phase of an O/W emulsion. In this situation, we enhance the degree of dispersion through optimizing ZnO particle dispersion in the oil phase using appropriate emollients or through adjusting the oil phase's droplet size. Effective skin coverage is accomplished through optimizing the emulsion's rheology, adjusting the droplet size, and utilizing film-forming agents [108].

3.3.4. Techniques for optimizing the performance of zinc oxide (ZnO) in sunscreen formulations

3.3.4.1. Dispersion

Good dispersion is critical for a sunscreen to function optimally. It enhances not only the UV ray protection but also the stability of the sunscreen products while decreasing whitening and increasing cosmetic attractiveness. To achieve a proper dispersion, appropriate emollients and proper processing procedures are utilized. Optical microscopy can be very useful in determining whether or not the dispersion is adequate. When a dispersion is looked at through an optical microscope, it

should have a uniform distribution of ZnO particles and not agglomerate to get a good result (http-26).

3.3.4.2. Dispersion of ZnO in oil phase

It is advisable to add ZnO as the final raw material in the oil phase when the oil phase is still hot, as this permits other solids to first melt. When zinc oxide is added to the oil phase, the oil phase viscosity decreases significantly. The oil phase mixture is then thoroughly mixed to moisten the particles, expel trapped air, and homogenize the phase mixture in order to optimize dispersion. The mixture must be homogenized thoroughly during emulsification; the ZnO particles should be invisible to the human eye and resemble paint. It is recommended that the final sunscreen product be "black-surface tested" to guarantee homogeneity and appropriate dispersion (http-26).

3.3.4.3. Dispersion of ZnO in water phase

For untreated ZnO particles, a water-dispersed approach may be explored. Pre-treatment with a water-soluble emollient or humectant can aid in dispersion. After this, it is recommended to mix thoroughly in the water phase until a homogeneous emulsion is achieved. A pH value of at least 7.1 is suggested. Below the pH value of 7, Zn^{2+} (divalent zinc ions) is formed, moves to the aqueous phase, and induces formulation instability. Zn^{2+} is capable of reacting with film formers, emulsifiers, and rheology modifiers. Utilizing a coated ZnO particles aids in reducing ion migration. Zn^{2+} is toxic to polymers (acrylate-derived), as it reacts and forms complexes with them, causing polymer matrix disruption and degradation of stability. This effect is exacerbated by using uncoated ZnO. Chelating agents are beneficial in the water phase. Chelating substances, like "disodium EDTA," might help mitigate the severity of these interactions by assisting in the binding of many of the ions which may be produced during the sunscreen formulation process. The pH value may increase during the formulation of the sunscreen. When the pH value of the formulation exceeds 7.5, buffering chemicals such as "lactic acid, citric acid, or others" are added to reduce the pH to a value not less than 7.1 (http-26).

3.3.4.4. Selection of emollient

Emollients are often chosen for their aesthetically pleasing addition to a formulation. However, other properties like polarity must be considered in their selection. ZnO particles that have not been treated require emollients with high polarity to produce homogenous dispersions, which should be incorporated into the oil phase. Emollients with a high polarity, such as "dibutyl adipate or cocoglycerides," are good fits for

untreated ZnO. Moreover, ZnO particles that have not been treated can be incorporated into the water phase. ZnO pre-mixed with an emollient soluble in water aids in dispersion and facilitates the integration of the water phase.

ZnO particles with a surface treatment provide great dispersion with a broader spectrum of emollients based on the coating. It takes less polarity in the emollient to get the best dispersion if the coating is more hydrophobic. Triethoxycaprylylsilane coated ZnO dispersed in a number of different types of emollients performed differently at ambient temperature. In contrast to cocoglyceride emollients, which have a higher polarity, emollients with low polarity, including "hydrogenated polyisobuten (http-26).

3.3.4.5. Choice of rheology modifier

The distinction between nonionic types of rheology modifiers and their ionic counterparts is very crucial. The nonionic type of rheology modifier is the best choice when utilized alongside inorganic UV filters. Xanthan gum, cellulose-based thickening agents, including "hydroxyethyl cellulose and hydroxypropylmethyl cellulose," and clays are all suitable thickeners for inorganic filters. Ionic types of rheology modifier have an effect on pH, UV performance, and aesthetic appeal. ZnO that has not been coated is problematic with ionic types of rheology modifiers (e.g., carbomers). While coated ZnO may be employed cautiously, the emulsion is prone to separation or displays characteristics of instability over time (http-26).

3.3.4.6. Emulsion type and choice of emulsifier

ZnO disperses easily in W/O or O/W emulsions. However, for inorganic sunscreen formulations, W/O emulsions are often advised. While W/O emulsions often have much better UV performance owing to a more uniform coating on the surface of the skin, it is feasible to achieve comparable UV performance in O/W sunscreen formulations. W/O emulsions impart a heavier, more pleasant feel to the formulation while also providing water resistance. The primary benefit of W/O is that pH is unimportant since the continuous phase is oil. Nonionic emulsifiers such as "polyglyceryl-3 diisostearate and polyglyceryl-2 dipolyhydroxystearate" are excellent choices for W/O emulsions. O/W emulsions impart a lighter, greater luxury feel to the product, which the consumer values highly. If an O/W emulsion formulation requires water resistance, water-resistant polymers have to be considered for utilization in the emulsion formulation. For O/W emulsions comprising ZnO, it is recommended to utilize only nonionic types of

emulsifiers as well as rheology modifiers. It is advised to avoid the ionic emulsifiers, particularly in O/W systems, since they may produce a pH change (increases or decreases), impairing the formulation's stability and affecting the aesthetic attractiveness and UV filtering efficacy of the emulsion products. "Glucosides, stearates, and oleates" are all examples of nonionic emulsifiers suitable for O/W systems. It is advised that the sunscreen formulation have a pH value of at least 7.1 and use nonionic thickening agents or natural gums. At higher loads of ZnO, the oil droplet density becomes higher than the aqueous phase, resulting in droplet agglomeration and settling. If this situation happens, it is advisable to increase the amount of both the emulsifiers and rheology modifiers. Whether producing a W/O or O/W emulsion, it is critical to follow the appropriate steps in order to achieve optimum dispersion. Proper dispersion is critical for reducing whitening and enhancing the formulation products' efficacy, cosmetic appeal, and stability (http-26).

3.4. Sunscreen Testing

After the formulation of sunscreens, they are subjected to certain tests in order to ensure that they possess the minimum standard requirements recommended by the regulatory authorities of the region where they are produced or utilised. These tests can be classified into biocompatibility tests and performance tests. A test such as a physiochemical test is also carried out to ensure the sunscreen possesses the properties and requirements to exhibit its sun protection ability.

3.4.1. Important terminologies

The understanding of some essential terminologies used in describing sunscreens is of uttermost importance. These terms include sun protection factor (SPF), broad spectrum protection, critical wavelength, etc.

3.4.1.1. Sun protection factor (SPF)

The SPF is the ratio of the energy needed to achieve MED (minimal erythema dose, i.e., sunburn or skin redness) when sunscreen is used to the energy needed to induce the same reaction when sunscreen is not used (see Equation 3.2). According to the US Federal Register, SPF represents the amount of UV radiation needed to induce one MED with a 2 mg/cm² sunscreen application on skin divided by the amount of UV radiation needed to induce one MED with no sunscreen application [9], [111].

$$SPF = \frac{MED_{Sunscreen\ application}}{MED_{No\ sunscreen\ application}} \quad (3.2)$$

The SPF value is used to ascertain how long it takes to stay in the sun without burning. For instance, according to theory, if an individual normally burns after 10 minutes in the sun when sunscreen is used, utilizing a sunscreen product with an SPF value of 15 may allow for approximately 150 minutes in the sun prior to having skin burn. Sunscreen products with an SPF value of 15 offer approximately 92 percent protection against UVB radiation; sunscreen products with an SPF value of 30 offer approximately 97 percent protection against UVB radiation, and so on [111]. Table 3.1 and Figure 3.10 show the percentage of UV rays filtered from and transmitted through the skin based on the sunscreen SPF value. SPF is only effective against UVB rays, while protection in the UVA ray region is only 10 percent UVB rating in sunscreens [111]. The SPF value of a sunscreen product can be determined using in vitro, in vivo, and in silico techniques.

Table 3.1. *UVB penetration reduction in percentage based on sunscreen SPF value [112]*

SPF	UV _B Absorption (%)*
2	50
4	75
8	87.5
15	93.3
20	95
30	96.7
45	97.8
50	98

*UV_B absorption (%) = 100 - (100/SPF)

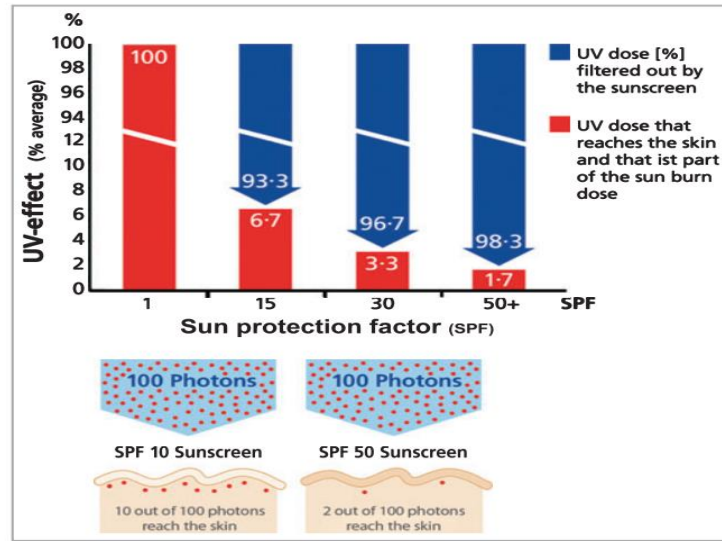


Figure 3.10. Filtered and transmitted UV rays based on SPF value [113]

3.4.1.2. Broad spectrum protection

This is used to denote the protection from UVA and UVB rays. It has been demonstrated that even sunscreen products with a high SPF rating do not offer adequate protection in the UVA region, which causes photoaging and skin cancer. As a result, protection against UVA and UVB radiation is necessary to avoid the long-term consequences of sun exposure [9].

3.4.1.3. Critical wavelength

The critical wavelength is used to establish if a sunscreen product can be labelled broad spectrum or not. It is used to denote the wavelength under which 90 percent of the entire UV absorbance curve area is found when the UV absorption measurement is taken from 290 to 400 nm. The sunscreen product must show at least 370nm mean critical wavelength before it can be labelled as broad-spectrum sunscreen [112]. Mathematically, critical wavelength is given in Equation 3.3.

$$\int_{290}^{\lambda_c} A(\lambda) d\lambda = 0.9 \int_{290}^{400} A(\lambda) d\lambda \quad (3.3)$$

In Equation 3.3, λ_c = critical wavelength, $A(\lambda)$ = mean absorption at every wavelength, and $d\lambda$ = between-measurements wavelength interval (http-27).

3.4.2. Method of testing sunscreen

The methods usually used for testing sunscreen products involve scientists monitoring individual volunteers in controlled testing of SPF as well as persistent darkening of the skin colour. In another way, sunscreen product efficacy can be measured

by spreading the product on a glass as well as an acrylic plate and then using a device known as a spectrophotometer to determine the quantity of light that passes through it. Furthermore, a mathematical model can also be used to figure out how a sunscreen can protect against the sun's rays considering the amount and types of active ingredients in the formulation. Evaluating the ability of sunscreen to prevent some UV ray attributed skin damages is an unusual but possibly quite important method. Each of these methods outlined above has advantages and disadvantages (http-28).

3.4.2.1. *In vivo methods of testing sunscreen (ISO 24442: 2011)*

The US FDA mandates that all sunscreens marketed in the United States be tested through the exposure of ten individual volunteers to UV lamps of high intensity. The following day, experts look for reddening on their skin. The FDA allows sunscreen producers to disregard three of the ten test subjects' results and base the labelled value of SPF on the dose of UV that induced sunburn in the other seven individuals. This method results in higher SPF values on sunscreen product labels. The use of volunteers for SPF tests is costly, and others claim that exposing individuals to harmful doses of UV light is morally wrong. The *in vivo* SPF testing method has the advantage of measuring direct skin response to UV lamp irradiation, but one important issue is that this test is unable to distinguish between UV_A protection that is good and poor (http-28). Additionally, the SPF testing results can differ significantly from one laboratory to the next, and usually, high SPF value sunscreen products are the most prone to poor repeatability. Another approach related to *in vivo* SPF testing is the test known as immediate pigment darkening (IPD). Here, individual volunteers are exposed to UV_A II rays to determine the amount of skin tanning that occurs. However, the IPD tests do not indicate the level of protection offered by the UV_A I rays. IPD testing is not required by the US FDA and, based on the paucity of data available, this testing method does not appear to be extensively employed. However, some sunscreen producers state that they do IPD tests for their sunscreen products (http-28).

3.4.2.2. *In vitro methods of testing sunscreen (ISO 24443: 2012)*

A spectrophotometry can be used in the lab to measure UV absorption. Scientists add a thin layer of sunscreen to an acrylic plate or quartz plate and measure the amount of UV reflected and what amount travels through the plate. *In vitro* testing is much cheaper and more repeatable than other testing methods. They can measure UV_A absorbance in the UV_A I range, unlike tanning. The data can be used in a variety of ways

to determine the amount of UV_A absorption and can be converted to a UV_A protection factor. The controlled laboratory setting makes calibration easier, but the kind of UV lamp utilized, the nature of the plate, and the degree of homogeneity of the sunscreen product on the plate can all affect the results (http-28).

3.4.2.3. In silico methods of testing sunscreen

These are UV protection models developed for the purposes of forecasting the efficacy of sunscreens, and they are based on the active components indicated on every product label as well as inactive components that may stabilise the sunscreen formulation. With the aid of Beer-Lambert's law, the model determines the amount of light that will travel through a sunscreen as well as the UV_B and UV_A protection. BASF's UV protection model is one of the in-silicon methods accessible to sunscreen formulators (http-28).

4. MATERIALS AND METHOD

Under this chapter, materials, chemicals, instruments, and procedures utilized in the experimental investigations, as well as experimental design, are discussed.

The primary chemical, ZnO, utilized in this study was obtained from different commercial sources. As shown in Table 4.1, MicNo-ZnO®, which is a patent-protected commercial product developed by Entekno Materials Inc. (Turkey), as well as other commercially available ZnO powders from two other suppliers in Turkey, were utilized. Other reagents and sunscreen formulation ingredients from various suppliers are shown in Tables 4.2 and 4.7, respectively.

Table 4.1. ZnO powders obtained

ZnO Powder	Supplier
MicNo-ZnO®*	Entekno Materials Inc.
30-50nm Spherical ZnO**	Nanografi Nano Technology
25-35nm Nano ZnO**	Nanografi Nano Technology
Sub-micron ZnO*	Hepsen Chemical Industry and Trade Limited Company (Hepsen Kimya)

*ZnO powders obtained from Suvaci Research Lab

** ZnO powders purchased with BAP funding

Table 4.2. Other reagents utilized

Reagent	Supplier/ Equipment
Isopropyl Alcohol (IPA)	Isik Kimya
Deionized Water	Millipore, Milli-Q Device

Apart from the chemical materials, other materials used are shown in Table 4.3.

Table 4.3. Other materials utilized

Material	Supplier
PMMA Plate (Helioplate HD6; 50 mm x 50 mm x 1.5 mm)	HelioScreen Labs
Microscope Slide Glass	IsoLab
Aluminium Foil	-
Sellotape	-

The method employed for this study is depicted on the flow chart shown in Figure 4.1.

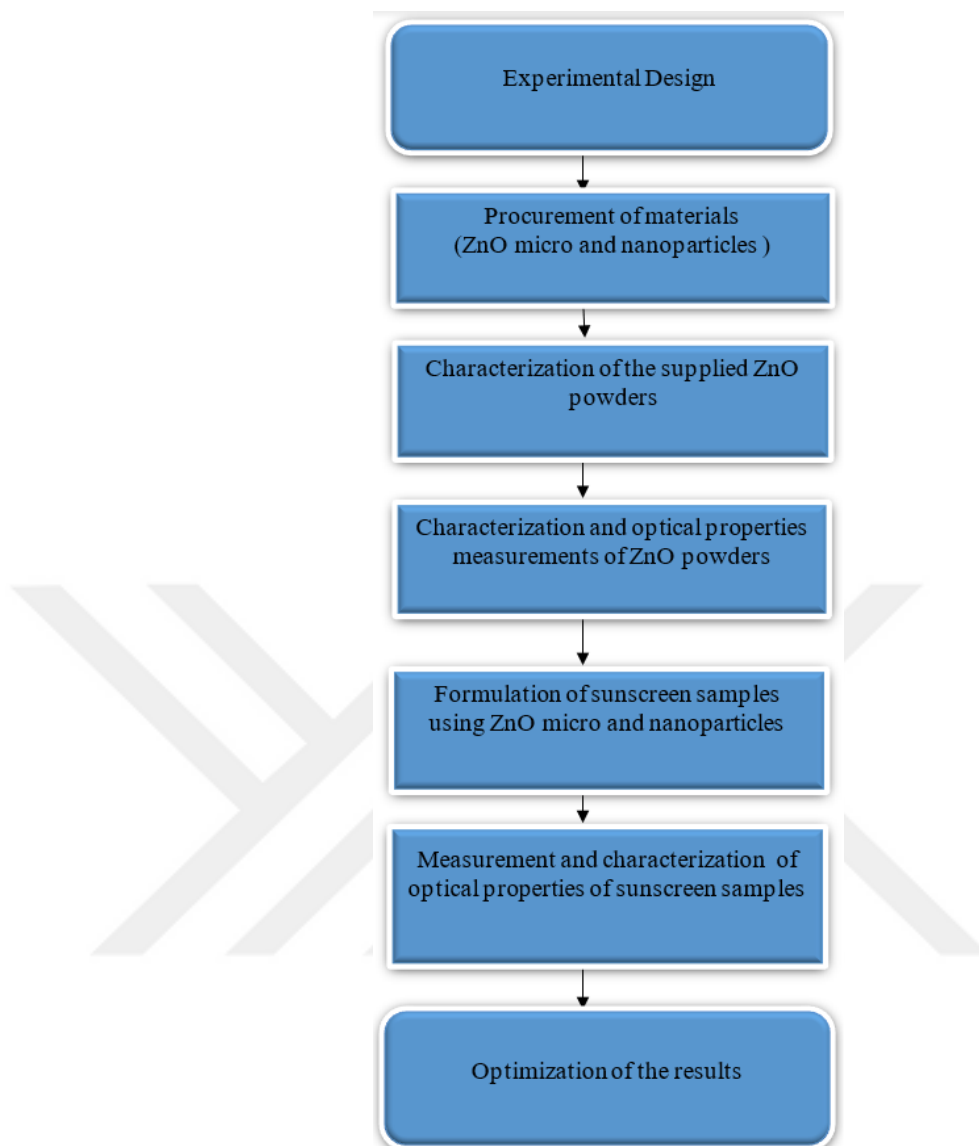


Figure 4.1. *Chemical formula of paracetamol*

4.1. Experimental Design and the ZnO Powder Procurement

This study employed the design of experiments technique to plan the experimental part in order to ensure that it was systematically conducted.

4.1.1. Procurement of the ZnO powder

Three different ZnO powders of different particle sizes and shapes were obtained from two suppliers, as indicated earlier in Table 4.1. The fourth powder, MicNo-ZnO®, was supplied by Entekno Materials Inc. at the Department of Materials Science and Engineering, Eskisehir Technical University (Turkey). This as-received MicNo-ZnO® was named the "Original MicNo-ZnO®."

4.1.2 Size reduction of the original MicNo-ZnO powder

A size reduction experiment was conducted on the original MicNo-ZnO in order to obtain a reduced size MicNo-ZnO. In the experiment, 30 g of original MicNo-ZnO was dispersed in 600 ml of isopropanol (IPA) in a glass beaker. The beaker was immersed in a larger, thicker glass beaker containing broken ice. The setup was placed under a Cole-Parmer 750-Watt ultrasonic processor (CP 750), which was operated at 30% amplitude and varied time (from 10 to 45 minutes). The powder solution was centrifuged (Joan-Thermo Electron Corporation KR 25, 6 Chambers), decanted, placed in laboratory watch glass dishes (about 180 mm size) covered with perforated aluminium foil, and then air dried in a fume cupboard for 3 days to obtain dry, reduced MicNo-ZnO powder. The schematic diagram of the size reduction experiment process is depicted in Figure 4.2. The reduced size MicNo-ZnO[®] utilised in this study was obtained using ultrasonic tip (ultrasonic processor) for 30 minutes at 30% amplitude.

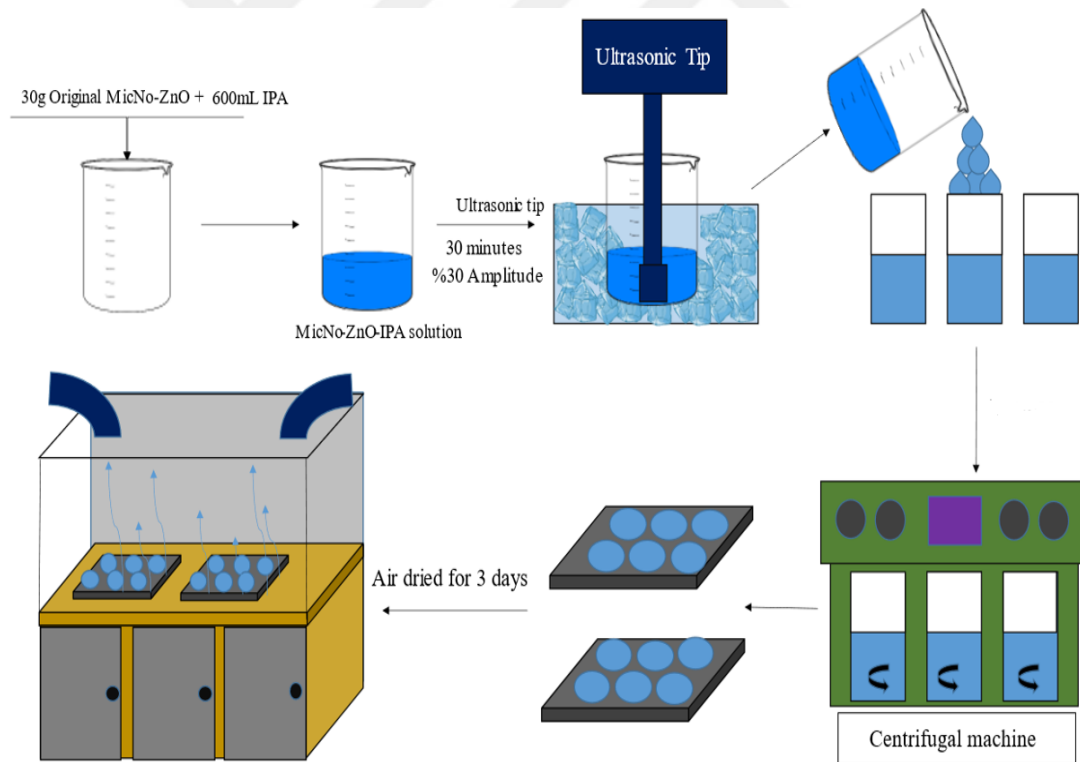


Figure 4.2. Schematic diagram of the particle size reduction experiment

4.1.3. ZnO powder utilized for the study

Following the size reduction of the MicNo-ZnO, a total of five ZnO samples were obtained for this study as shown in Table 4.4.

Table 4.4. *ZnO powders utilized*

Number of Sample	ZnO Powder
1	Original MicNo-ZnO [®]
2	Reduced Size MicNo-ZnO [®]
3	30-50nm Spherical ZnO
4	25-35nm Nano ZnO
5	Sub-micron ZnO

4.2. Characterization of the ZnO Powder Samples

Various powder characterization techniques were used to characterize both as-received and modified ZnO powder particles. These techniques are described in the subsections below, and the laboratory instruments used are listed in Table 4.5.

Table 4.5. *List of instruments utilized*

Instrument	Brand/model
Benchtop X-ray diffractometer	Bruker D2 Phaser
Brunauer-Emmett-Teller	Quantachrome Instruments, Autosorb-1
Simultaneous Thermal Analyzer	TA Instruments SDT Q600
FTIR spectrophotometer	Shimadzu IR Tracer-100 with DRS-8000A attachment
Scanning Electron Microscope (SEM)	Zeiss EVO 50 LP
Particle Size Analyzer	Malvern Mastersizer 2000 Hydro S
Particle Size and Zeta Potential Analyzer	Malvern Zeta Sizer Zen 3600
Portable Ultrasonic Cleaner	JeioTech
Ultrasonic Processor	Cole-Parmer 750-Watt (CP 750)
UV-VIS-NIR Spectrophotometer	Shimadzu UV-3600 Plus, MPC-603A Integrating Sphere
Large Capacity Refrigerated Centrifuge	Thermo- Joan (Thermo Electron Corporation, KR 25i)
Analytical Balance	Mettler Toledo
pH Meter	Mettler Toledo
Light Duty Mechanical Stirrer	IsoLab
Modular Microscope	Zeiss Axioscope 5
Digital Precise Water Bath	Wisd-Wisebath WB11
High Shear Laboratory Mixer	Silverson L5M-A

Table 4.5. (Continued) *List of instruments utilized*

Instrument	Brand/model
Precision Balance	Precisa ES Series
Sputter Coater for SEM	Agar Scientific
Digital micrometer	Mitutoyo

4.2.1. Morphology of powder samples

The term "particle morphology" is used to describe the particle shape, size, and surface roughness, and these parameters have a significant impact on powder performance [114]. This study utilised scanning electron microscopy and particle size analysis techniques to ascertain the shape and particle size of the ZnO samples.

4.2.1.1. Scanning electron microscopy (SEM)

The morphological characterization of the ZnO samples was conducted using a scanning electron microscope (Zeiss EVO 50 LP) with an energy dispersive spectrometer attachment. The ZnO samples were dispersed in an isopropanol solution using a portable ultrasonic cleaner (JeioTech) for 10 minutes, after which they were prepared on smaller pieces of glass substrates (IsoLab microscope glass slides) attached to the SEM sample holder using carbon tape, followed by placing inside a dry heat sterilizer oven for about 10 minutes. The sample was then coated with gold using an Agar sputter coater. All the samples were scanned under the same condition of a voltage of 5–10 kV.

4.2.1.2. Particle size analysis

The particle size distribution of original MicNo-ZnO[®], reduced size MicNo-ZnO[®], and submicron ZnO was determined using a particle size analyser (Malvern, Mastersizer 2000 Hydro S) with the powder particles dispersed in deionized water with the aid of a portable ultrasonic cleaner (JeioTech) to well disperse the particles, and immediately followed by measurements. Particle size distribution of nanoparticles (30-50nm Spherical ZnO and 25-35nm Nano ZnO) was determined using Malvern (Zeta Sizer Zen 3600) due to its measuring range down to smaller particle sizes. Isopropanol (IPA) was used to disperse the powders, followed by placing them under a Cole-Parmer 750-Watt ultrasonic processor (CP750), which was operated at 30% amplitude for 2 minutes, after which measurements were taken.

4.2.2. X-ray diffraction analysis (XRD)

This technique was carried out to determine the phase identification and analysis of the ZnO powder particles using x-ray diffractometer (Bruker, D2 Phaser) with $\text{CuK}\alpha$ ($\lambda = 1.54060 \text{ \AA}$) radiation and X-ray source operating voltage of 40 kV. The powder samples were scanned in the ($10^\circ - 80^\circ$) 2θ range and Scherrer equation (Equation 4.1) was used to determine the crystallite size of particles from the XRD data. Where $K = 0.94$ (shape factor), $\lambda = 1.54060 \text{ \AA}$ (wavelength of X-rays), $\beta = \text{FWHM}$ (in radians), $\theta =$ (Peak position), $\beta_o =$ experimental broadening observed, and $\beta_i =$ instrumental broadening. FWHM is the full width at half maximum intensity of the broadened peak after the instrumental broadening is removed.

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (4.1)$$

$$\beta = \beta_o - \beta_i \quad (4.2)$$

4.2.3. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of 30-50 nm spheres of ZnO powder was done using TA Instruments SDT Q600. This was because the XRD data of the ZnO seemed to have additional peaks different from the ZnO peaks. 10–15 mg of ZnO sample was placed in the sample holder and heated to 900°C at a rate of $10^\circ\text{C}/\text{min}$ from room temperature. The mass loss observed in the samples was reported as a function of the temperature.

4.2.4. Fourier transform infrared spectroscopy (FTIR)

FTIR analysis of 30-50 nm spherical ZnO was conducted in order to identify any polymeric coating on the surface of the ZnO. The IR vibrational modes of 30-50 nm spherical ZnO powder were examined using an IR spectrophotometer (Shimadzu, IR Tracer-100) with a diffuse reflectance spectroscopy (DRS-8000A) attachment. FTIR spectra were acquired by scanning the 30-50 nm spherical ZnO powder mixed with KBr from the 650 to 4000 cm^{-1} wavenumber range.

4.3. Optical Properties Measurements of ZnO Solid Samples

The absorbance, transmittance, and reflectance measurements were obtained from powder samples using the UV-VIS-NIR spectrophotometer (Shimadzu, UV-3600 Plus with MPC-603A integrating sphere compartment) in a wavelength range of 260 – 1200 nm . At the time of writing this thesis, the UV-VIS-NIR spectrophotometer has solid sample holders for reflectance measurement, while there are currently no solid sample holders designed to measure absorbance and transmittance except for the use of cuvettes

where the powder particles are dispersed in deionized water. Due to the fact that MicNo-ZnO[®] undergoes sedimentation faster than the other powder systems utilised for this study, using the cuvette method to measure the absorbance was expected not to provide a fair comparison of five powder samples. Thus, a novel method was designed to measure the absorbance and transmittance of solid powder samples using HelioScreen PMMA HD6 plates.

4.3.1. Designed method to measure absorbance and transmittance of ZnO solid powder

The rough surfaces of two HelioScreen PMMA HD6 plates were separately decorated with 0.05 g of dried powder samples for 1 minute per plate. The two rough surfaces containing 0.05 g of ZnO powder each were placed on top of each other, positioning the powder layer in between the two plates to produce one absorbance and transmittance sample. Hence, 0.1 g of ZnO was used for each sample. To ensure the powder was firmly held in between the two plates, the edges of the two plates were sealed with sellotape. This process is shown in Figure 4.3 (a)-(d).

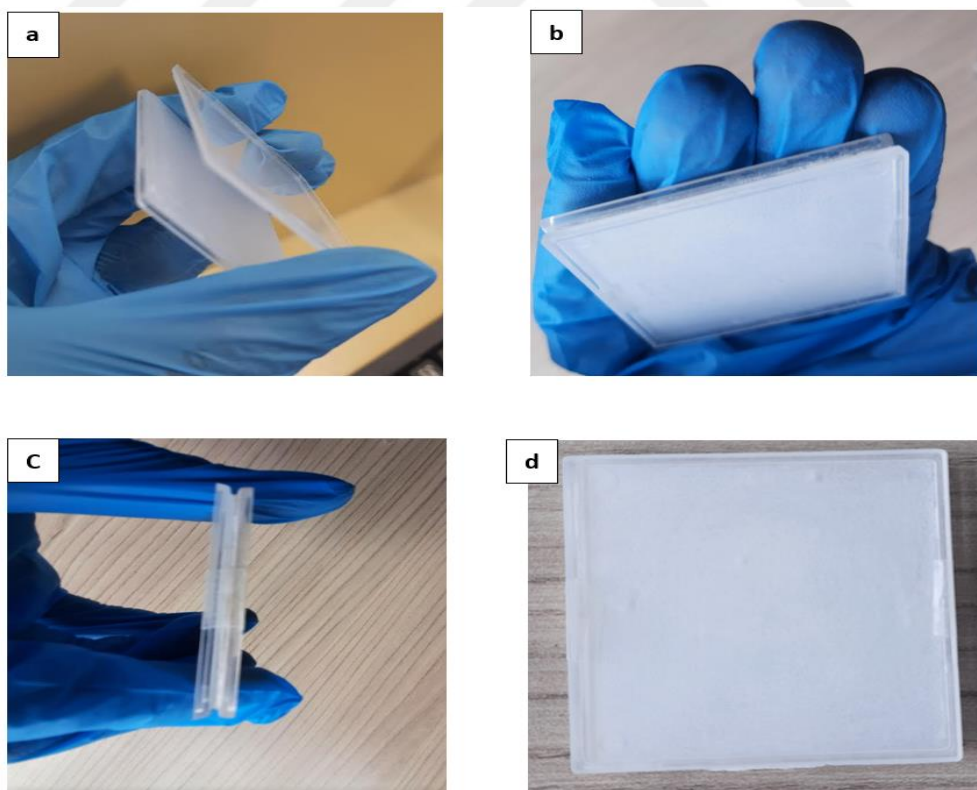


Figure 4.3. *The absorbance and transmittance sample preparation process*

Four HelioScreen PMMA HD6 plates prepared in the same way as above with no ZnO powder served as two reference materials for baseline measurement (see Figure 4.4). Each of the prepared ZnO samples was labelled and preserved in a clear small plastic zip bag as shown in Figure 4.5.

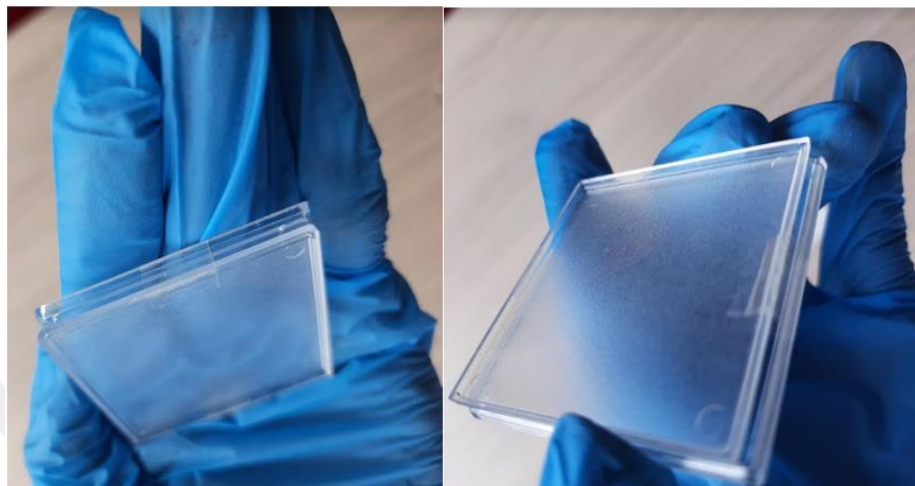


Figure 4.4. Prepared absorbance and transmittance reference samples

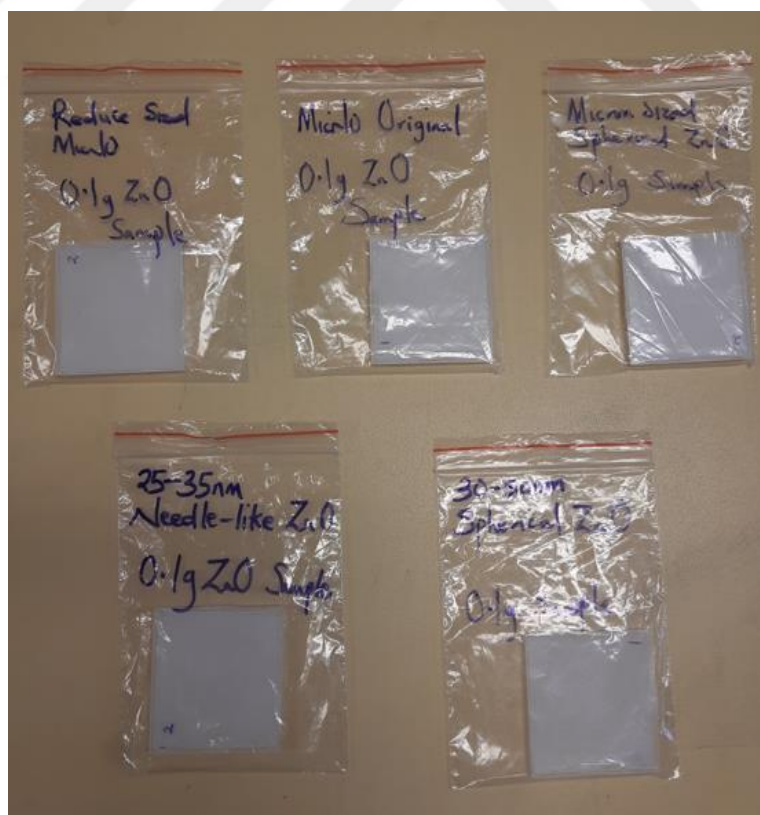


Figure 4.5. Prepared absorbance and transmittance ZnO samples

4.3.1.1. Optical microscopy analysis of ZnO decorated PMMA plates

An optical microscope (Zeiss Axioscope 5) was utilized in order to observe the surface coverage ability of the prepared solid ZnO powder samples. The microscopy images were taken after the sellotape used to seal the edges of each sample was removed. Thus, each prepared PMMA sample was separated into two, and the first and second faces as shown in Figure 4.6. The optical images of each face of the prepared PMMA sample were then taken separately at various points on the PMMA sample. These plates were mainly separated due to the fact that the microscope could not capture the surface coverage of the powder samples sealed within the PMMA plates.

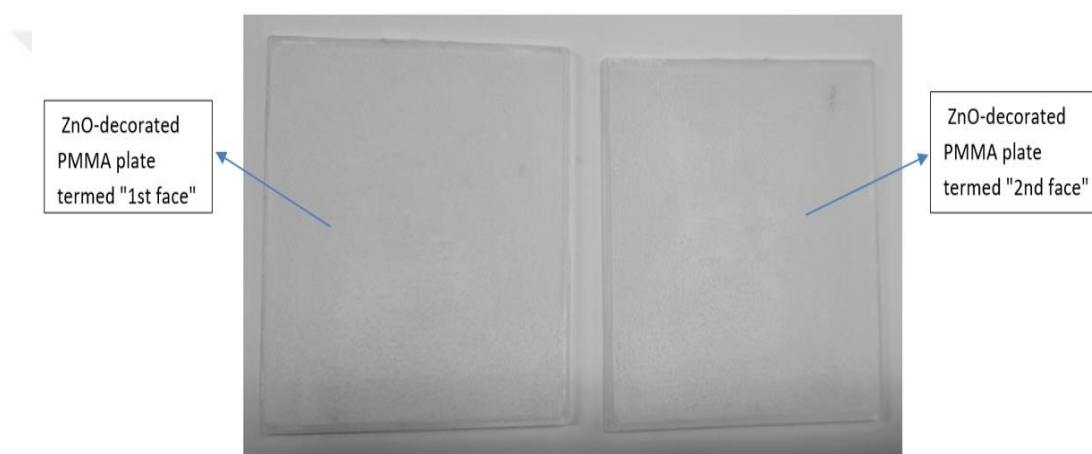


Figure 4.6. Separated ZnO-decorated PMMA plates

4.3.1.2. Absorbance and transmittance measurements of ZnO solid powder samples

Absorbance and transmittance measurements were taken with the aid of the MPC-603A integrated sphere compartment of the UV-3600 Plus UV-VIS-NIR Shimadzu device. Figures 4.7 (a) and (b) show the interior of the integrated sphere from the top and the left side of the integrated compartment, respectively. The vivid lime green and ruby red colours represent the measuring and reference lights, respectively, with respect to absorbance and transmittance measurements. Prior to taking the absorbance and transmittance measurements, the UV-VIS-NIR Shimadzu device was configured as shown in Table 4.6 and the prepared reference plates were placed both on the plate holder facing the measuring and the reference lights (see Figure 4.8).

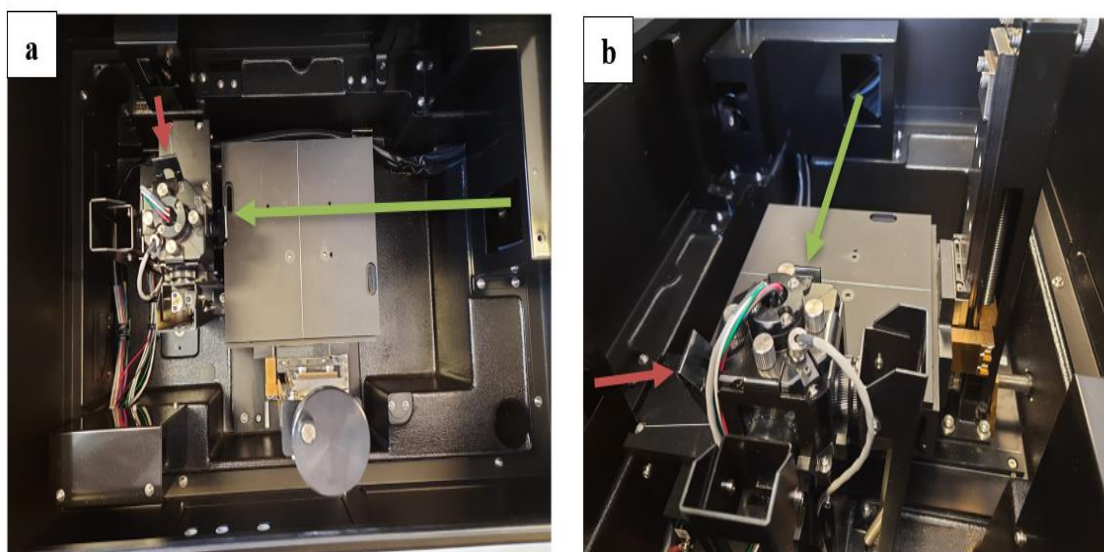


Figure 4.7. MPC-603A integrated sphere compartment interior

Table 4.6. UV-VIS-NIR Shimadzu device configuration for absorbance/transmittance measurements

Measurement Properties	
Wavelength Range (nm)	260.0 to 1200.0
Scan Speed	Medium
Sampling Interval	1.0
Auto Sampling Interval	Disabled
Scan Mode	Single
Instrument Properties	
Instrument Type	UV-3600Plus Series
Measuring Mode	Absorbance
Slit Width	32
Time Constant	0.1 sec
Source Lamp	Auto
Light Source Change Wavelength	310.00 nm
Detector Unit	External (3 Detectors)
Detector Change Wavelength	870.00 nm 1650.00 nm
Grating Change Wavelength	760.00 nm
S/R Exchange	Normal
Detector Lock	Auto
Slit Program	Normal
Beam Mode	Double
Stair Correction	Enable

Table 4.6. (Continued) *UV-VIS-NIR Shimadzu device configuration for absorbance/transmittance measurements*

Measurement Properties	
Attachement Properties	
Attachement	None
Operation	
Threshold	0.0010000
Points	4
InterPolate	Disabled
Average	Disabled
Sample Preparation Properties	-

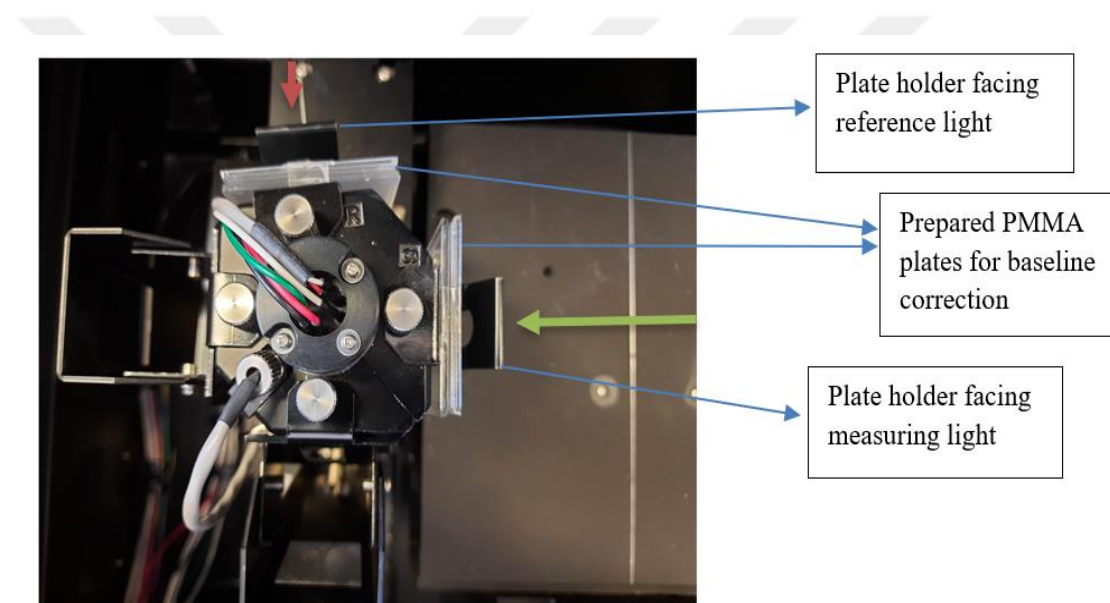


Figure 4.8. *Positioning the PMMA plates for baseline correction and absorbance/transmittance measurement*

After the baseline correction, one of the prepared reference plates (placed on the plate holder facing the measuring light) was substituted for the ZnO samples to be measured as shown in Figure 4.9 (a). The measurements were taken from a total of nine different points on each face of the ZnO plate samples, as depicted in Figure 4.9 (b). For the purpose of comparison, absorption measurements were also taken randomly from a total of nine points on the two faces of each ZnO plate sample, but still within the points indicated on the diagram depicted in Figure 4.9 (b).

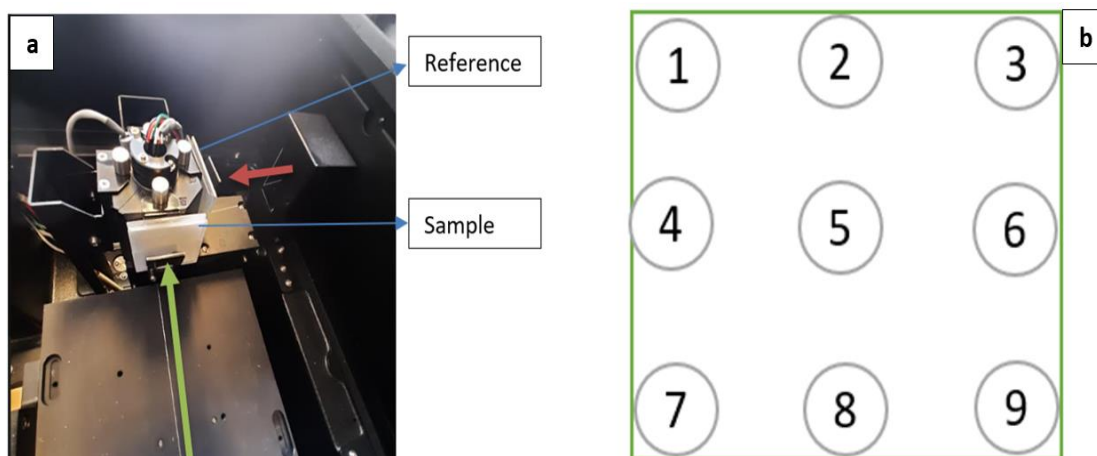


Figure 4.9. Absorbance/transmittance measurements: (a) Sample position (b) points on the PMMA plate where the measurements were taken

4.3.1.3. Measurement of sample thickness for extinction coefficient determination

The thickness of the prepared samples was measured with the aid of a Mitutoyo micrometre for the purpose of generating extinction coefficient data from the measured absorbance (see Figure 4.10 (a)). The thickness of prepared PMMA samples with and without ZnO particles was measured from five different points on the PMMA plates (earlier depicted in Figure 4.9) as indicated in Figure 4.10 (b), from which their average values were used in order to determine the thickness of the powder samples placed in between the PMMA plates.

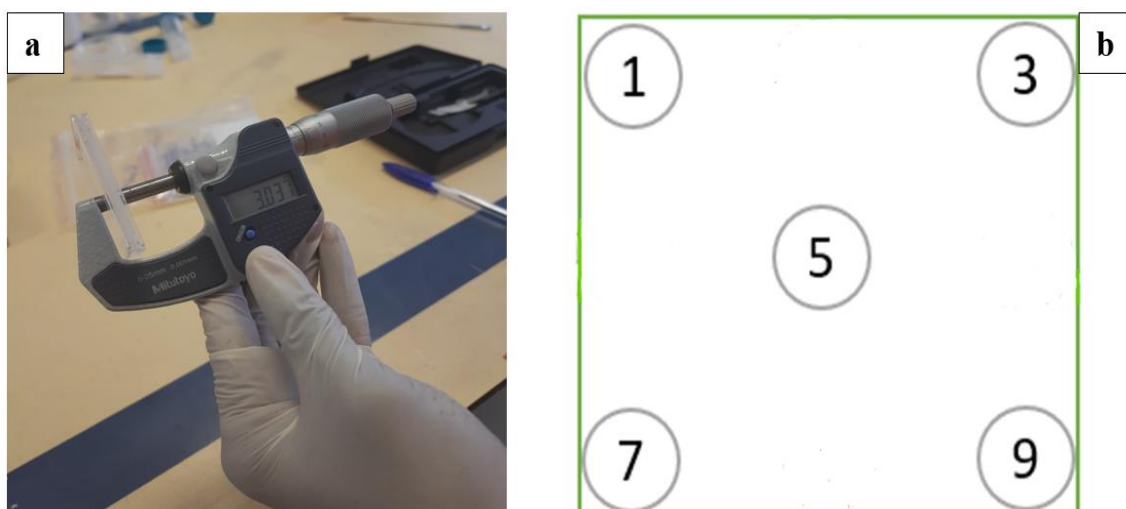


Figure 4.10. (a) Thickness measurement using Mitutoyo micrometer (b) points on the PMMA plates where thickness measurements were recorded

4.3.1.4. ZnO samples weighing after absorbance and transmittance measurements

After the absorbance and transmittance measurements, the ZnO samples were weighed on an analytical balance (Mettler Toledo). The aim was to observe whether significant amounts of ZnO powders fell off during absorbance and transmittance measurements.

4.3.2. Concept of reflectance measurement of solid samples

Reflectance is characterized by directing an incident light on a powder sample and measuring the reflected light. Reflected light is made up of diffuse reflected light and specular reflected light, the combination of which is called the total reflected light, as shown in Figure 4.11.

From Figure 4.11, the specular reflected light (red arrow line) has the same angle as the incident light (black arrow line), while the diffuse reflected light (blue arrow line) produces reflection in different directions on the powder surface. Reflectance measurements can be obtained in terms of the relative or absolute amount of light reflected (http-29).

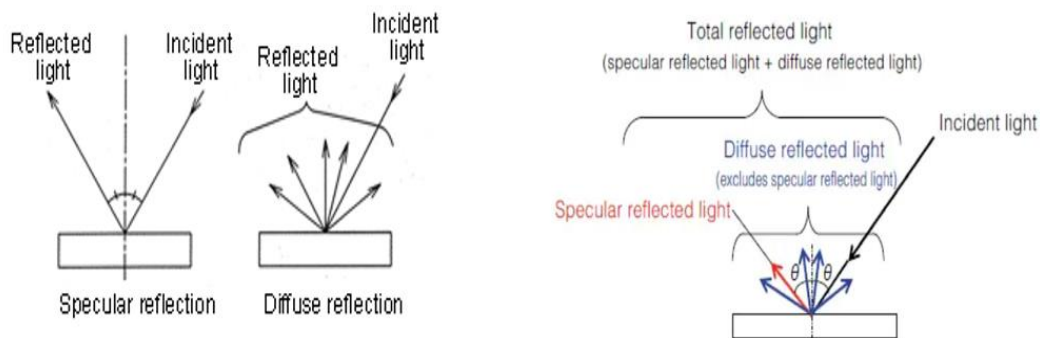


Figure 4.11. Types of light reflected from solid sample (http-29)

4.3.2.1. Reflectance measurement of ZnO solid samples

The MPC-603 integrated sphere compartment of the UV-3600 Plus UV-VIS-NIR Shimadzu device has three powder sample holders for reflectance measurement, of which only two can be used at a time (see Figure 4.12). In the reflectance measuring experiment, two clean and dried sample holders were first filled with barium sulfate powder for baseline correction. After the baseline correction, one of the sample holders was fixed with barium sulfate, which was used as the reference powder. The other sample holders

were properly cleaned, dried, and filled with 0.1 g ZnO samples to be measured as shown in Figure 4.13.



Figure 4.12. Integrating sphere powdered sample holder (<http-30>)



Figure 4.13. Sample holders filled with ZnO samples

Proper cleaning and drying of the sample holders were ensured each time a new sample of ZnO was filled into the sample holder. In this study, relative reflectance measurements (diffuse and total relative reflectance) were taken using the integrated sphere. This type of reflectance measures the light reflected from the sample (ZnO powder) relative to the light reflected by the reference sample (barium sulfate) as shown mathematically in Equation 4.3.

$$\text{Relative Reflectance (R\%)} = \frac{\text{Amount of Light Reflected from the sample}}{\text{Amount of Light Reflected from the Reference Plate}} \quad (4.3)$$

4.3.2.2. Relative diffuse reflectance of ZnO solid samples

The relative diffuse reflectance measurements, which are utilised for samples with rough surfaces, were taken for the ZnO solid samples. For the baseline correction, two solid sample holders containing barium sulfate only were positioned opposite to both the sample beam (1) and the reference beam (2) as depicted on the left diagram in Figure 4.14. When measuring the relative diffuse reflectance in the integrated sphere, the barium sulfate reference powder at position (1) was replaced by measurement samples (0.1 g ZnO powders). During this measurement, the specular reflected light is reflected through the inlet port of the sample measuring beam, thus only the relative diffuse reflected light was detected by the detector as shown on the right diagram in Figure 4.14. For each ZnO sample, four reflectance measurements were taken, and the sample holder was refilled with a "fresh" ZnO sample after each measurement was recorded.

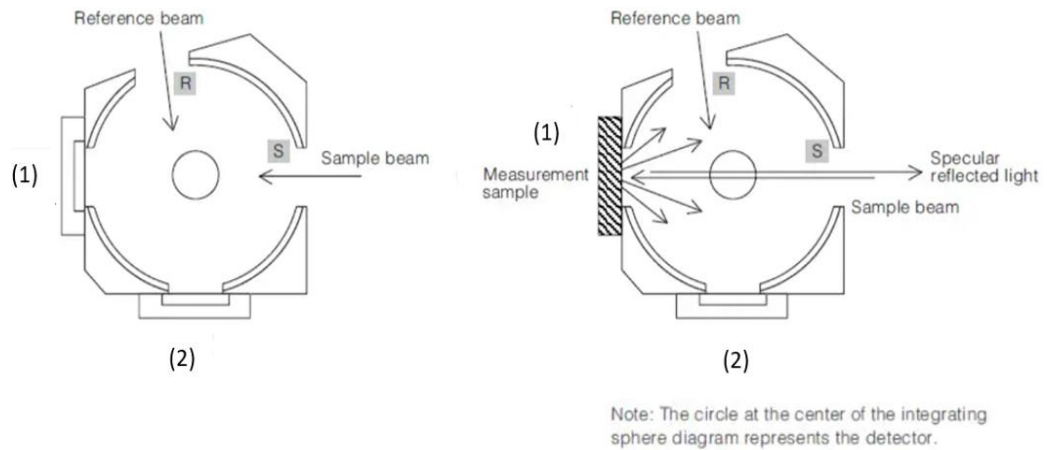


Figure 4.14. Schematic diagram of reference and sample positions in the integrated sphere compartment for relative diffuse reflectance measurements ([http-29](#))

Following this procedure, the experimental diagram is shown in Figure 4.15. The device configuration was the same as that in Table 4.6 except that reflectance was selected as the measuring mode.

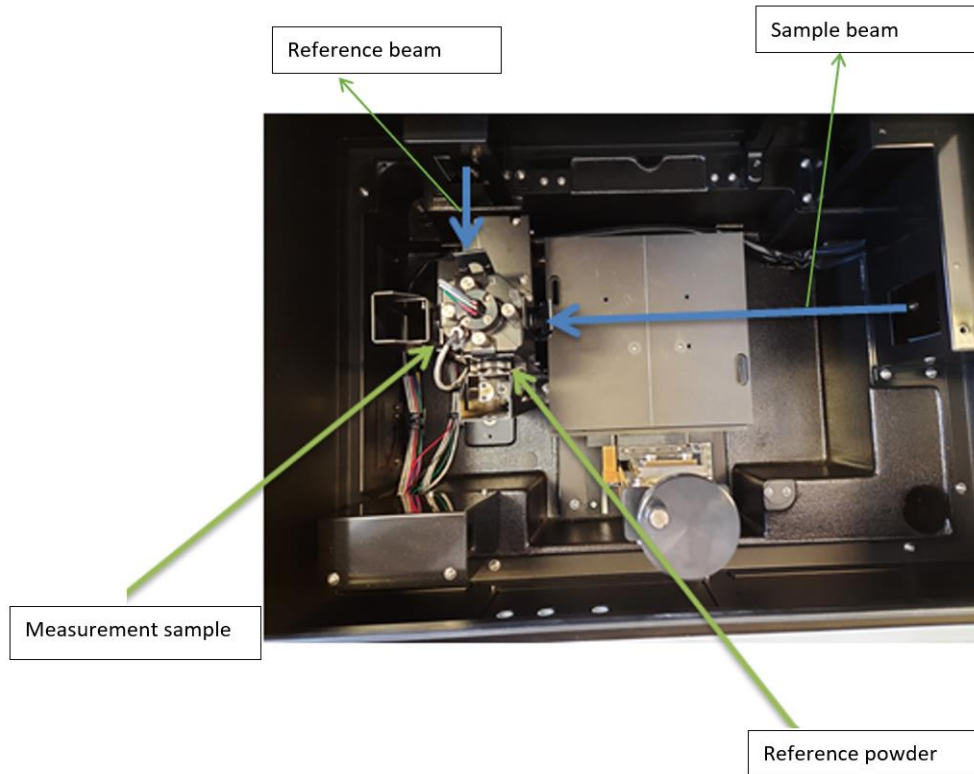


Figure 4.15. *Experimental diagram showing the reference and sample positions in integrated sphere compartment for relative diffuse reflectance measurements*

4.3.2.3. Relative total reflectance of ZnO samples

Relative total reflectance comprises of both relative diffuse and specular reflected beams. The measuring procedure and the device configuration setting were the same as for relative diffuse reflectance except that the sample and the reference beams were reversed through the S/R exchange setting, and it was changed from normal to inverse in Table 4.6. Thus, the reference beam in the case of relative diffuse reflectance became the sample beam for relative total reflectance and vice versa. This exchange of the sample to the reference beam occur automatically after "inverse" was selected in place of "normal." Consequently, the positions of sample and reference were swapped. Figures 4.16 and 4.17 show the schematic and the experimental diagram of the relative total reflectance measurement respectively.

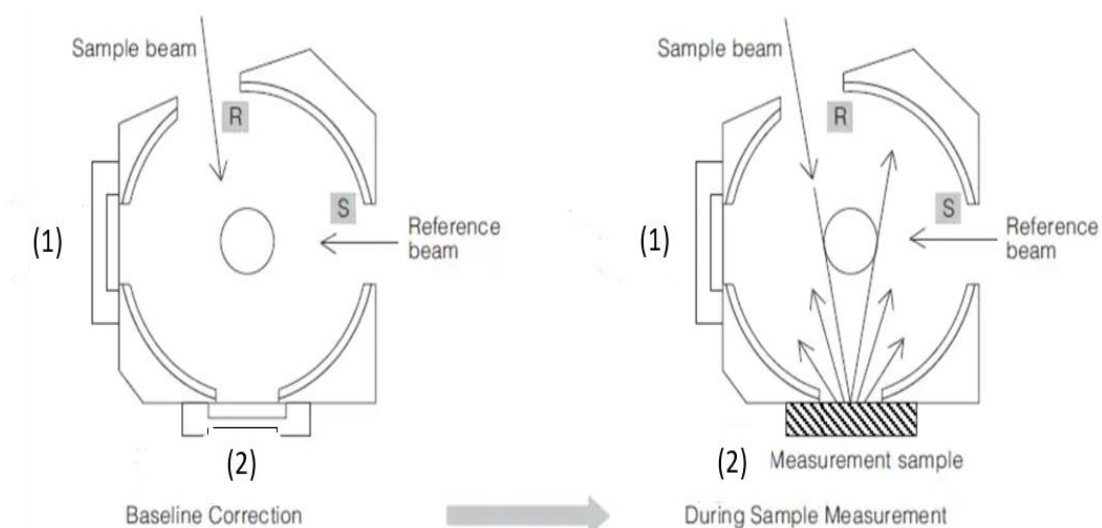


Figure 4.16. Schematic diagram showing the reference and sample positions in integrated sphere compartment for relative total reflectance measurement ([http-29](http://29))

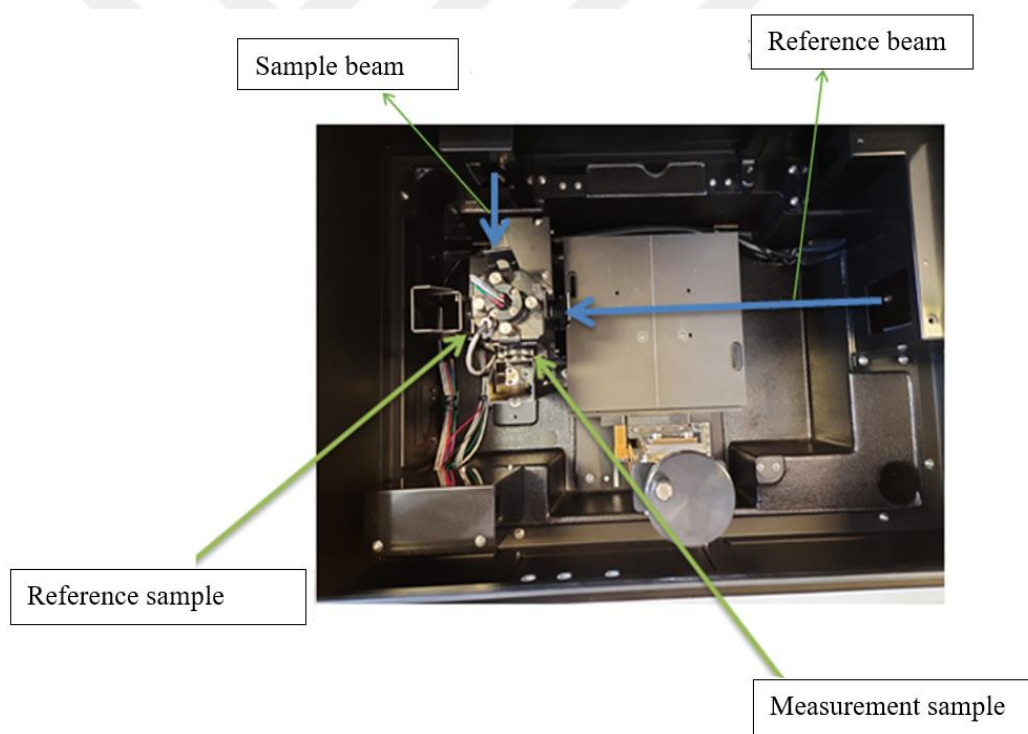


Figure 4.17. Experimental diagram showing the reference and sample positions in integrated sphere compartment for relative total reflectance measurement

4.4. Sunscreen Formulations

The standard formulation of the five powder systems stated in Table 4.4 were prepared using the formulation constituents in Table 4.7.

Table 4.7. *Sunscreen formulation constituents*

No	Product Name	Ingredient INCI Name	Application	Structural features	%	Mass (g)	Phase
1	Crodamol™ GTCC	Caprylic Capri Triglyceride	Emollient	polar	7	14	A
2	Cithrol™ PG ₃ PR	Polyglyceryl-3 Polyricinoleate	Emulsifier	-	3	6	
3	Cithrol™ PG ₃ 2IS	Polyglyceryl-3 Diisostearate	Emulsifier	-	2	4	
4	Jojoba Oil	Simmondsia Chinensis seed oil	Moisturizer	apolar	10	20	
5	Beeswax	Cera Alba	Moisturizer	-	4	8	
6	Miglyol Coco 810	Coco- Caprylate / Caprate	Emollient	polar	8	16	
7	Zinc Oxide	Zinc Oxide	UV filter	-	20	40	C
8	Deionized water	Deionized water	-	-	45.4	90.8	B
9	MgSO ₄ .7H ₂ O	Magnesium Sulphate Heptahydrate	-	-	0.6	1.2	

4.4.1. Formulation procedures

The ingredients classified under the A phase (oil phase) were added sequentially in the same beaker according to the proportion stated in Table 4.7 using a precision balance (Precisa, ES Series). In a similar way, the ingredients making up the B phase (water phase) were measured in a separate beaker. The C phase (one of the ZnO samples) was also measured in a separate beaker and the three phases (A, B, and C) were covered with aluminium foil as shown in Figure 4.18. The A and B phases were placed in a digital water bath (Wisd-Wisebath, WB11), which was heated up and maintained at a temperature of 80 °C for about 20 minutes to allow complete melting of the ingredients (see Figure 4.19). The A phase was then removed and immediately placed under a mechanical stirrer (IsoLab) for 2 minutes at about 500 rpm, after which the C phase was slowly added to the A phase under the mechanical stirrer and the speed was increased to 2000 rpm. The mixture of A and C phases was mixed for 10 minutes, as shown in Figure

4.20 (a). Because of the heat balance of the two phases (A and C), their mixture was placed back into the water bath.

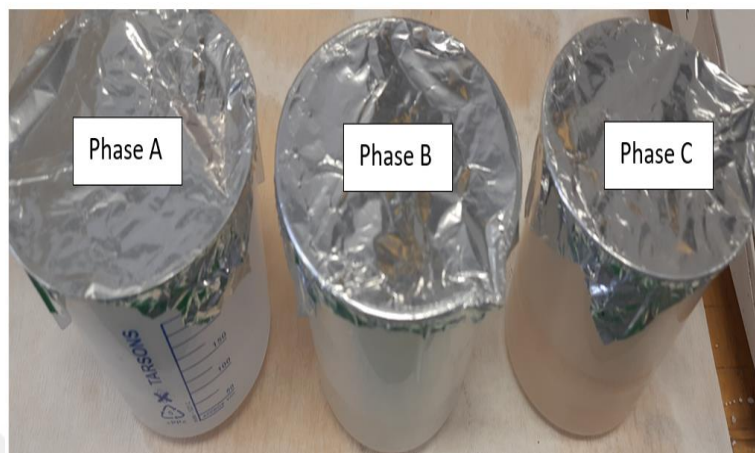


Figure 4.18. Separately measured formulation phases



Figure 4.19. A and B phases placed in a digital water bath at 80 °C

The B phase was then added slowly into the mixture of A and C and then homogenized with the aid of a high shear mixer (Silverson, L5M-A) which was operated for 30 minutes at 3000 rpm (see Figure 4.20 (b) and (c)). It was mixed in a paddle mixer and the temperature was monitored until the formulated sunscreen fell below 30 °C (see Figure 4.20 (d)), after which the cream was poured into the plastic-covered container as shown in Figure 4.21. The same procedure was exactly repeated for the other four ZnO samples.

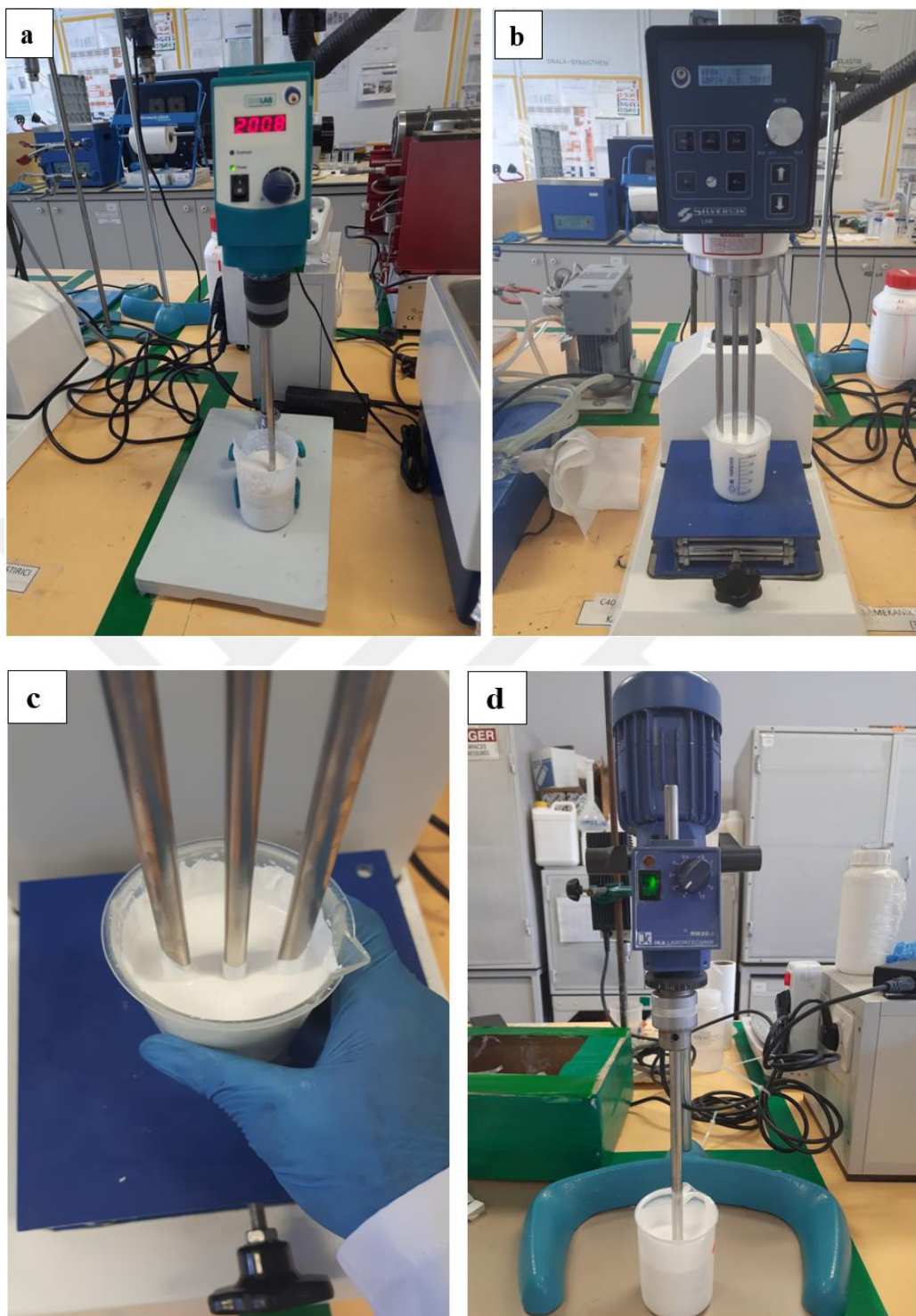


Figure 4.20. (a) A and C phases under mechanical stirrer (b) homogenization of phases A, C and B (c) complete homogenization of the three phases (d) cooling of the formulated sunscreen using a paddle mixer

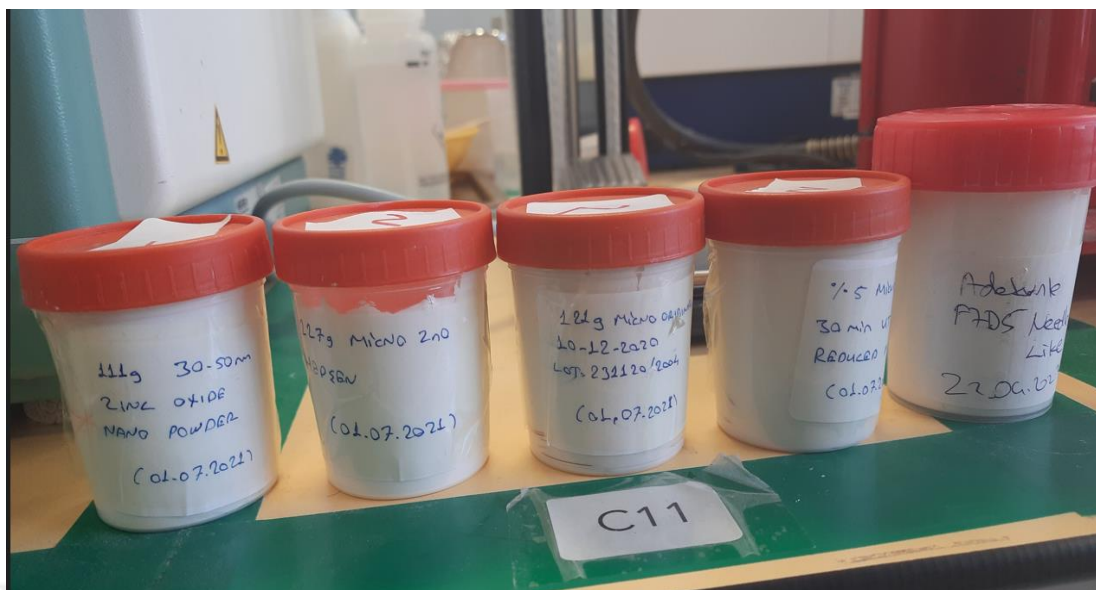


Figure 4.21. Formulated sunscreens from the five powder systems

4.4.2. SPF and optical measurements of formulated sunscreens

The SPF and optical properties of the formulated sunscreens were determined according to the 2011 COLIPA guidelines for testing sunscreens with the aid of the MPC-603 integrated sphere compartment of the UV-3600 Plus UV-VIS-NIR Shimadzu device.

4.4.2.1. Measuring procedure

Each formulated sunscreen was applied on Helioscreen HD6 plate (6 μm roughness and 2500 mm^2 surface area) at a rate of $1.3\text{mg}/\text{cm}^2$ (i.e., 0.033g) and then rubbed using a finger cot in three different directions (see Figure 4.22). The Helioscreen PMMA plate represented by the rectangle ABCD was rubbed for a total of 1 minute; circular direction for 30 seconds, horizontal and vertical forward and backward directions for 30 seconds, covering the entire rough surface of the plate. The plate was then left to dry for 15 minutes after which the measurement was taken according to COLIPA guideline, using the integrated sphere of the UV-VIS-NIR Shimadzu device in the 290-400 nm wavelength range.

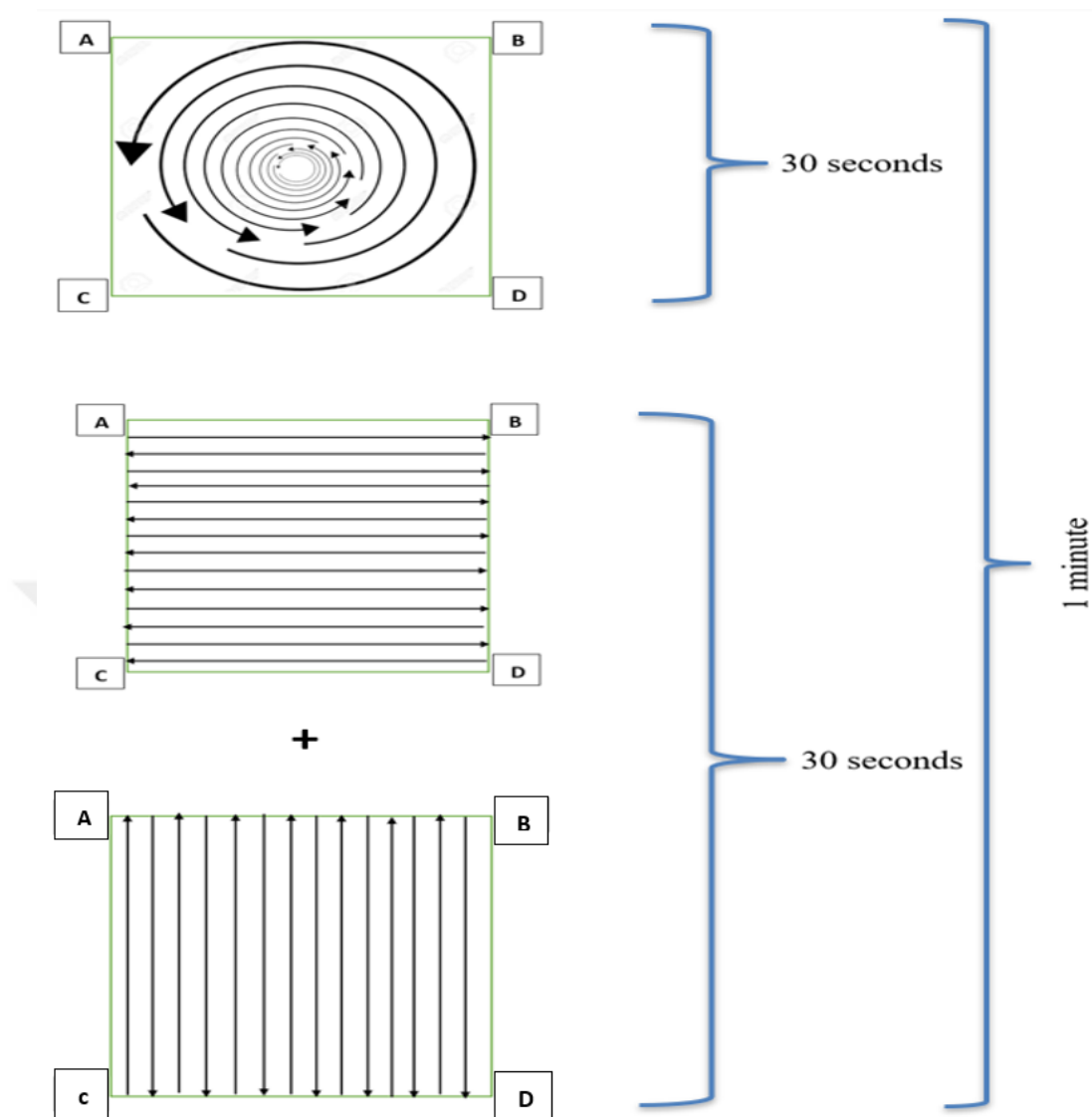


Figure 4.22. Rubbing directions of formulated sunscreens on PMMA plates

5. RESULTS AND DISCUSSIONS

In this chapter, powder particles characterization results, measured optical properties results, sunscreen formulations and their optical properties results are presented and discussed.

5.1. Powder Particles Characterization Results

Under this section, the results of various techniques used for the characterization of both as-received and modified powders are presented.

5.1.1. X-ray powder diffraction analysis results

This technique was utilized so as to be able to identify the crystallographic phases present in the sample powders. The individual results of X-ray powder diffraction (XRD) of the five powder systems are shown in Figures 5.1 (a)-(e). These results are also combined in Figure 5.2.

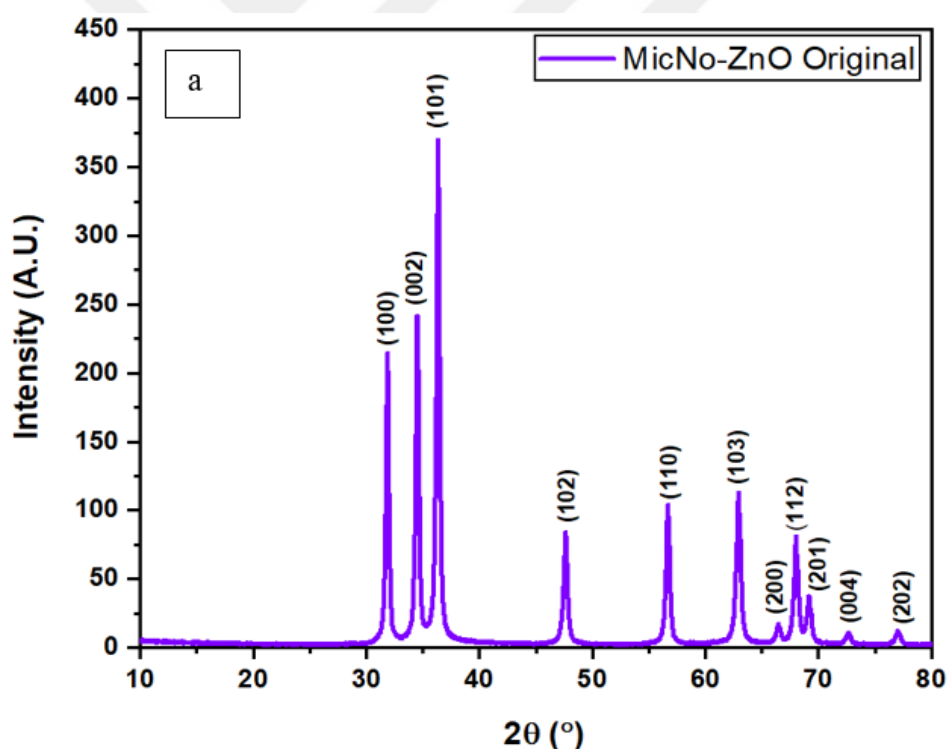


Figure 5.1. X-ray diffraction patterns (a) Original MicNo-ZnO (b) reduced size MicNo-ZnO (c) 25-35nm nano ZnO (d) 30-50nm spherical ZnO (e) submicron ZnO

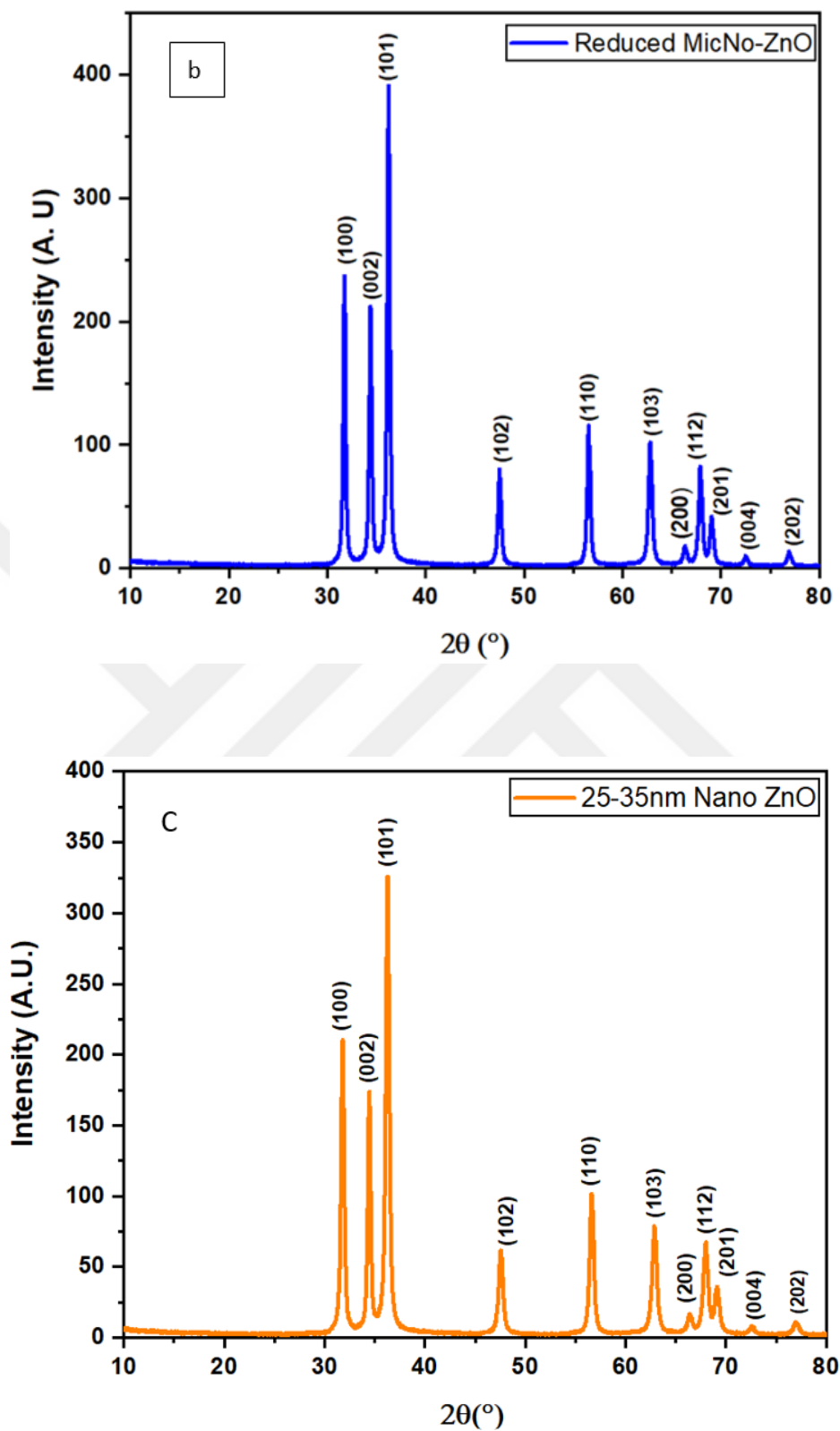


Figure 5.1. (Continued) X-ray diffraction patterns (a) Original MicNo-ZnO (b) reduced size MicNo-ZnO (c) 25-35nm nano ZnO (d) 30-50nm spherical ZnO (e) submicron ZnO

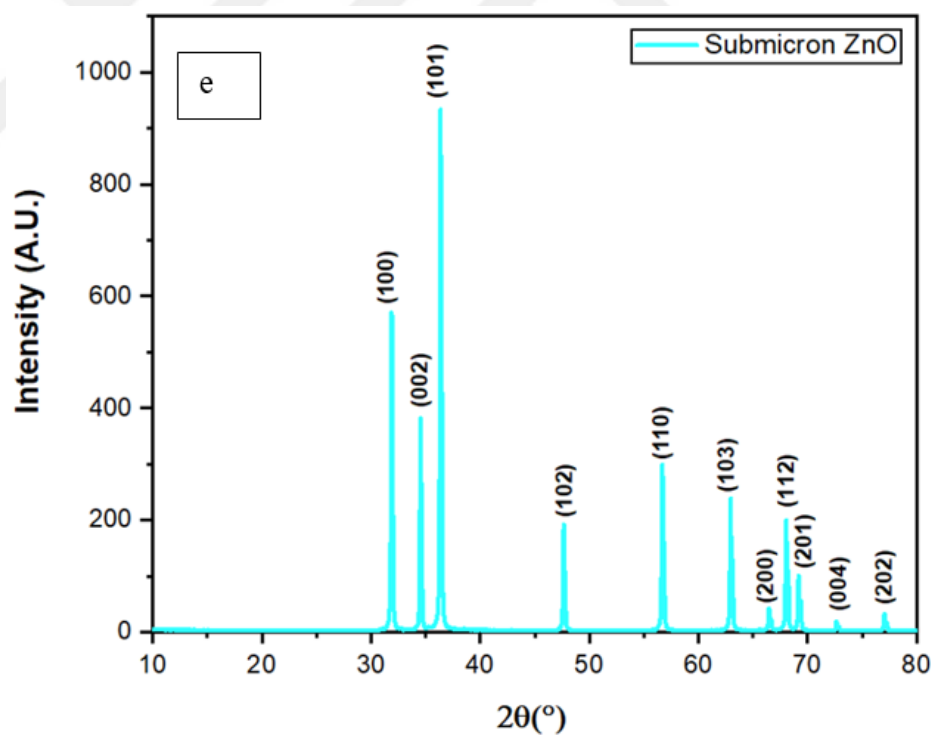
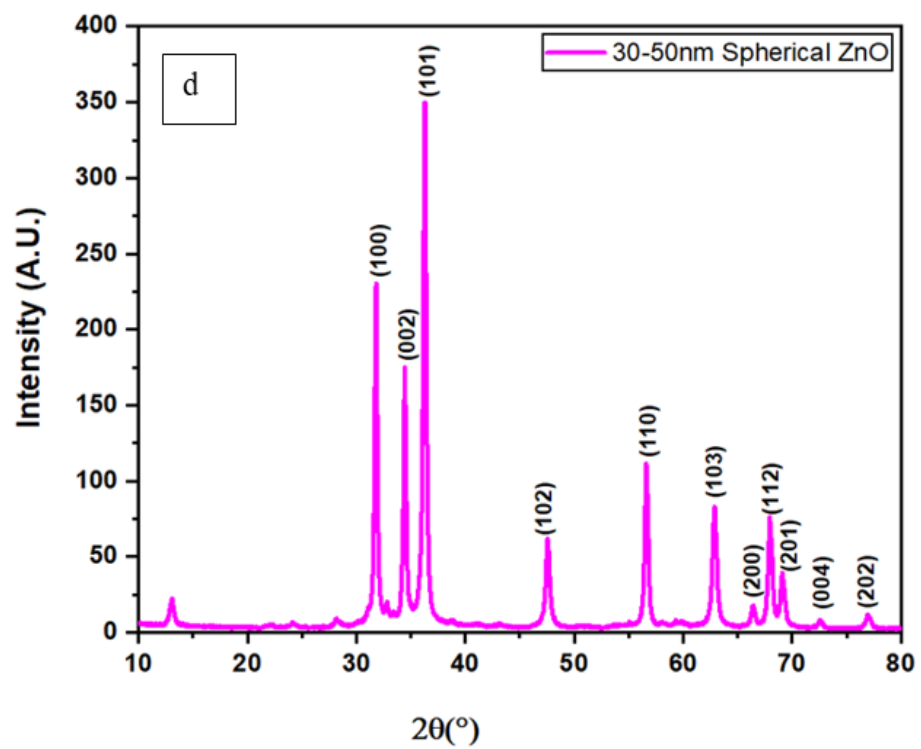


Figure 5.1. (Continued) X-ray diffraction patterns (a) Original MicNo-ZnO (b) reduced size MicNo-ZnO (c) 25-35nm nano ZnO (d) 30-50nm spherical ZnO (e) submicron ZnO

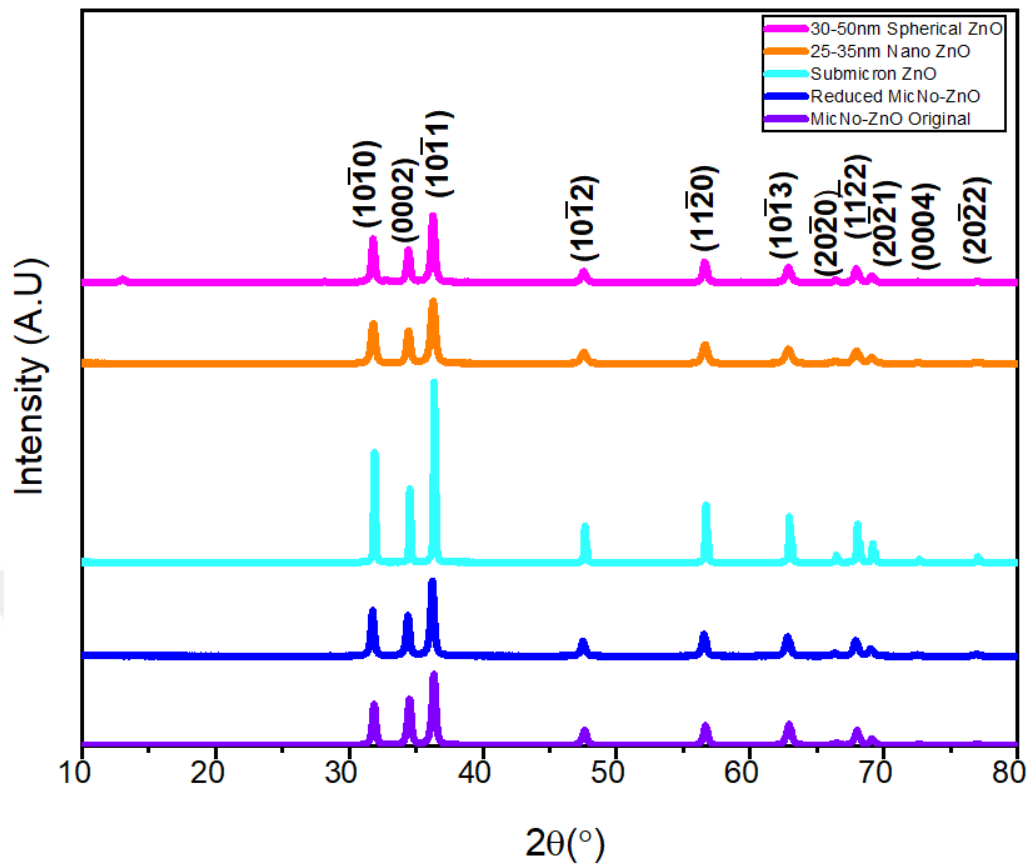


Figure 5.2. X-ray diffraction pattern of the combined five powder systems

The five powder samples were indexed at eleven distinct peaks corresponding to the ZnO crystal structure of hexagonal wurtzite (ICDD PDF Card Number: 01-082-3143). While the original MicNo-ZnO, reduced size MicNo-ZnO, 25-35nm nano ZnO, and submicron ZnO have no other peaks apart from the peaks of standard ZnO, 30-50 nm spherical ZnO seems to have additional peaks different from those of ZnO, with the most pronounced in terms of the peak intensity around $2\theta = 13^\circ$, as indicated in Figure 5.1 (e). The average crystallite size of five powder systems was calculated from information in Tables 5.1 to 5.5 using Scherrer's equation as indicated in Equation 4.1, for which the most intense peak (101) of each powder was utilized. The instrumental broadening contribution to the broadening observed from the experiment was removed for each powder using Equation 4.2. The instrumental broadening was determined using silicon powder (99+%, 325 mesh) obtained from Acro Organics (ThermoFisher Scientific). The X-ray diffraction pattern of the silicon powder and the polynomial fit of the FWHM (broadening) versus the 2θ are shown in Figures 5.3 and 5.4, respectively. The silicon peaks were observed at 28.436,

47.322, 56.109, 69.118, and 76.362. The crystallite size results of the five powder systems are stated in Table 5.6.

Table 5.1. Experimentally observed XRD data of MicNo-ZnO data

S/N	Peak position (2 θ)	FWHM (2 θ)	(khl)
1	31.85889	0.33107	100
2	34.50526	0.33847	002
3	36.33738	0.35951	101
4	47.61842	0.4532	102
5	56.67755	0.42662	110
6	62.92854	0.49313	103
7	66.47007	0.39752	200
8	68.0274	0.43379	112
9	69.15897	0.51686	201
10	72.63098	0.52259	004
11	77.03384	0.56355	202

Table 5.2. Experimentally observed XRD data of reduced size MicNo-ZnO data

S/N	Peak position (2 θ)	FWHM (2 θ)	(khl)
1	31.74579	0.31277	100
2	34.39289	0.3063	002
3	36.2258	0.34247	101
4	47.51287	0.42683	102
5	56.57638	0.40873	110
6	62.83234	0.46666	103
7	66.36674	0.40662	200
8	67.93031	0.37917	112
9	69.06083	0.47817	201
10	72.53825	0.45659	004
11	76.9514	0.53828	202

Table 5.3. Experimentally observed XRD data of nano ZnO data

S/N	Peak position (2 θ)	FWHM (2 θ)	(hkl)
1	31.79361	0.38994	100
2	34.44037	0.33748	002
3	36.27258	0.42753	101
4	47.56135	0.54673	102
5	56.62673	0.51336	110
6	62.88458	0.58176	103
7	66.42608	0.45847	200
8	67.98533	0.50808	112
9	69.09438	0.68092	201
10	72.58119	0.60726	004
11	76.99758	0.72378	202

Table 5.4. Experimentally observed XRD data of submicron ZnO data

S/N	Peak position (2 θ)	FWHM (2 θ)	(hkl)
1	31.89774	0.1657	100
2	34.55075	0.16143	002
3	36.38286	0.17751	101
4	47.67187	0.21708	102
5	56.72787	0.24477	110
6	62.99081	0.27303	103
7	66.50828	0.27115	200
8	68.0804	0.28434	112
9	69.2213	0.30392	201
10	72.66513	0.14923	004
11	77.09055	0.34078	202

Table 5.5. Experimentally observed XRD data of 30-50 nm spherical ZnO data

S/N	Peak position (2 θ)	FWHM (2 θ)	(hkl)
1	31.79054	0.29927	100
2	34.43497	0.29031	002
3	36.27055	0.34914	101
4	47.56327	0.47598	102
5	56.63249	0.3895	110
6	62.88979	0.48136	103
7	66.4295	0.39644	200
8	67.98873	0.3796	112
9	69.11786	0.50393	201
10	72.58864	0.46433	004
11	77.00857	0.57887	202

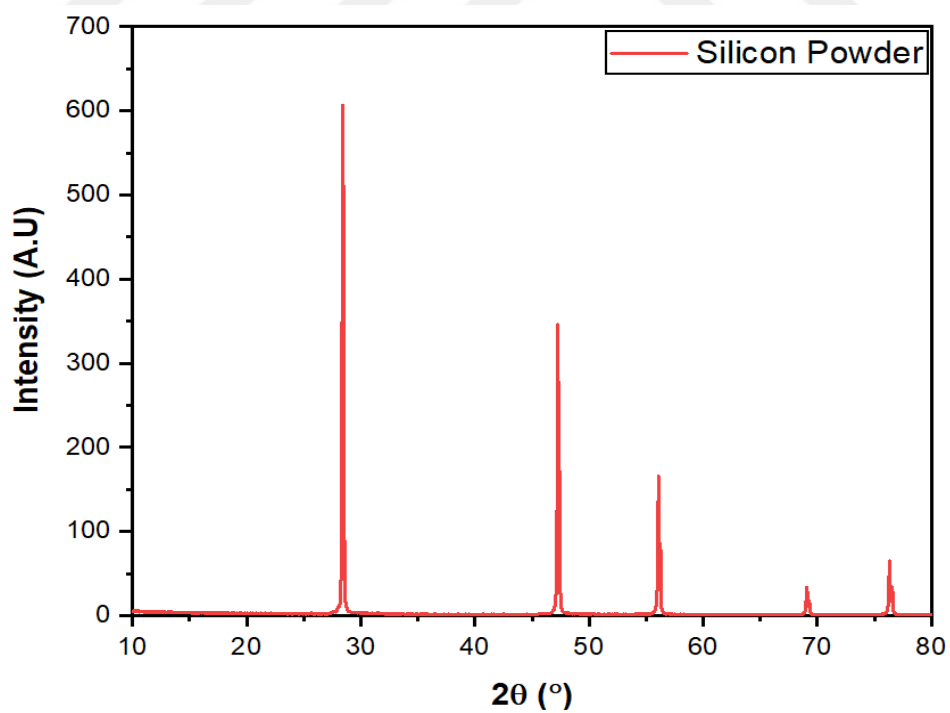


Figure 5.3. X-ray diffraction pattern of silicon powder

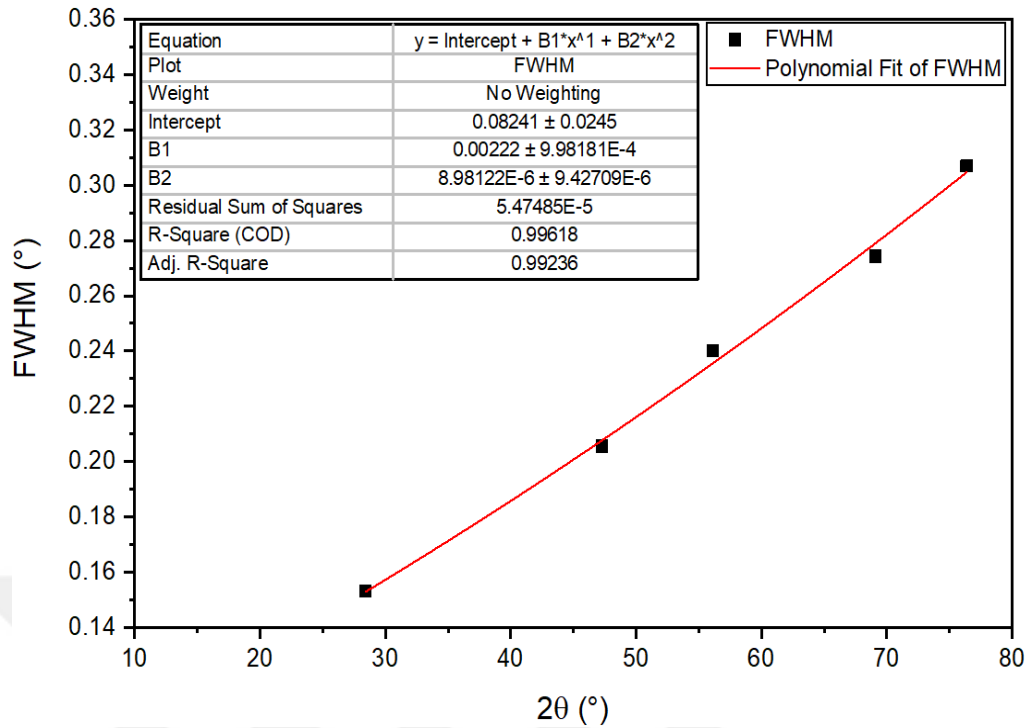


Figure 5.4. Plot of FWHM vs 2θ for silicon powder

Table 5.6. Crystallite size calculated using Scherer's equation

S/N	ZnO Sample	Peak position (2θ)	β_0 (°)	β_i (°)	β (°)	Average crystallite size (nm)
1	MicNo-ZnO	36.33738	0.35951	0.1749	0.18461	47.304
2	Reduced size MicNo-ZnO	36.22580	0.34247	0.1746	0.16787	52.004
3	25-35 nm Nano ZnO	36.27258	0.42753	0.1748	0.25273	34.547
4	Submicron ZnO	36.38286	0.17751	0.1751	0.00241	3624
5	30-50 nm Spherical ZnO	36.27055	0.34914	0.1747	0.17444	50.052

The submicron ZnO in table 5.6 seemed very large. This is because the x-ray broadening is only applicable to particles <100 nm which causes peak broadening. Therefore, the average crystallite size result for the submicron ZnO should be ignored.

5.1.2. SEM and EDX results

The images of the five powder systems obtained from a scanning electron microscope (Zeiss EVO 50 LP) with an energy dispersive spectrometer attachment are shown in Figures 5.5 (a)-(e).

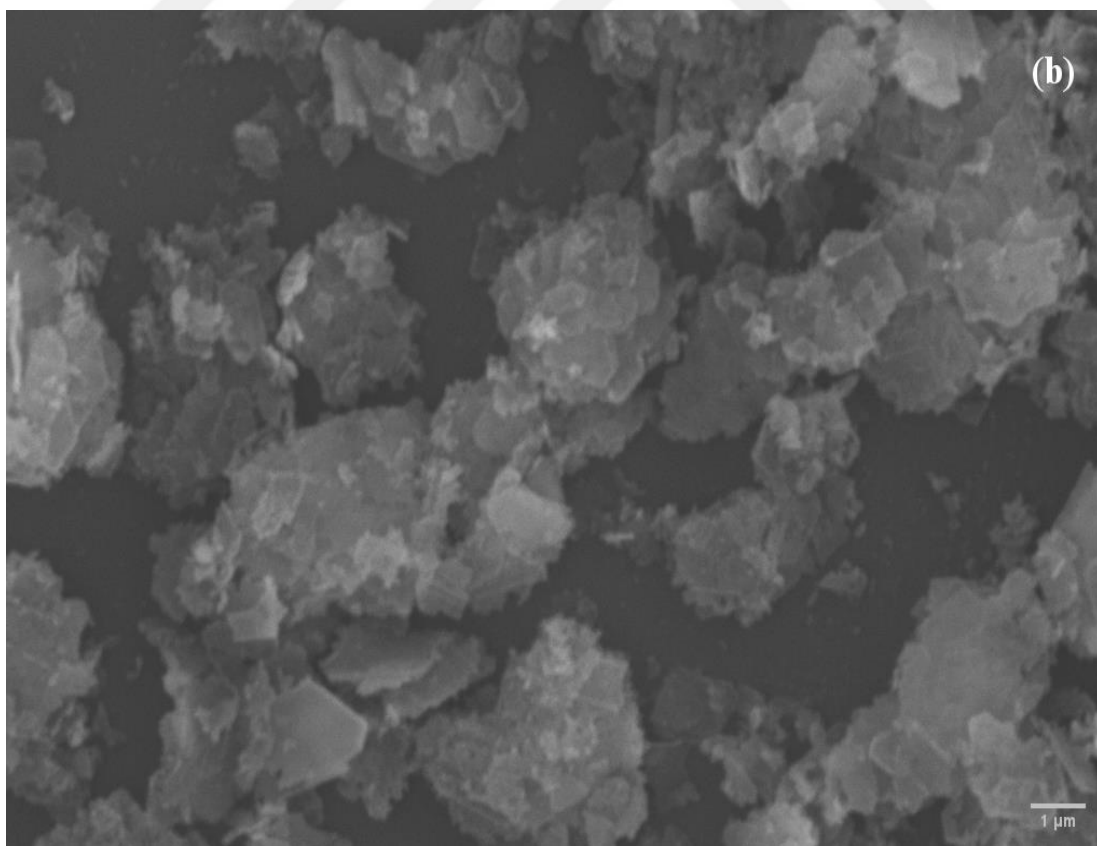
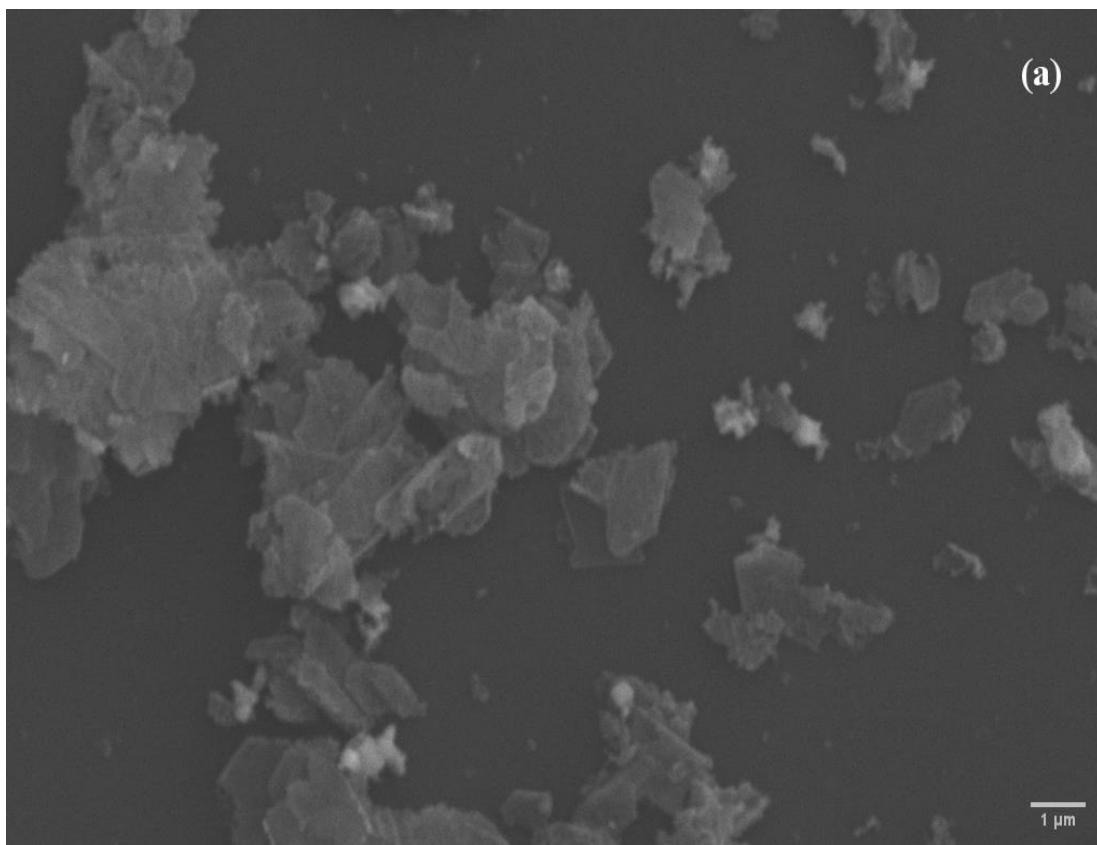


Figure 5.5. SEM images (a) Original MicNo-ZnO (b) reduced size MicNo-ZnO
(c) submicron ZnO (d) 25-35nm nano ZnO (e) 30-50nm spherical ZnO

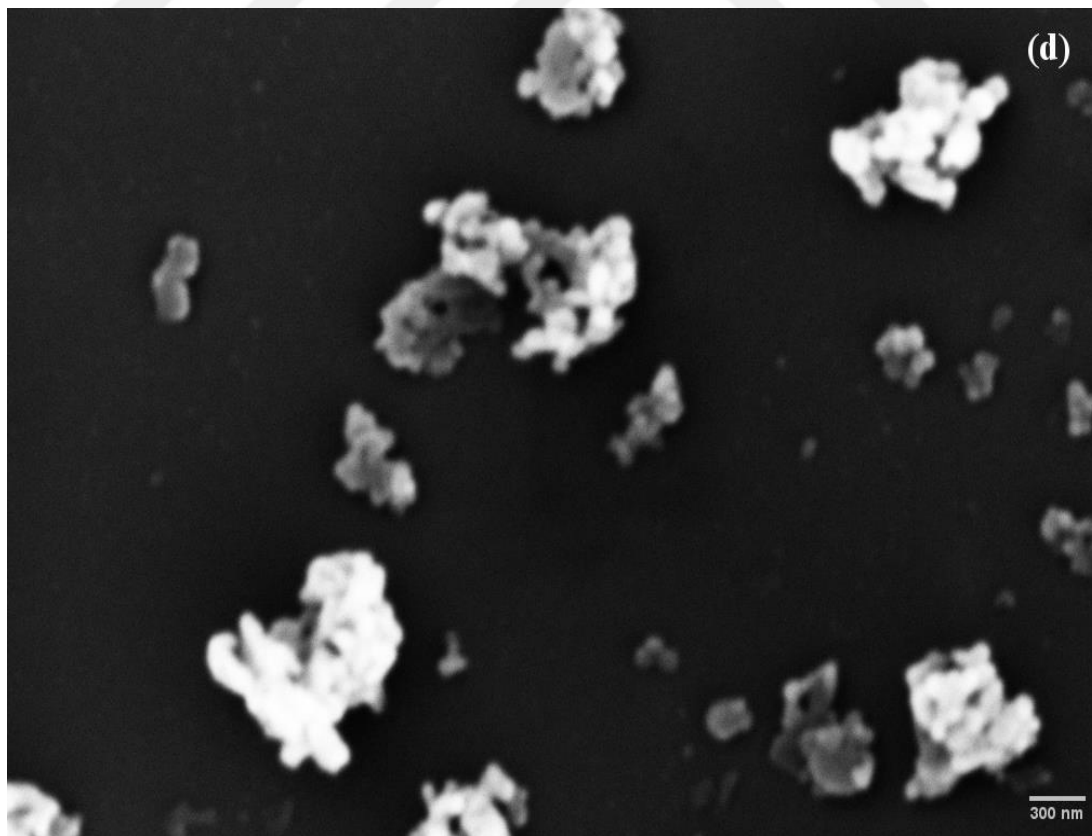
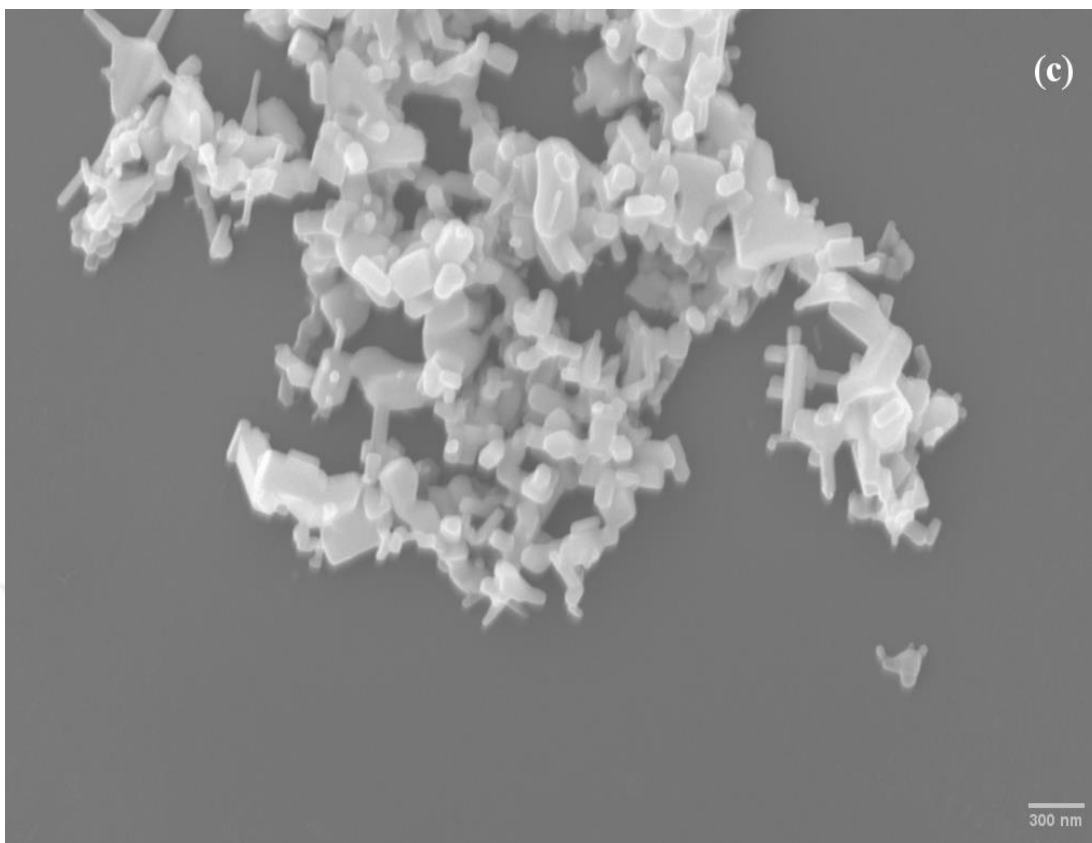


Figure 5.5. (Continued) SEM images (a) Original MicNo-ZnO (b) reduced size MicNo-ZnO (c) submicron ZnO (d) 25-35nm nano ZnO (e) 30-50nm spherical ZnO

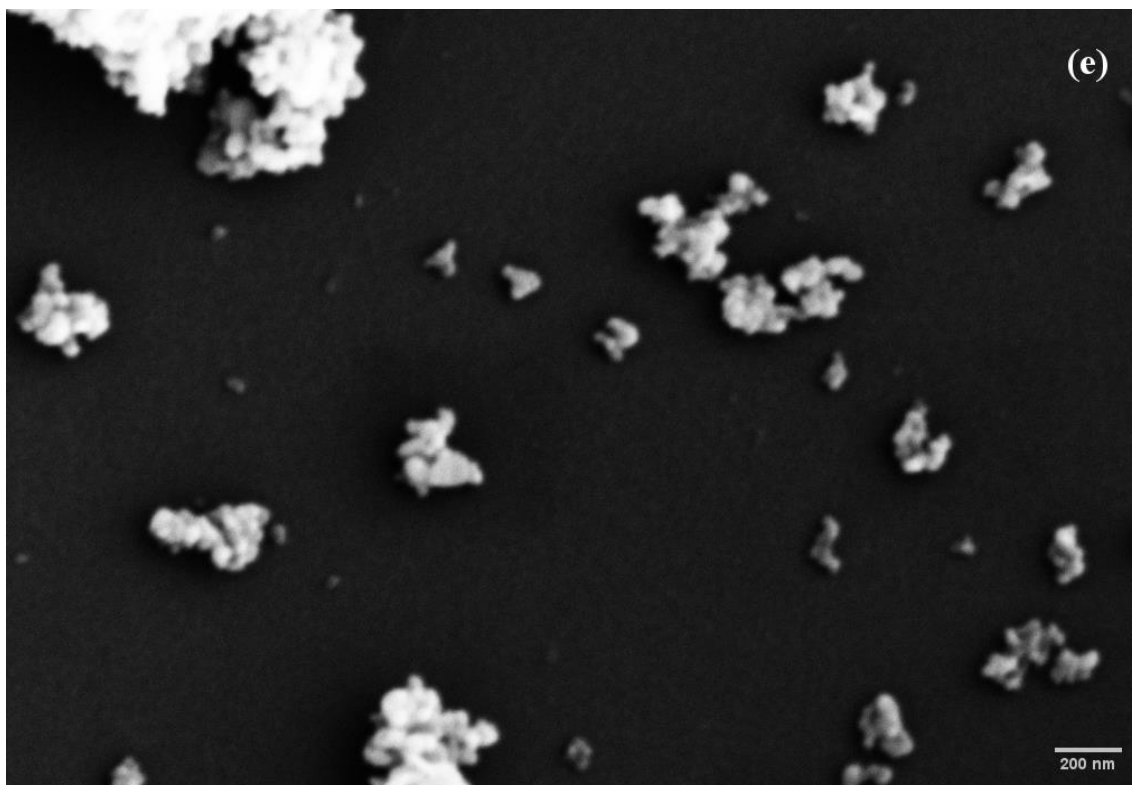


Figure 5.5. (Continued) SEM images (a) Original MicNo-ZnO (b) reduced size MicNo-ZnO (c) submicron ZnO (d) 25-35nm nano ZnO (e) 30-50nm spherical ZnO

From the SEM images, hexagonal platelet morphology was observed in original MicNo-ZnO and a few in reduced size MicNo-ZnO. Because of the aggressive effect of the ultrasonic processor on the original MicNo-ZnO particles during the size reduction experiment, the reduced size MicNo-ZnO morphology was dominated by irregular polygonal platelets resulting from broken hexagonal platelets. Submicron ZnO consisted of different types of morphologies, including equiaxial, rod-like, and irregularly shaped particles. While a needle-like shape was not observed in the images obtained for 25-35 nm nano ZnO as claimed by the manufacturer, but rather rice-like and irregular-shaped morphologies, the morphology of that of 30-50 nm ZnO seemed approximately spherical. Due to the unidentified peaks observed in the XRD data of 30-50 nm spherical ZnO, EDX analysis was conducted to identify the unknown phase as shown in Figure 5.6. 80.50% and 17.98% were observed for zinc (Zn) and oxygen (O), respectively, although two other elements, calcium (Ca) and copper (Cu), were also present in smaller amounts, as stated in Table 5.7.

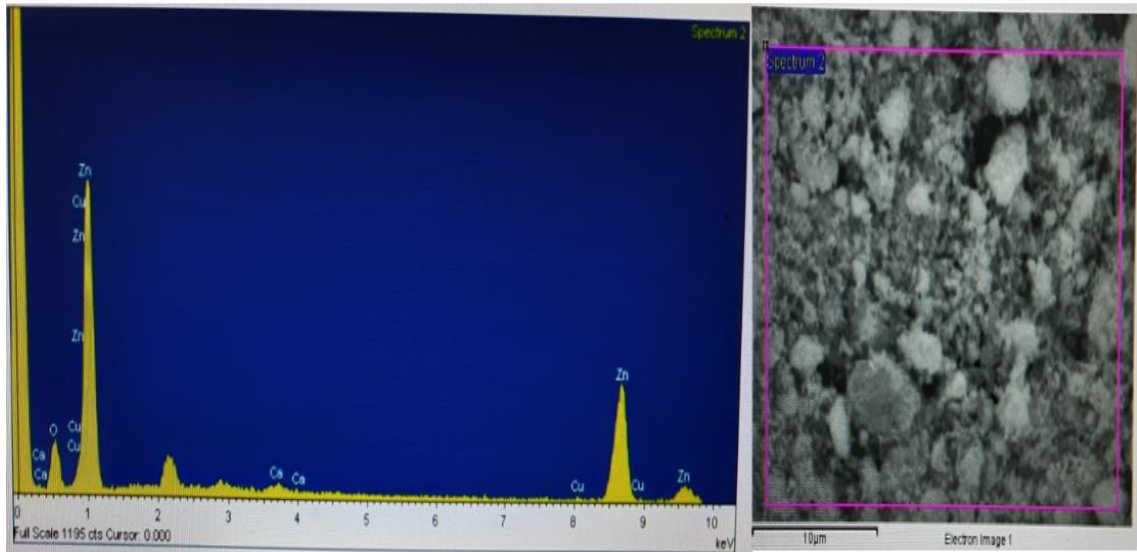


Figure 5.6. EDX Analysis result of the 30-50 nm spherical ZnO powder sample.

Table 5.7. Elemental composition of 30-50 nm spherical ZnO

Element	Weight %	Atomic %
O K	17.98	47.13
Ca K	0.56	0.58
Cu K	0.92	0.61
Zn K	80.55	51.68
Total	100	

5.1.3. Particle size results

The results from the laser diffraction method utilized for the particle size determination of original MicNo-ZnO, reduced size MicNo-ZnO, and submicron ZnO are depicted in Figure 5.7. The size reduction experiment reduced the original MicNo-ZnO size from $d(0.5) = 8.716 \mu\text{m}$ to $d(0.5) = 4.499 \mu\text{m}$ while submicron ZnO had an average particle size of $d(0.5) = 2.902 \mu\text{m}$ (see Table 5.8). The obtained size distributions for the two nano powders are shown in Figure 5.8. The average particle size values of 188.5 nm and 229.4 nm were obtained for 25–35 nm nano and 30–50 nm spherical ZnO, respectively (see Table 5.9). These results were higher than the sizes stated by the manufacturer due to the agglomeration of the nano powders when dispersed in isopropanol during particle size measurement.

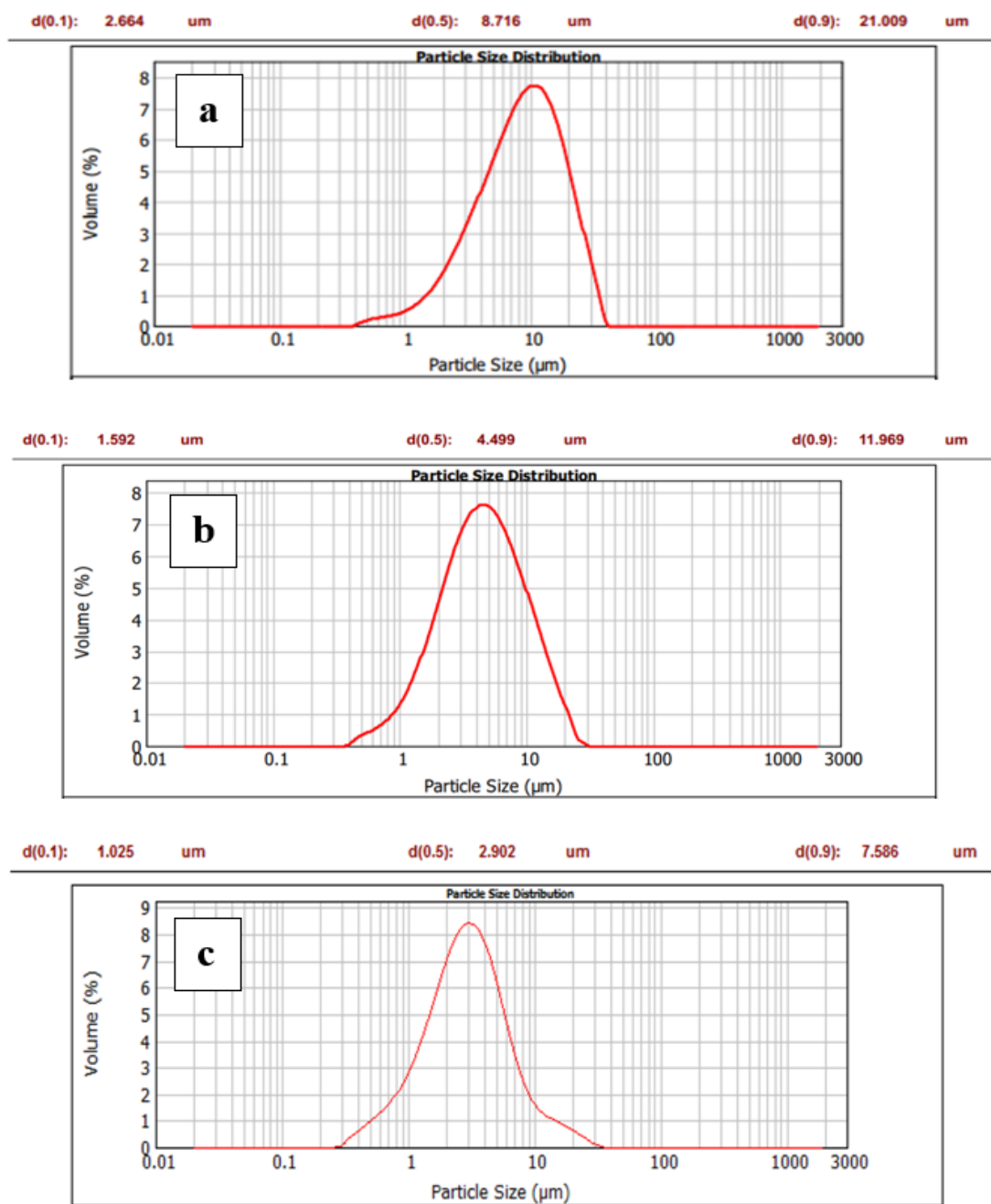


Figure 5.7. Particle size distributions (a) original MicNo-ZnO, (b) reduced size MicNo-ZnO, and (c) submicron ZnO

Table 5.8. $D(0.1)$, $d(0.5)$ and $d(0.9)$ values obtained from the Mastersizer particle size analyzer

ZnO Powder	$d(0.1) \mu\text{m}$	$d(0.5) \mu\text{m}$	$d(0.9) \mu\text{m}$
Original MicNo-ZnO	2.664	8.716	21.009
Reduced Size MicNo-ZnO	1.592	4.499	11.969
Submicron-ZnO	1.025	2.904	7.586

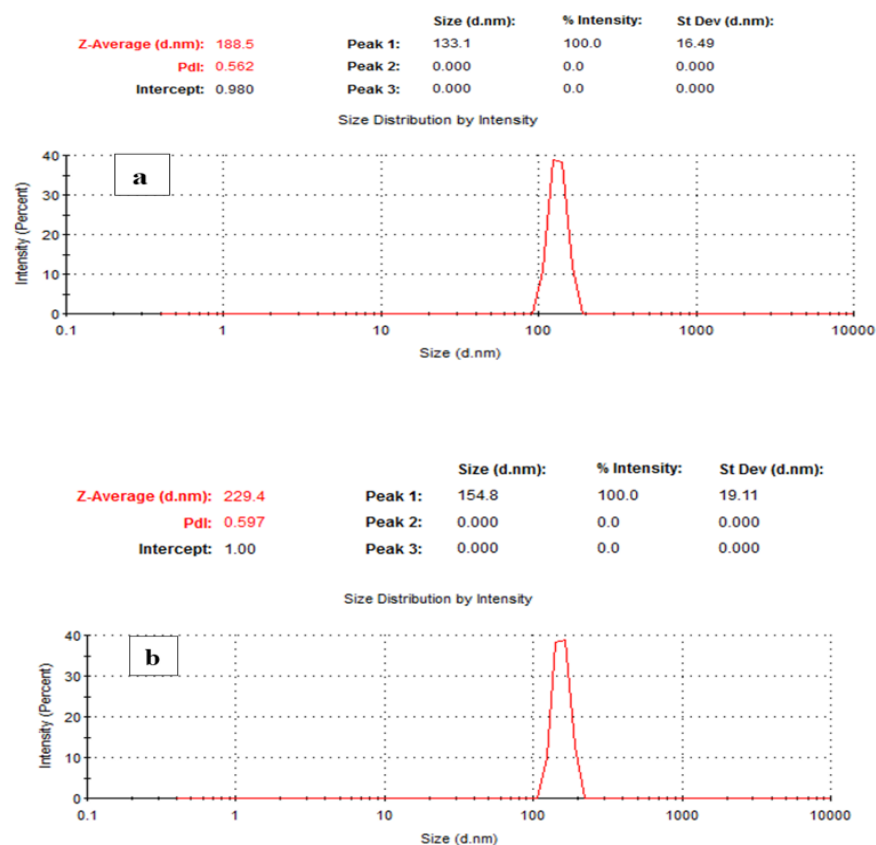


Figure 5.8. Nanoparticle size distributions of (a) 25-35 nm nano ZnO and (b) 30-50 nm spherical ZnO

Table 5.9. Average particle size of nano powders obtained from Zetasizer particle size analyzer

ZnO Powder	Z-average (d.nm)
25-35 nm nano ZnO	185.5
35-50 nm spherical ZnO	229.4

5.1.4. Thermogravimetric analysis result of 30-50 nm spherical ZnO (TGA-DTA)

The TGA-DTA of 30-50 nm spherical ZnO revealed a weight loss of 6.460%, which occurred until around 891.47°C as shown in Figure 5.9. The two minimal weight losses of 0.51% (50°C - 137°C) and 0.91% (137°C - 242.36°C) were due to the dehydration of absorbed moisture on the ZnO powder surface [115]. The most significant weight loss from this powder sample, 3.26% (242.36°C - 270.41°C), was attributed to the loss of CO₂. A weight loss of 1.78% (270.41°C - 891.47°C) was further observed. The endothermic peak at around 260°C and the dramatic weight loss between 242.36°C and 270.41°C could be associated to the decomposition of precursor material used [115].

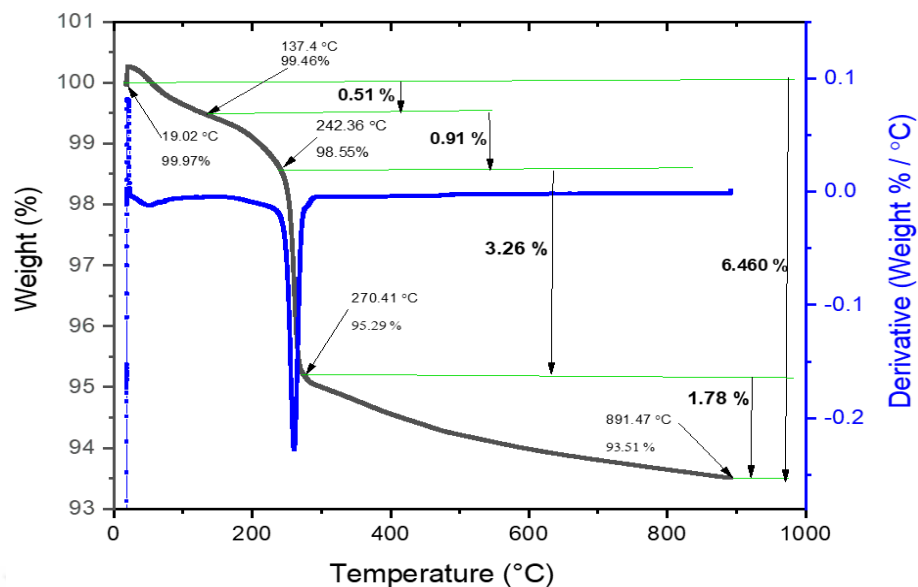


Figure 5.9. TGA-DTA graphs of 30-50nm spherical ZnO

5.1.5. Fourier transform infrared spectroscopy result of 30-50 nm spherical ZnO

The analyzed FTIR transmittance spectrum of 30-50 nm spherical ZnO is shown in Figure 5.10. The peak at 522 cm^{-1} was assigned to the presence of ZnO. Peaks at 1519 cm^{-1} and 3057 cm^{-1} were ascribed to asymmetric bond stretching of CO_2 . Also, the peak at 2353 cm^{-1} was attributed to C=O stretching of CO_2 . The peak observed around 3429 cm^{-1} was related to O-H stretching [115].

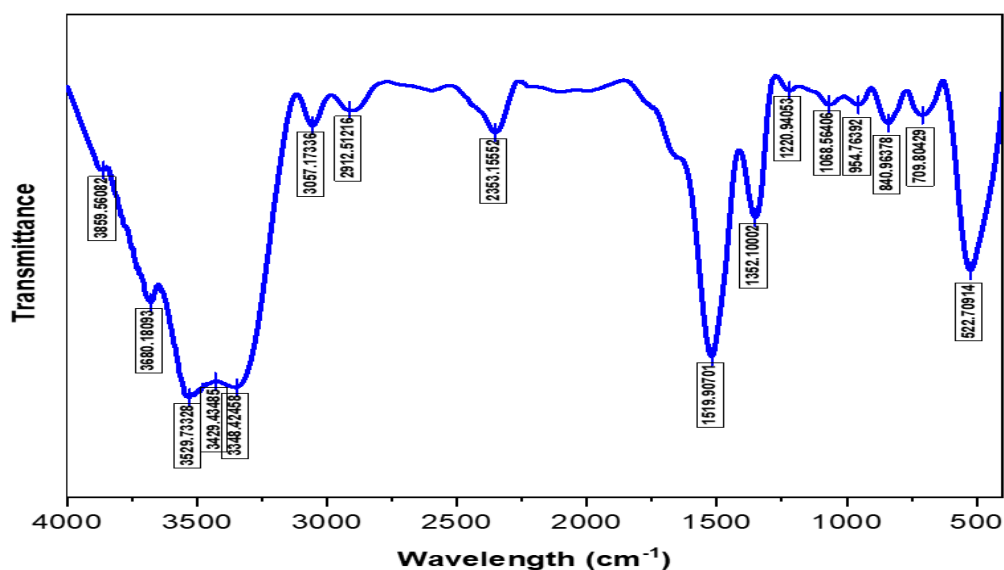


Figure 5.10. Analyzed FTIR transmittance spectrum of 30-50nm spherical ZnO

5.2. Optical Properties Measurement Results of ZnO Solid Samples

This subsection discussed the results of absorbance, transmittance, and reflectance (relative diffuse and total reflectance) of the ZnO powder particles. Optical microscopy images of PMMA samples as well as the observed mass of ZnO samples remaining after all measurements are also presented.

5.2.1. Optical microscopy images of ZnO PMMA plates

The selected microscopy images taken in order to observe the surface coverage ability of the prepared solid ZnO powder samples are shown in Figures 5.11–5.15 (the complete optical microscopy images are provided in Appendix-1, Figures 0.1–0.10). A total of 18 images were taken for each ZnO sample: 9 images each at different points on the 1st and 2nd faces of the PMMA plate. The white colouration on the images represents ZnO particles.

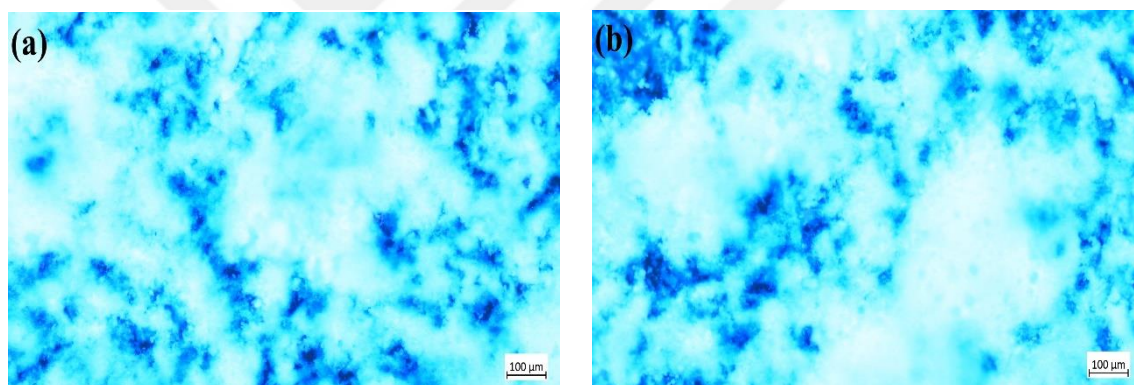


Figure 5.11. Optical microscopy images of MicNo- ZnO (a) PMMA 1st face (b) PMMA 2nd face

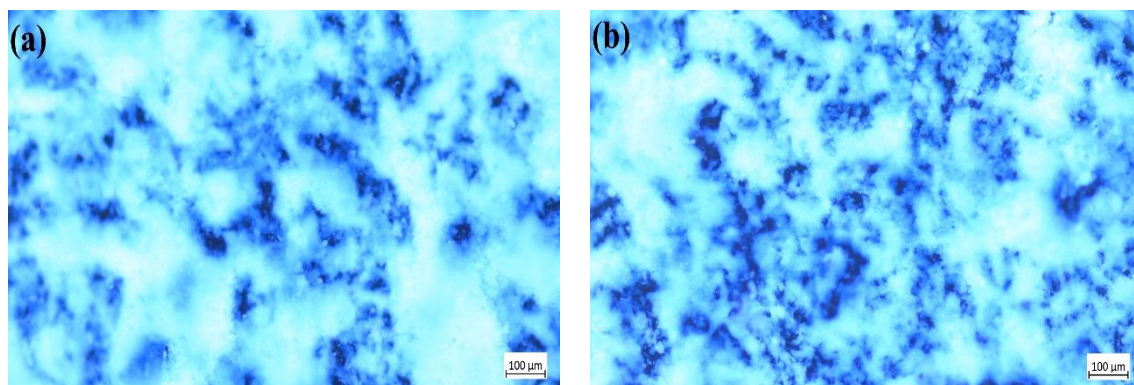


Figure 5.12. Optical microscopy images of reduced size MicNo-ZnO (a) PMMA 1st face (b) PMMA 2nd face

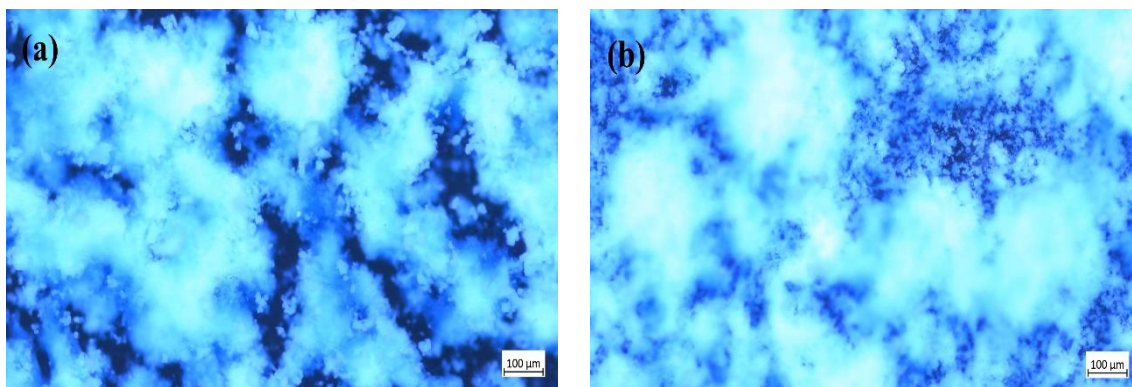


Figure 5.13. Optical microscopy images of 25-35 nano ZnO (a) PMMA 1st face (b) PMMA 2nd face

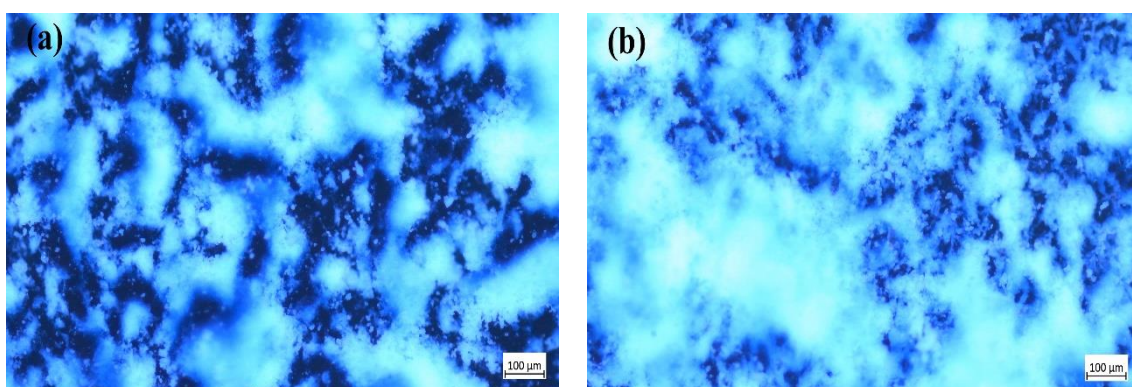


Figure 5.14. Optical microscopy images of 30-50 nm spherical ZnO (a) PMMA 1st face (b) PMMA 2nd face

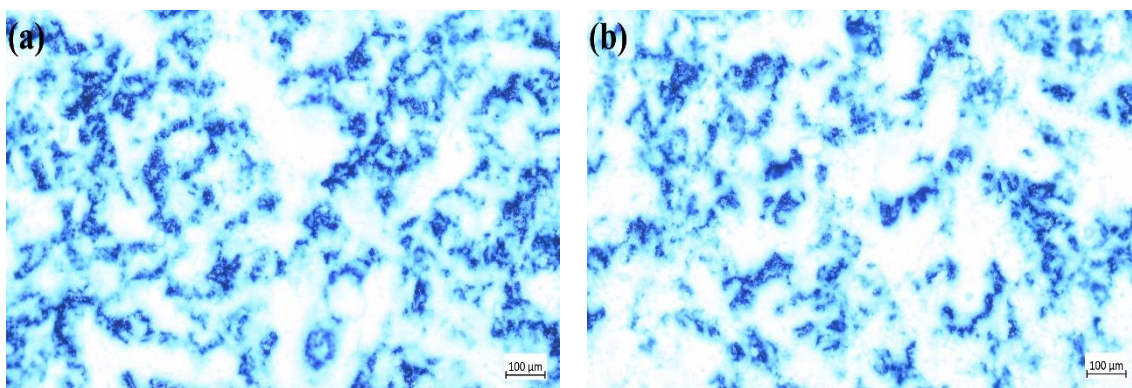


Figure 5.15. Optical microscopy images of submicron ZnO (a) PMMA 1st face (b) PMMA 2nd face

From the complete optical microscopy images of the five sample which were taken after all the absorbance and transmittance measurements, it was observed that MicNo particles (original and reduced size) and submicron spread and covered the surface PMMA plates better than their nanoparticles counterparts.

5.2.2. ZnO PMMA plates weighing results

The mass of each of the plates used for the absorbance and transmittance measurements were determined by an analytical balance (Mettler Toledo). Table 5.10 shows the total mass of each ZnO PMMA sample comprising the mass of each plate and the mass of ZnO sample which was placed in between the plates. Following all absorbance and transmittance measurements, the prepared ZnO PMMA samples were weighed after removing the sellotape used to hold the ZnO powders in between the plates as shown in Table 5.11. The amounts of ZnO powder remaining for each sample was determined by subtracting the mass ZnO PMMA sample obtained after absorbance and transmittance measurements from the total mass of ZnO PMMA sample initially obtained, and the results are shown in Table 5.12. Figure 5.16 shows a clustered column comparing the initial mass of ZnO powder placed in between the plates to the mass of the ZnO powder remaining.

Table 5.10 Total Mass of ZnO PMMA samples prepared for absorbance and transmittance measurements

ZnO PMMA sample	Mass of PMMA 1 (g)	Mass of PMMA 2 (g)	Total mass of ZnO placed in between the plates (g)	Total mass of ZnO PMMA sample (g)
Original MicNo-ZnO	4.6395	4.6513	0.1	9.3908
Reduced size MicNo-ZnO	4.6408	4.6509	0.1	9.3917
25-35nm Nano ZnO	4.9784	4.6451	0.1	9.7235
30-50nm Spherical ZnO	4.7068	4.6468	0.1	9.4536
Submicron ZnO	4.6532	4.6554	0.1	9.4086

Table 5.11. Mass of ZnO PMMA samples after absorbance and transmittance measurements

ZnO PMMA sample	Mass of ZnO PMMA sample (g)
Original MicNo-ZnO	9.3309
Reduced size MicNo-ZnO	9.3328
25-35nm Nano ZnO	9.6580
30-50nm Spherical ZnO	9.3789
Submicron ZnO	9.3461

Table 5.12. Mass of ZnO powder remaining after absorbance and transmittance measurements

ZnO PMMA Sample	Mass of ZnO PMMA sample remaining (g)
Original MicNo-ZnO	0.0599
Reduced size MicNo-ZnO	0.0589
25-35nm Nano ZnO	0.0655
30-50nm Spherical ZnO	0.0747
Submicron ZnO	0.0625

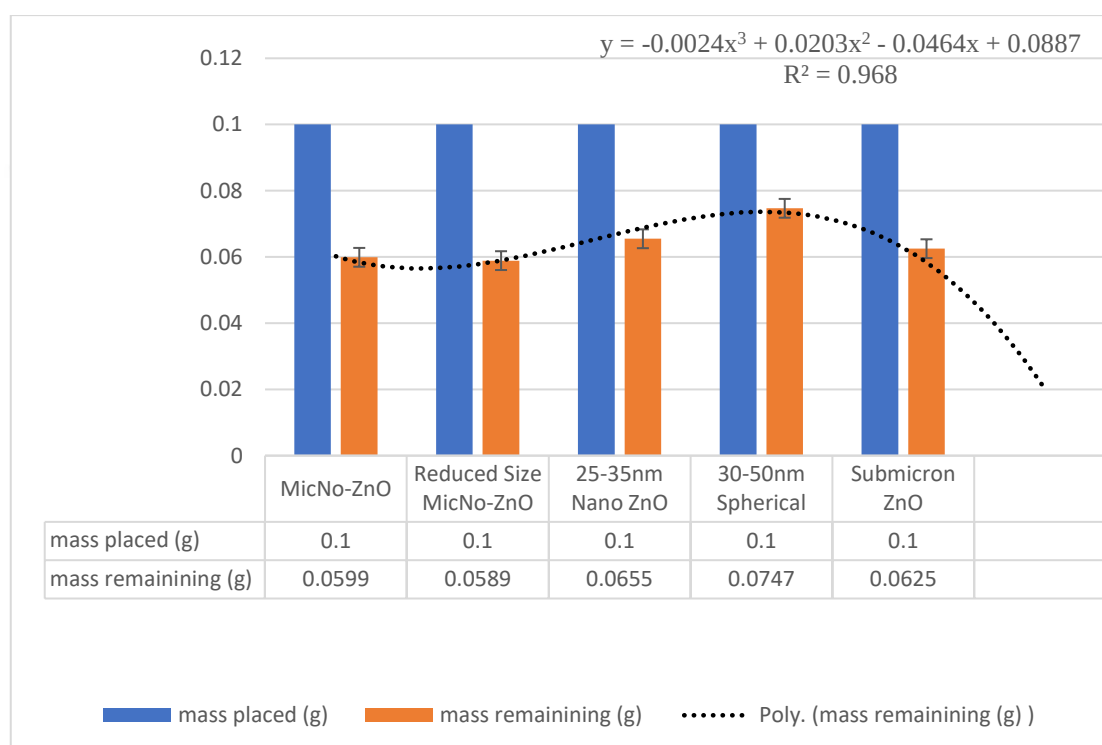


Figure 5.16. Mass of ZnO samples placed vs mass remaining after measurements

5.2.3. Absorbance measurement results

Absorbance and transmittance results in the wavelength range of 260 nm to 1200 nm are discussed herein.

5.2.3.1. Absorbance results for the first set of data obtained

The first set of absorbance measurements was comprised of 9 different points on each face of the PMMA plate samples. Hence, a total of 18 data points (1st face = 9 data and 2nd face = 9 data) were generated. For each of the two faces, an average data curve calculated from the 9 data points was plotted, while the highest and the lowest data curve were indicated (see Appendix-2, Figures 0.11 – 0.22).

5.2.3.2. Absorbance results for the second set obtained

The second set of absorbance data was comprised of 9 different data points taken randomly from any of the two PMMA plate faces within the specified measuring positions indicated in Figure 4.9. Again, an average data curve calculated from the 9 data points was plotted, while the highest and the lowest data curve from the 9 data point were indicated as shown in Appendix-3, Figures 0.21 – 0.25.

5.2.3.3. Comparison of the first and second set of absorbance data

The average graphs of the 1st and 2nd faces from the first absorbance data as well as the second absorbance data set were plotted separately and compared as shown in Figures 5.17 and 5.18. The measurements from both the 1st and 2nd faces were combined for each powder and their average values were plotted and compared with the second data obtained as shown in Figure 5.19.

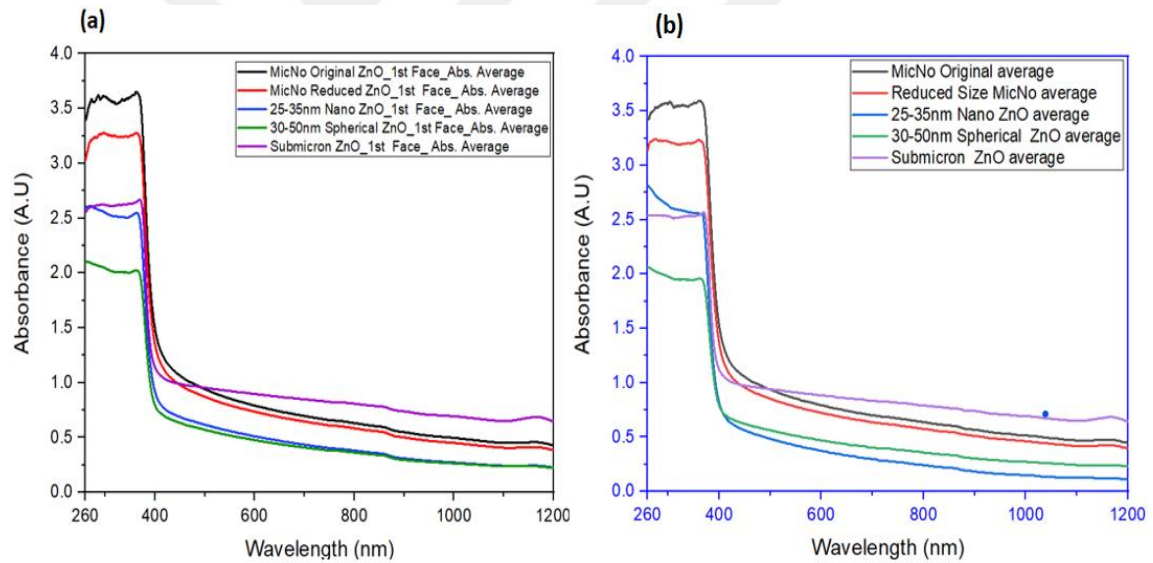


Figure 5.17. Absorbance graph comparison (a) first data set 1st face (b) second data set

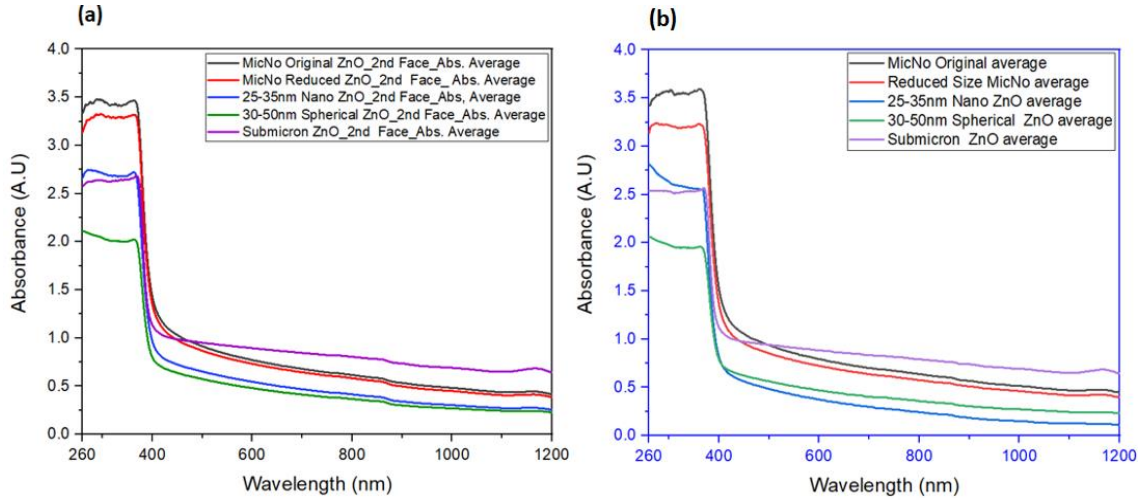


Figure 5.18. Absorbance graph comparison (a) first data set 2nd face (b) second data set

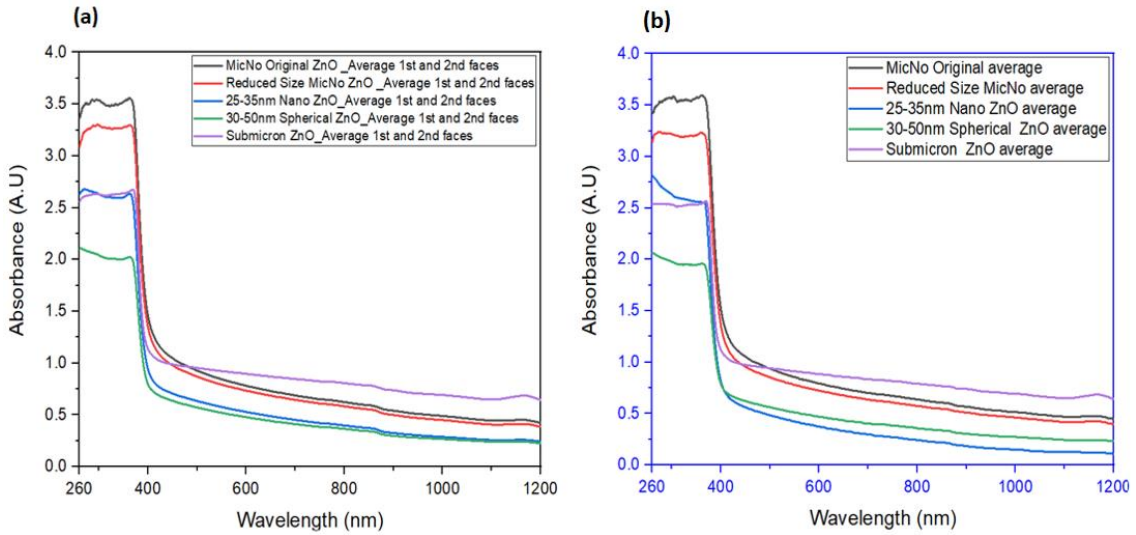


Figure 5.19. Absorbance graph comparison (a) first data set 1st and 2nd faces combined (b) second data

5.2.3.4. Extinction coefficient determination from absorbance data

A crucial parameter needed in order to calculate the extinction coefficient in this work is the powder thickness, t . Figure 5.20 shows the cross-section of the sample during absorbance and transmittance measurements. The total thickness (T) of the sample containing two PMMA plates and each of the ZnO powder sample as well as the thickness of two PMMA plates without ZnO were measured as described in Chapter 4. The average thickness of two PMMA plates without ZnO was calculated as shown in Table 5.13, and the powder thickness of each sample was estimated by subtracting the average thickness of two PMMA plates without ZnO from the average total thickness (T) as shown in Table 5.14.

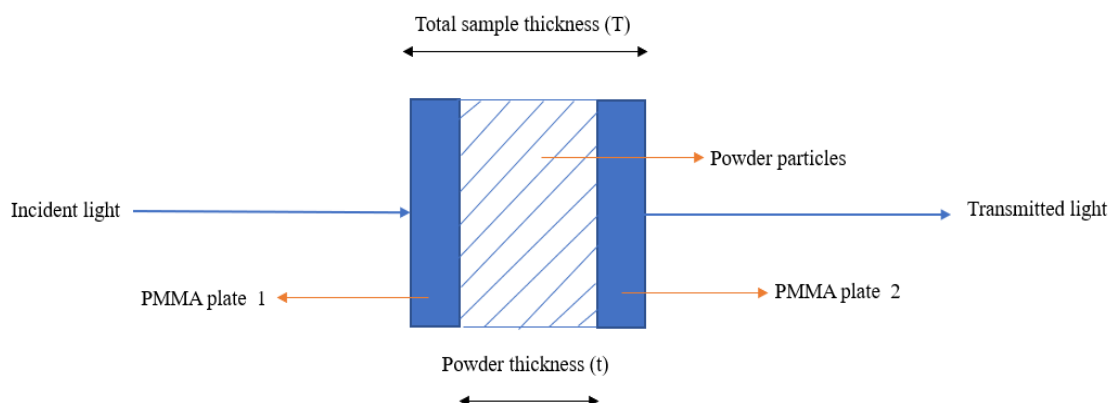


Figure 5.20. Cross section of the prepared samples during absorbance and transmittance measurements

Table 5.13. Average thickness of two PMMA plates without ZnO powder

2 PMMA Plates	Thickness of two PMMA plates without ZnO (mm)					Average (mm)
	1 st	2 nd	3 rd	4 th	5 th	
Baseline sample 1	3.060	3.038	3.082	3.036	3.091	3.061
Baseline sample 2	3.097	3.109	3.089	3.092	3.087	3.095
Extra baseline sample	3.023	3.038	3.026	3.023	3.007	3.023
Average of the three samples without ZnO = 3.0599 mm						

Table 5.14. Estimated average thickness of ZnO powder samples

Sample ZnO	Total sample thickness (T) (mm)					Average total sample thickness (T) (mm)	Average powder thickness (t) (mm)
	1 st	2 nd	3 rd	4 th	5 th		
Original MicNo-ZnO	3.144	3.134	3.140	3.125	3.141	3.1368	0.0769
Reduced Size MicNo-ZnO	3.132	3.142	3.138	3.144	3.135	3.1382	0.0783
30-50nm Spherical ZnO	3.152	3.158	3.148	3.162	3.137	3.1514	0.0915
25-35nm Nano ZnO	3.246	3.269	3.275	3.281	3.256	3.2654	0.2055
Submicron ZnO	3.131	3.139	3.126	3.123	3.144	3.1326	0.0727

A parameter which has to be calculated before the extinction coefficient can be determined is the absorption coefficient. The absorption coefficient (α) and extinction coefficient (k) were calculated using Equations 5.1 and 5.2 respectively, where A_{abs} stands for the measured absorbance, t is average powder thickness (cm), and λ is wavelength. The absorption and extinction coefficients of first absorbance data (1st face, 2nd face, and combination of 1st and 2nd faces) and their comparisons with second absorbance data are shown in Figures 5.21 and 5.22.

$$\alpha = \frac{A_{\text{abs.}}}{t} \times \ln(10) \quad (5.1)$$

$$k = \frac{\lambda \alpha}{4\pi} \quad (5.2)$$

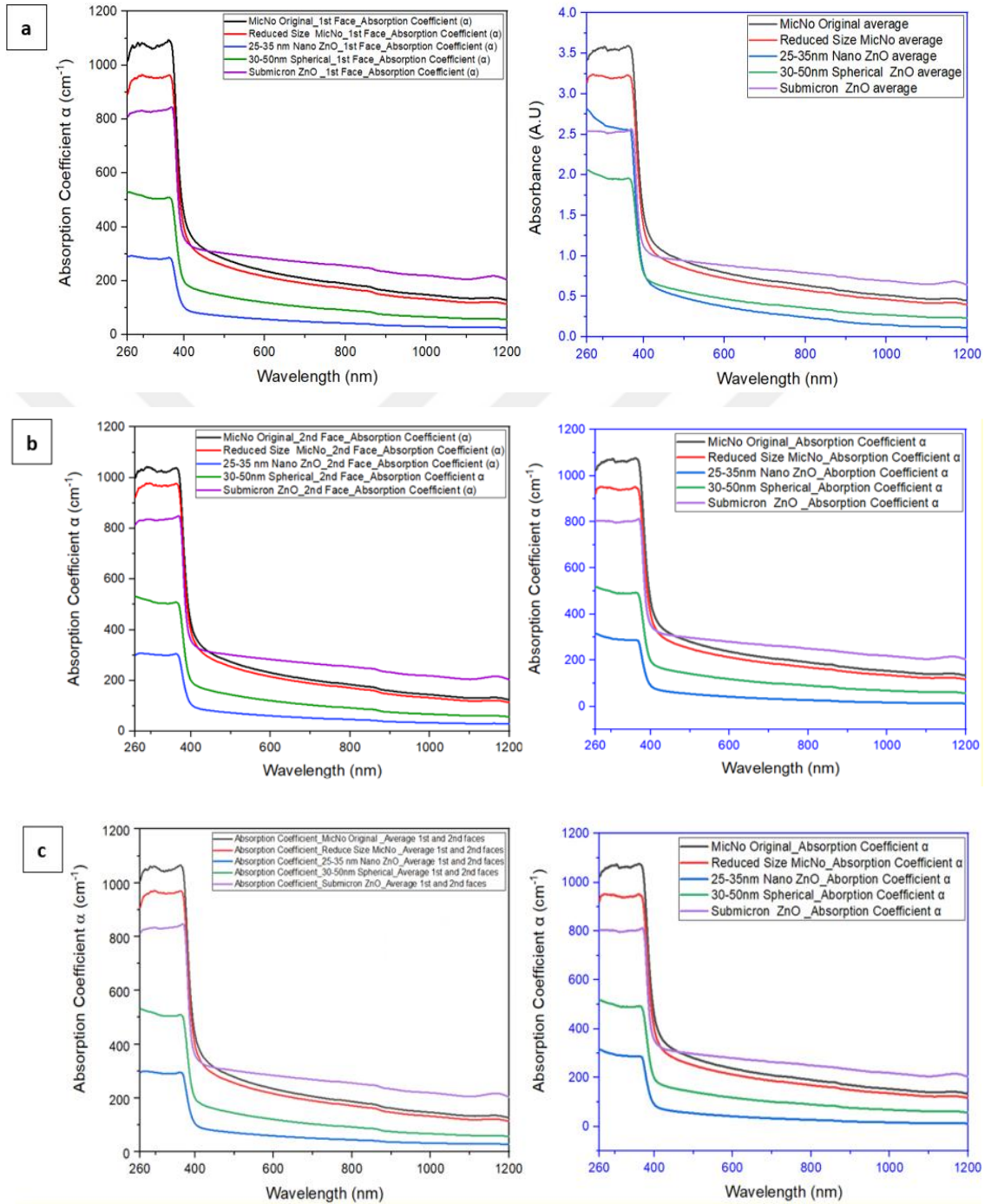


Figure 5.21. Absorption coefficient (a) first data set 1st face and second data set (b) 2nd face and second data set (c) Combined 1st & 2nd faces and second data set

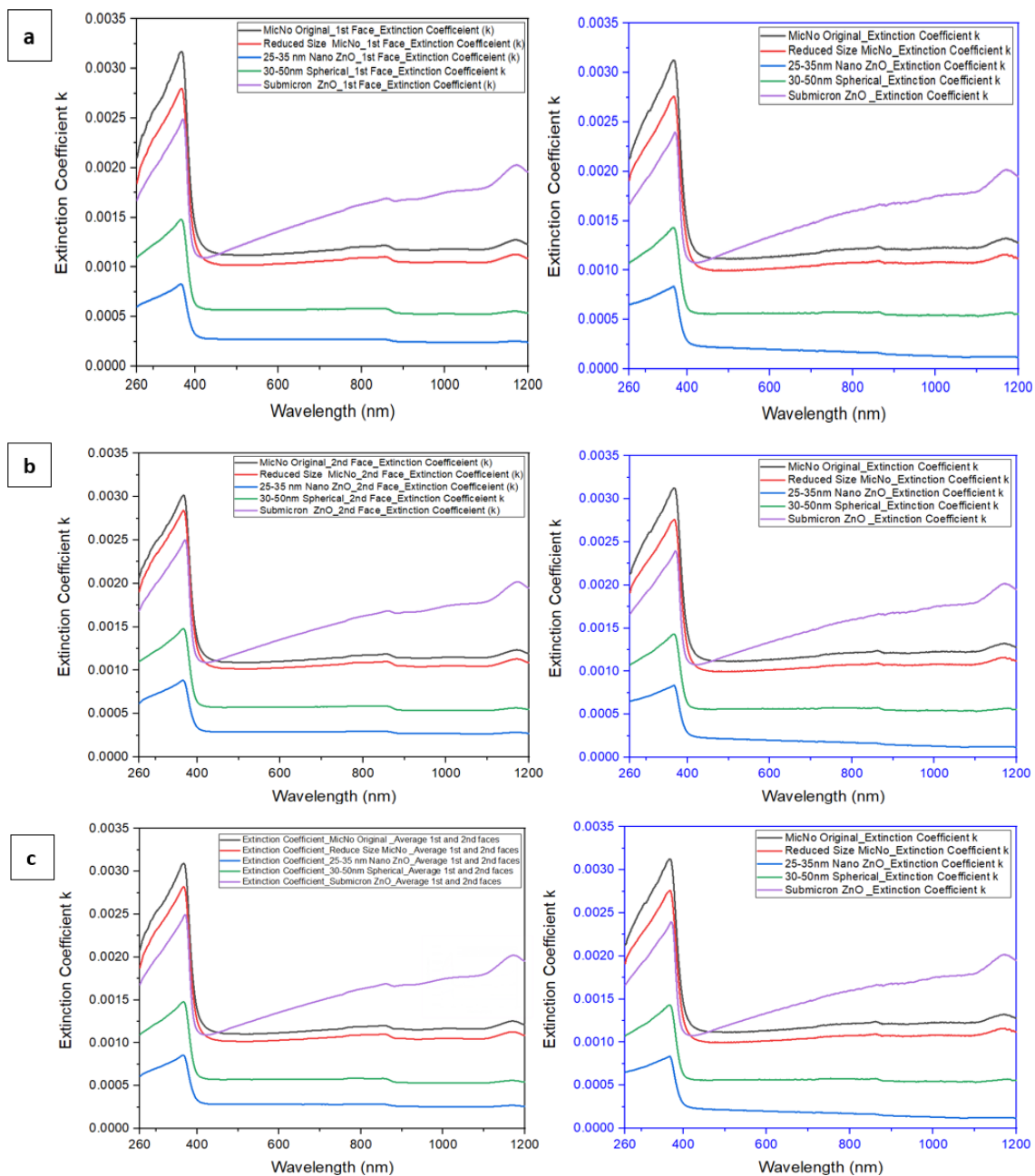


Figure 5.22. Extinction coefficient (a) first data set 1st face and second data set (b) 2nd face and second data set (c) combined 1st & 2nd faces and second data set

From the average absorbance results of the first data (1st face, 2nd face, and combined 1st and 2nd faces) and second data set represented above, MicNo-ZnO particles (original and reduced size) were observed to possess excellent UV absorbance in the UV_A and UV_B regions. Due to the peculiar morphology which combines spherical nano primary particles firmly connected together to form hexagonal platelet secondary particles, MicNo-ZnO exhibits nano and micro-particles behaviors. While the size of the primary particle provides excellent absorbance characteristics for original and reduced

size MicNo-ZnO, the unique shape/morphology also plays a crucial role in the UV ray attenuation. The original MicNo-ZnO was observed to absorb UV_A and UV_B more than its reduced size counterpart. This was because hexagonal platelets in the original MicNo-ZnO were broken during the size reduction experiment to form polygonal plates, resulting in a reduced size MicNo-ZnO, although a few hexagonal platelets were observed in the SEM images of the reduced size MicNo-ZnO. The primary particles of reduced size MicNo-ZnO were not broken into smaller particles during the reduction process. Attenuation of UV_B by absorption is primary particle size dependent. The smaller the particle size, the higher the absorption characteristic of the particle. The primary particle size observed for MicNo-ZnO particles was 47 nm (albeit higher than those reported in [3], [116]), was attributed to their higher absorption. Since the primary particle size of the reduced size MicNo-ZnO was not affected during the size reduction process, the difference in their absorbance characteristics can be attributed to the shape and secondary particle size. The hexagonal platelets in reduced MicNo-ZnO were distorted, leaving polygonal platelets, which contributed to its lower absorbance properties compared to the original MicNo-ZnO. The secondary particle size plays a vital role in the attenuation of UV ray by scattering. In this case, original MicNo-ZnO has an advantage over the reduced size MicNo-ZnO because of its larger particle size. ZnO attenuation of UV rays by absorption covers almost the entire UV range, but around $\lambda = 360$ nm (UV_A), absorption is 90% [92]. Since UV ray attenuation is dominated by absorption within the UVA region, MicNo-ZnO has higher absorbance in this region owing to its primary particles, which are kept intact within the hexagonal platelet shape, than its reduced-size particles, which have distorted hexagonal platelets (resulting in irregular polygonal platelets). The 25-35 nm nano ZnO (rice-like and irregular-shaped morphologies) was observed to have followed the MicNo-particles (original and reduced size) in absorbance rank, which can be attributed to its smaller particle size and morphology. The submicron ZnO containing mixed morphologies (equiaxial, rod-like and irregular shaped particles) was observed to have higher absorbance than 30-50 nm spherical ZnO in spite of its larger particle size. Perhaps, the additional peaks found in the XRD pattern of 30-50nm spherical may have contributed to its lower absorbance performance compared to the other powders.

The visible light wavelength range (400-500 nm) known as blue light (most energetic visible light) has been reported [117]–[119] to have damaging effects on the skin and in the eyes. Therefore, protection against blue light is paramount. The MicNo-

ZnO powder (original and reduced size) and the submicron ZnO were observed to provide very good protection in the blue light region compared to their nano powder counterparts. From the average absorbance results of the first data set (1st face, 2nd face, and combined 1st and 2nd faces), the original and reduced size MicNo-ZnO were observed to have the highest and second highest blue light protection, respectively, until they were surpassed by submicron ZnO. This occurred in the results of the first data set at the wavelength range (486 ± 7 nm) and (442 ± 5 nm) for the original and reduced size MicNo-ZnO, respectively. In the same data set, 25-35 nm nano ZnO was observed to be more effective for the protection against blue light than 30-50 nm spherical ZnO. The average absorbance result of the second data set shows that the original MicNo-ZnO is the most effective throughout the blue light region. The reduced size MicNo-ZnO had the second highest blue light protection until it was surpassed by the submicron ZnO at 443 nm. Unlike the results obtained for the first data set (1st face, 2nd face, and combined 1st and 2nd faces), 30-50 nm spherical ZnO was observed to be more effective for the protection against blue light than 25-35 nm nano ZnO in the second data set. The larger particles, original and reduced size, MicNo-ZnO (secondary particle) and submicron ZnO are more effective than the nano powders due to attenuation by scattering of visible light, which is predominately larger particle dependent.

The absorption trend, which started in the blue light region, continued through the visible regime (500-700 nm) to the IR regime (700-1200 nm). The submicron ZnO, which surpassed the MicNo-ZnO particles (original and reduced size) in the blue wavelengths as discussed above, continued the same trend through the visible regime (500-700 nm) to the IR regime (700-1200 nm). The two nanoparticles, 25-35 nm nano ZnO and 30-50 nm spherical ZnO, were observed to maintain the same curve trend exhibited in the blue light region for both the first and second data sets. The higher absorption of visible light (500-700 nm) results in less transparency which is an undesirable feature in sunscreens. For cosmetic applications, lower visible light absorption in the visible range of 500–700 nm was observed for MicNo-ZnO particles, and the nano particles are advantageous for aesthetical reasons.

The quantity of light or photons absorbed by a material is determined by the absorption coefficient, and the extinction coefficient is the amount of light lost owing to both absorption and scattering per unit length of the penetrating material medium. The extinction coefficient indicates how effectively a material absorbs and scatters

electromagnetic radiation. Electromagnetic radiation can pass freely through a material with a low extinction coefficient [120]. In the first data (1st face, 2nd face, and combined 1st and 2nd faces) and second data sets, the absorption coefficient was highest for original MicNo-ZnO, followed by reduced size MicNo-ZnO, submicron ZnO, 30-50nm spherical ZnO, and 25-35 nm nano ZnO having the lowest absorption coefficient value in the UV_A and UV_B regions where absorption dominates over scattering. The absorption coefficient is dependent on the thickness of the powder particle placed in between the PMMA sample plates. Although the same powder amount was utilized for each of the PMMA samples, it does not translate to the same powder thickness because of the differences in morphology, surface roughness, and degree of uniformity of particles on the PMMA plates. The highest thickness value was observed for 25–35 nm nano ZnO in Table 5.14, and despite having a higher absorbance than 30–50 nm spherical ZnO, its absorption coefficient was the lowest due to its thickness. In the blue light region, submicron ZnO seemed to surpass MicNo-ZnO particles, original and reduced size, in the wavelength range (456 ± 10 nm) and (418 ± 2 nm), respectively, in both the first and second data sets, while the two nanoparticles remained below the MicNo-ZnO particles. This trend continued through the visible regime (500-700nm) to the IR regime (700-1200nm). The extinction coefficient curves from the first and second data sets show that MicNo particles (original and reduced size) have excellent extinction coefficients in the UV_A and UV_B regions. The third highest extinction value was observed for submicron ZnO, followed by 20-30 nm spherical ZnO and 25-35nm ZnO having the lowest. In the blue light region, submicron ZnO seemed to surpass MicNo-ZnO particles, original and reduced size, in the wavelength range (458 ± 6 nm) and (417 ± 1 nm), respectively. The submicron ZnO curve was observed to continue to rise as the wavelength increased. This was due to more scattering in submicron ZnO particles than in other ZnO particles from blue light to visible regime (500-700nm) to IR regime (700-1200nm).

5.2.4. Transmittance results

The transmittance data were measured directly from the spectrophotometer in the same way as the absorbance data were obtained, and the same samples prepared for absorbance were utilized. As exactly measured for absorbance, two sets of data were obtained for transmittance; the first, which comprised of measurements taken separately from the 1st and 2nd faces of the PMMA plates; the second, which comprised of measurements taken randomly from the two faces.

5.2.4.1. Transmittance results obtained for the first data set

The graphs of the first transmittance data, comprising of 9 data points, and the other indicating the average, highest, and lowest curves from the 9 data points, are shown in Appendix-4, Figures 0.26 – 0.30.

5.2.4.1. Transmittance results obtained for the second data set

The graphs of the second transmittance data, comprising of 9 data points, and the other indicating the average, highest, and lowest curves from the 9 data points, are shown in Appendix-5, Figures 0.31 – 0.35

5.2.4.3. Comparison of the first and the second set of transmittance data

The average graphs of the 1st and 2nd faces from the first transmittance data as well as the second transmittance data set were plotted separately and compared as shown in Figures 5.23 and 5.24. The measurements from both the 1st and 2nd faces were combined for each powder and their average values were plotted as shown in Figure 5.25 and this can be compared to the average values of transmittance obtained for the second data shown in Figure 5.26.

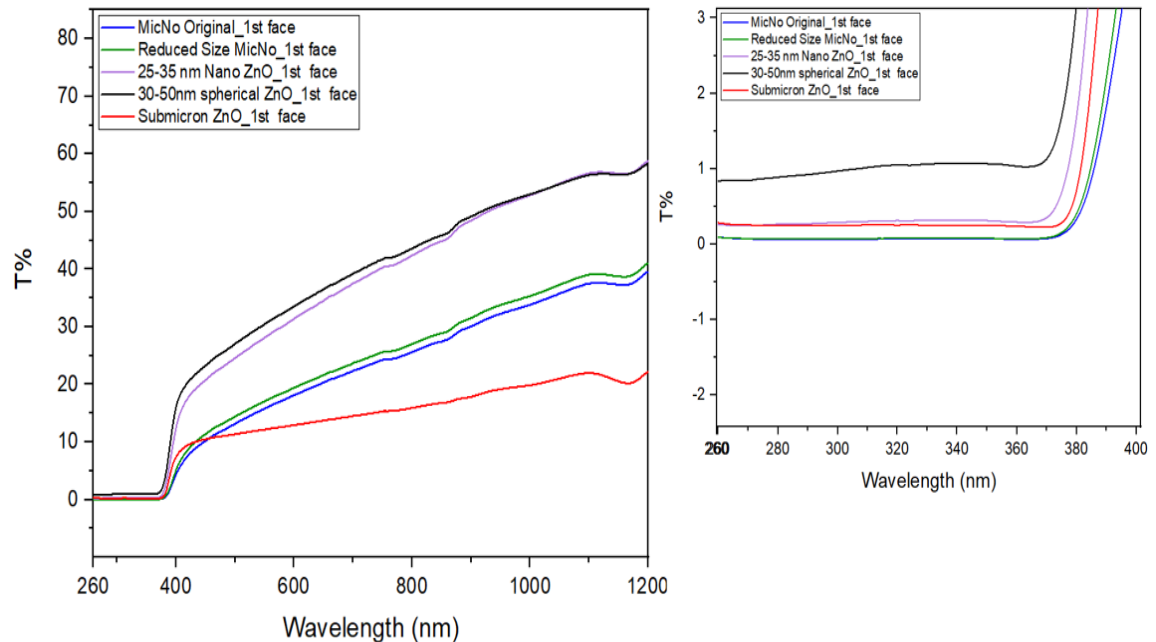


Figure 5.23. Transmittance graphs of 1st face of the first data set

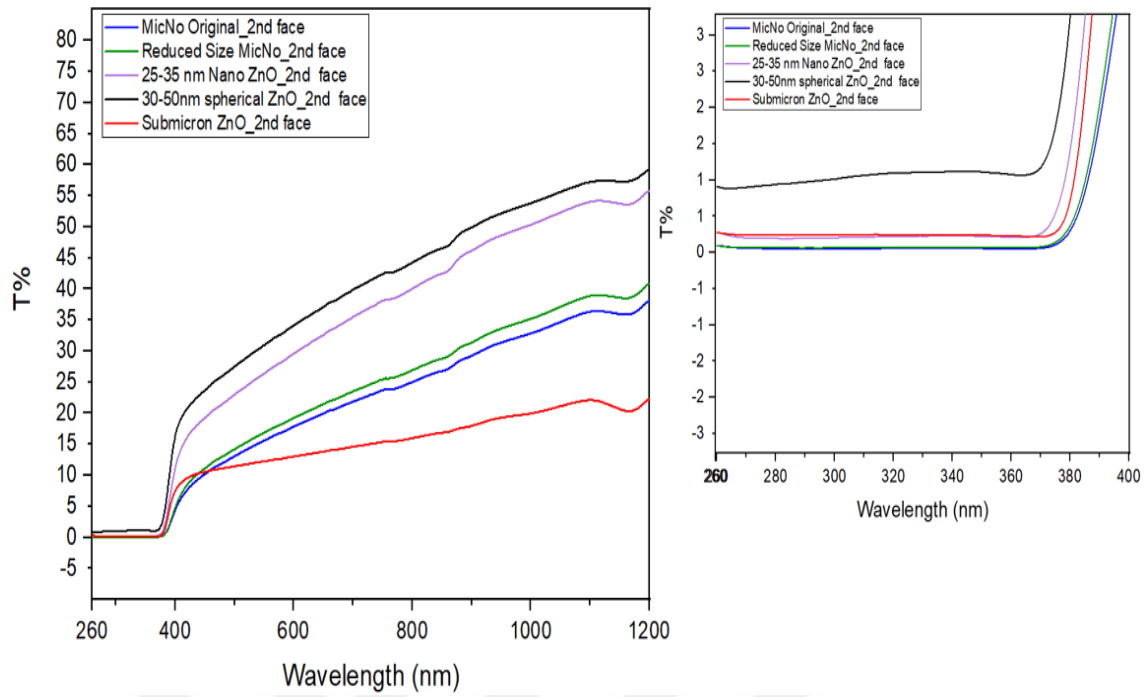


Figure 5.24. Transmittance graphs of 2nd face of the first data set

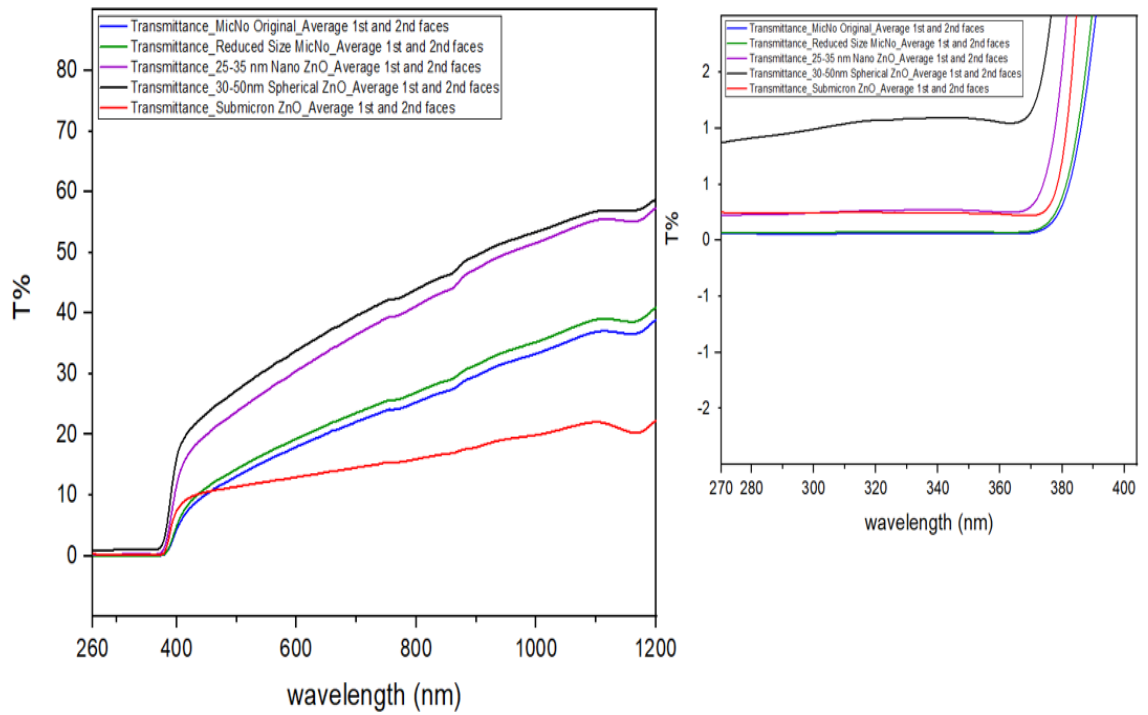


Figure 5.25. Transmittance graphs of combined 1st and 2nd faces of the first data set

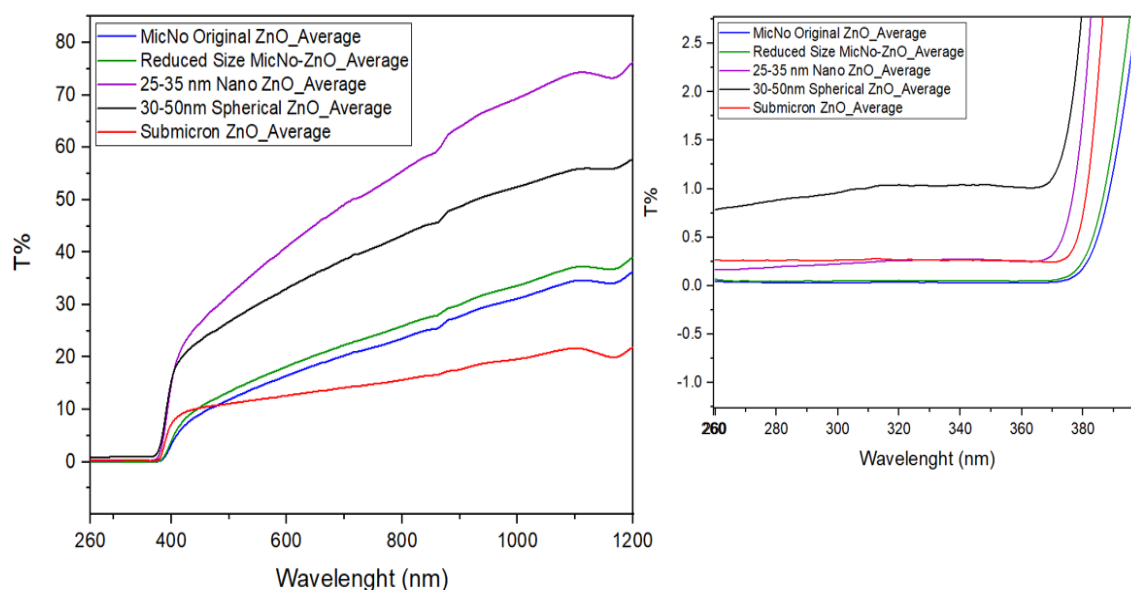


Figure 5.26. Transmittance graphs of the second data set (taken from the two faces)

From the transmittance data presented above, low transmittance values were observed for the UV_B and UV_A regions due to high UV absorption. The transmittance results of the first data set (1st face, 2nd face, and combined 1st and 2nd faces) show that 30-50 nm spherical ZnO has the highest transmittance value, followed by 25-35 nm nano ZnO, submicron ZnO, reduced size MicNo-ZnO, and original MicNo-ZnO, which were observed to have the least transmittance in the UV_B region. This was because MicNo particles (original and reduced size) have stronger absorbance than other powders in the UV_B region. The percentage transmittance ranges observed in the region were: 30-50 nm spherical ZnO (0.84-1.1%); 25-35nm nano ZnO (0.19-0.31%); submicron ZnO (0.24-0.25%); reduced size MicNo-ZnO (0.06-0.08%); and original MicNo-ZnO (0.05-0.07%). In the second data set, only the 25–35 nm nano ZnO and submicron ZnO interchanged positions, making submicron ZnO the second highest transmittance in the UV_B region. The percentage transmittance ranges observed in the region were: 30-50 nm spherical ZnO (0.88-1%); submicron ZnO (0.26-0.27%); 25-35nm nano ZnO (0.20-0.26%); reduced size MicNo-ZnO (0.05-0.06%); and original MicNo-ZnO (0.03-0.04%). In the UVA region, the first and second data sets were observed to have similar transmittance trends. 30-50 nm spherical ZnO has the highest transmittance value, followed by 25-35 nm nano ZnO, submicron ZnO, reduced size MicNo-ZnO, and original MicNo-ZnO. In the first data set, the percentage transmittance ranges observed were: 30-50 nm spherical ZnO (1.05-16.31%); 25-35nm nano ZnO (0.22-12.43%); submicron ZnO (0.25-7.5%);

reduced size MicNo-ZnO (0.07-5.1%); and original MicNo-ZnO (0.06-4.36%). The percentage transmittance ranges in the second data set were: 30-50 nm spherical ZnO (1.04–15.54%); 25–35nm nano ZnO (0.26–14.99%); submicron ZnO (0.27–7.25%); reduced size MicNo-ZnO (0.06-4.04%); and original MicNo-ZnO (0.04–3.35%). In the entire visible region (400-700nm), nanoparticles were observed to show higher transparency than other powder particles because larger particles scatter visible light more than smaller particles in the visible region. The percentage transmittance ranges observed for the first data set in the visible region (400-700nm) were: 30-50 nm spherical ZnO (16-39.9%); 25-35nm nano ZnO (11.14-37.5%); reduced size MicNo-ZnO (4.88-23.67%); and original MicNo-ZnO (4.34-22.35%); and submicron ZnO (7.41-14.6%). The percentage transmittance ranges observed for the second data set in the visible region (400-700nm) were: 25–35nm nano ZnO (14.99–49.14%); 30-50 nm spherical ZnO (15.54–38.62%); reduced size MicNo-ZnO (4.04-22.32%); original MicNo-ZnO (3.35–20.32%); and submicron ZnO (7.25–14.18%). The thickness of the ZnO samples placed in between the PMMA plates also plays a vital role in the transmittance measurement. Transmittance increases with a decrease in the thickness and this trend occurred in the percentage transmittance ranges observed for the second data set in the visible region (400-700nm).

5.2.5. Reflectance measurement results

For each type of the reflectance measured in this study, relative diffuse and total reflectance, four measurements were taken for each sample. The relative diffuse reflectance behaviors were measured twice.

5.2.5.1. Relative diffuse reflectance measurement results

The graphs of the first relative diffuse reflectance data obtained in this study as well as their graphs indicating the average, highest, and lowest curves are shown in Appendix-6, Figures 0.36 – 0.40. The average value of the data (first measurements) of each powder was plotted for the purpose of comparison as shown in Figure 5.27. Similarly, the graphs of the second relative diffuse reflectance data as well as their graphs indicating the average, highest, and lowest curves are shown in Appendix-7, Figures 0.41 – 0.45. The average value of the data (second measurements) of each powder was plotted for the purpose of comparison as shown in Figure 5.28.

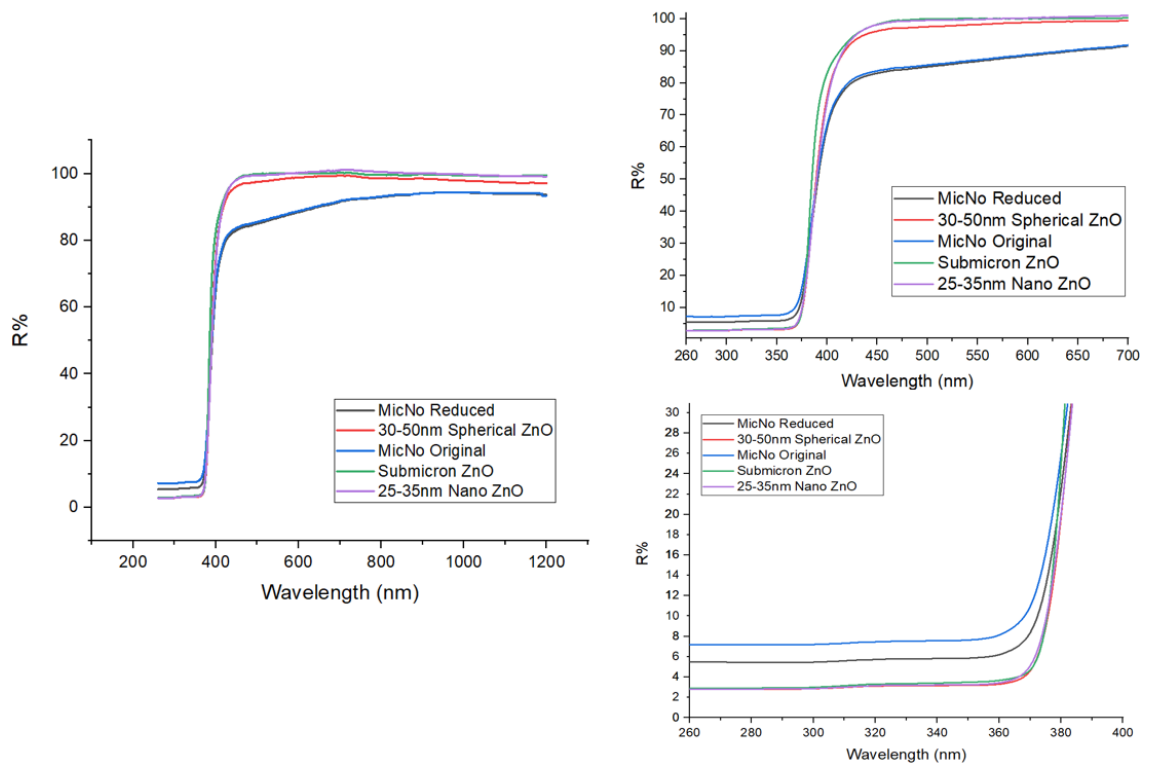


Figure 5.27. Relative diffuse reflectance graphs of the average values of each ZnO sample (first data)

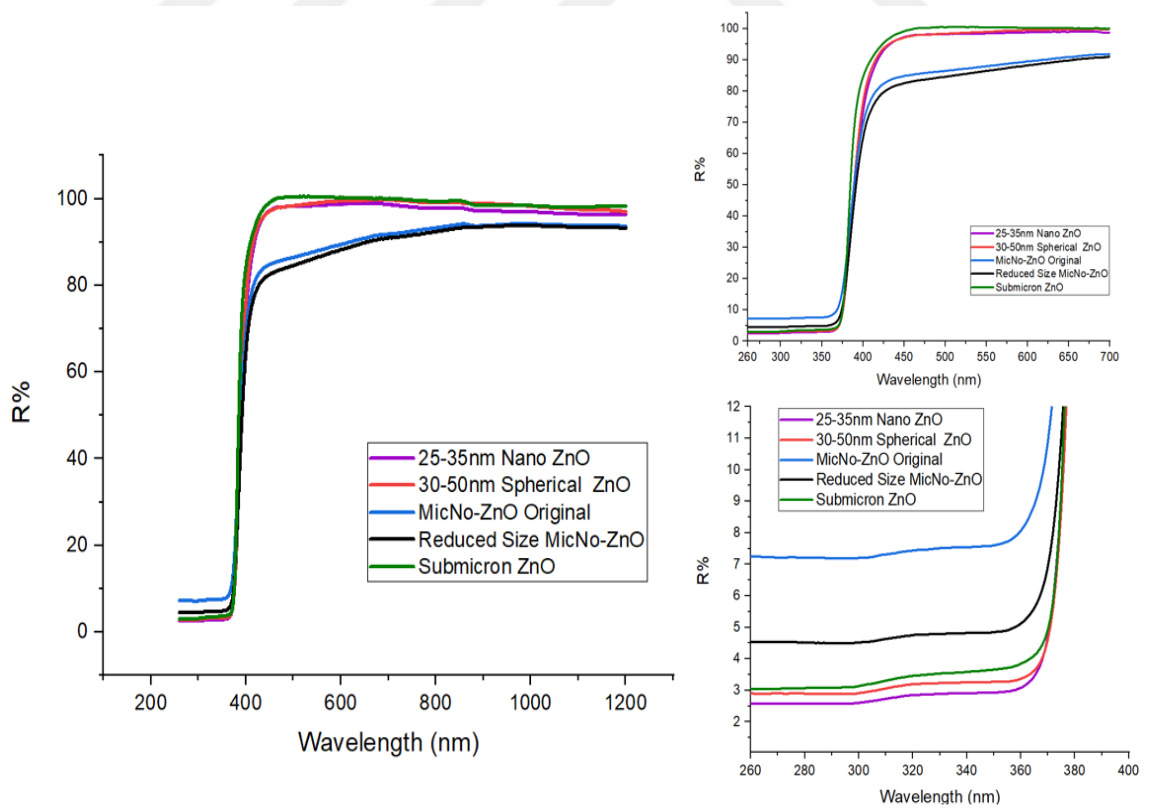


Figure 5.28. Relative diffuse reflectance graphs of the average values of each ZnO sample (second data)

The average values of first and second relative diffuse reflectance measurements of the same powder were compared to each other as shown in Figure 5.29. Relative diffuse reflectance graphs of the average values of each ZnO sample (first and second measurements) in Figures 5.27 and 5.28 were compared in the UV region as shown in Figure 5.30.

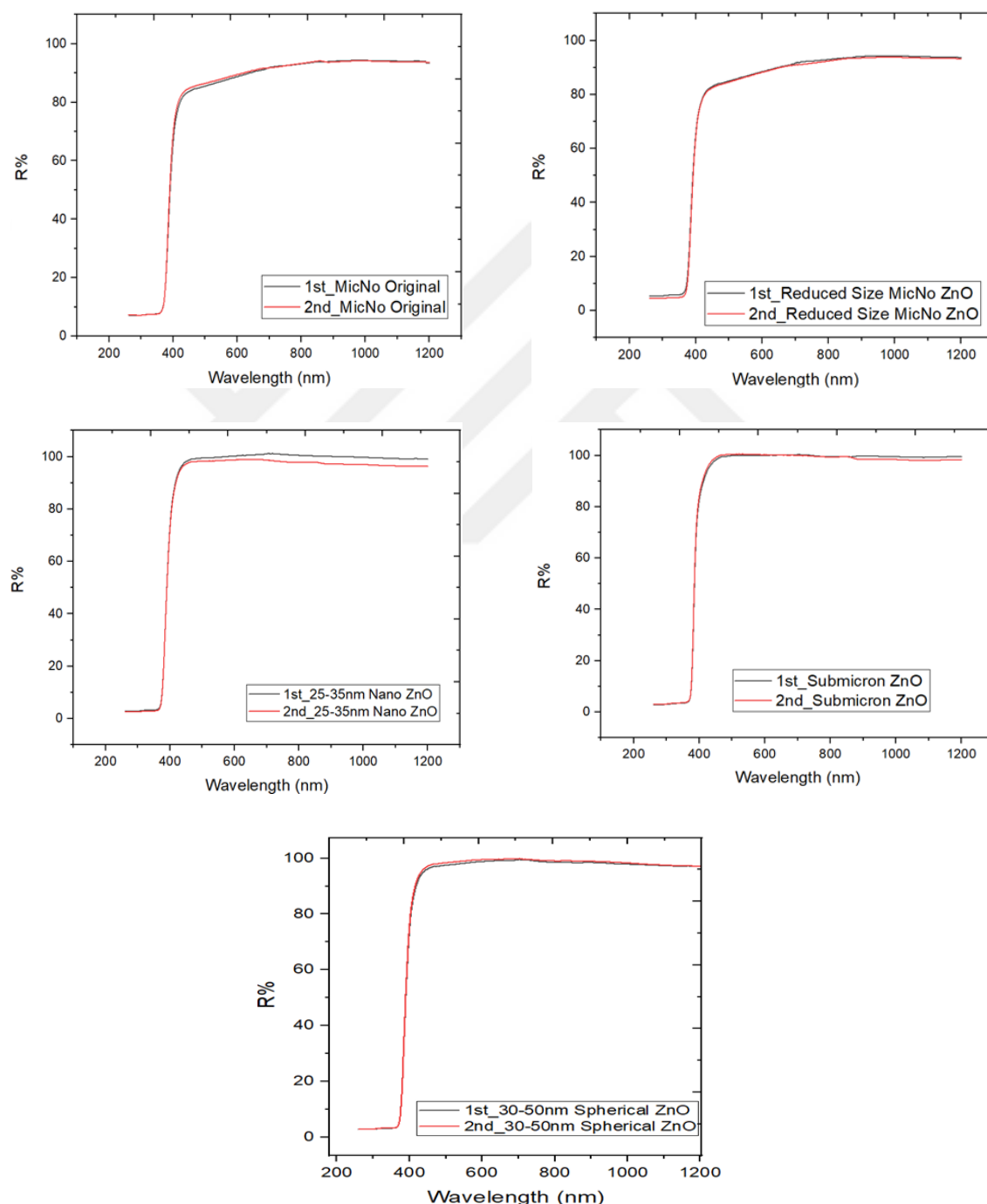


Figure 5.29. Relative diffuse reflectance comparison of 1st and 2nd measurements of each powder

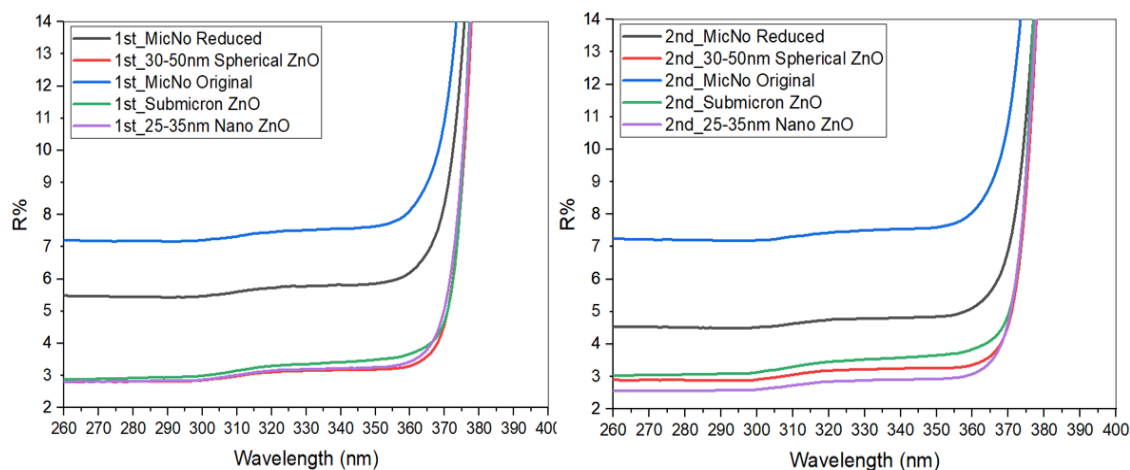


Figure 5.30. Relative diffuse reflectance graphs of the average values of each sample (1st and 2nd data)

5.2.5.2. Relative total reflectance measurement results

The relative total reflectance measurements of the five powder systems were obtained as described in Chapter 4. Unlike the relative diffuse reflectance, only one set of data was taken for the relative total reflectance. The graphs of the relative total reflectance data as well as their graphs indicating the average, highest, and lowest curves are shown in Appendix-8, Figures 0.46 – 0.50. The average value of the data of each powder was also plotted for the purpose of comparison as shown in Figure 5.31.

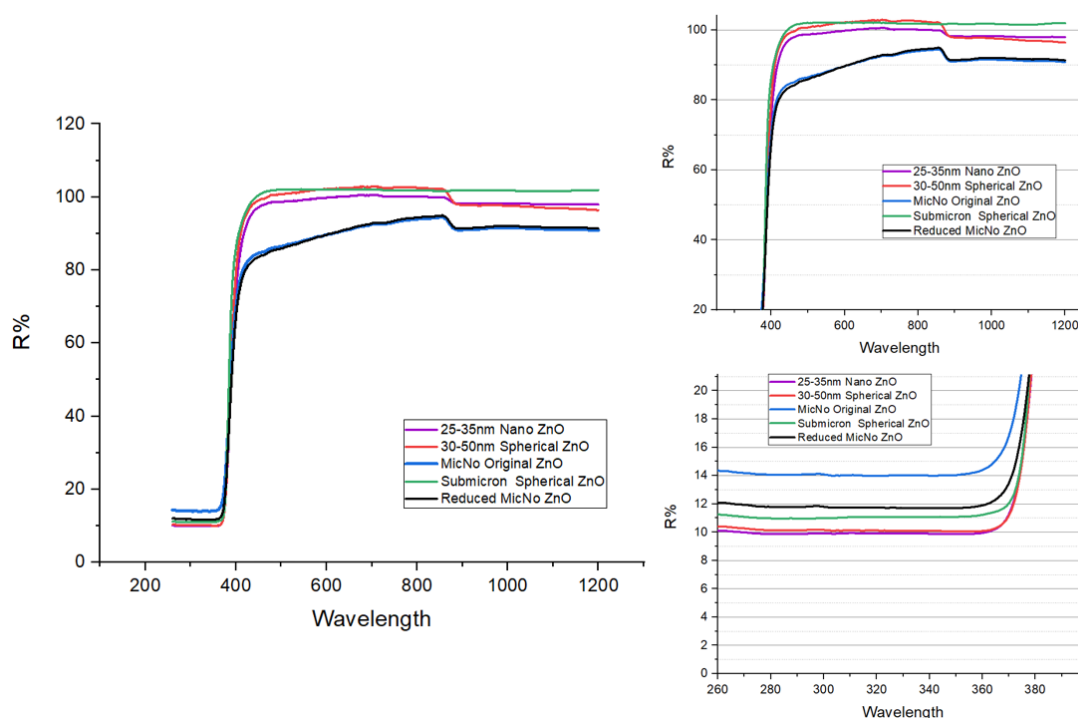


Figure 5.31. Relative total reflectance graphs (average values) of the five powder systems

5.2.5.3 Comparison of relative diffuse and relative total reflectance results

The two sets of data obtained for relative diffuse reflectance were plotted with the relative total reflectance, utilizing their average values. The graphs are shown in Figures 5.32 and 5.33.

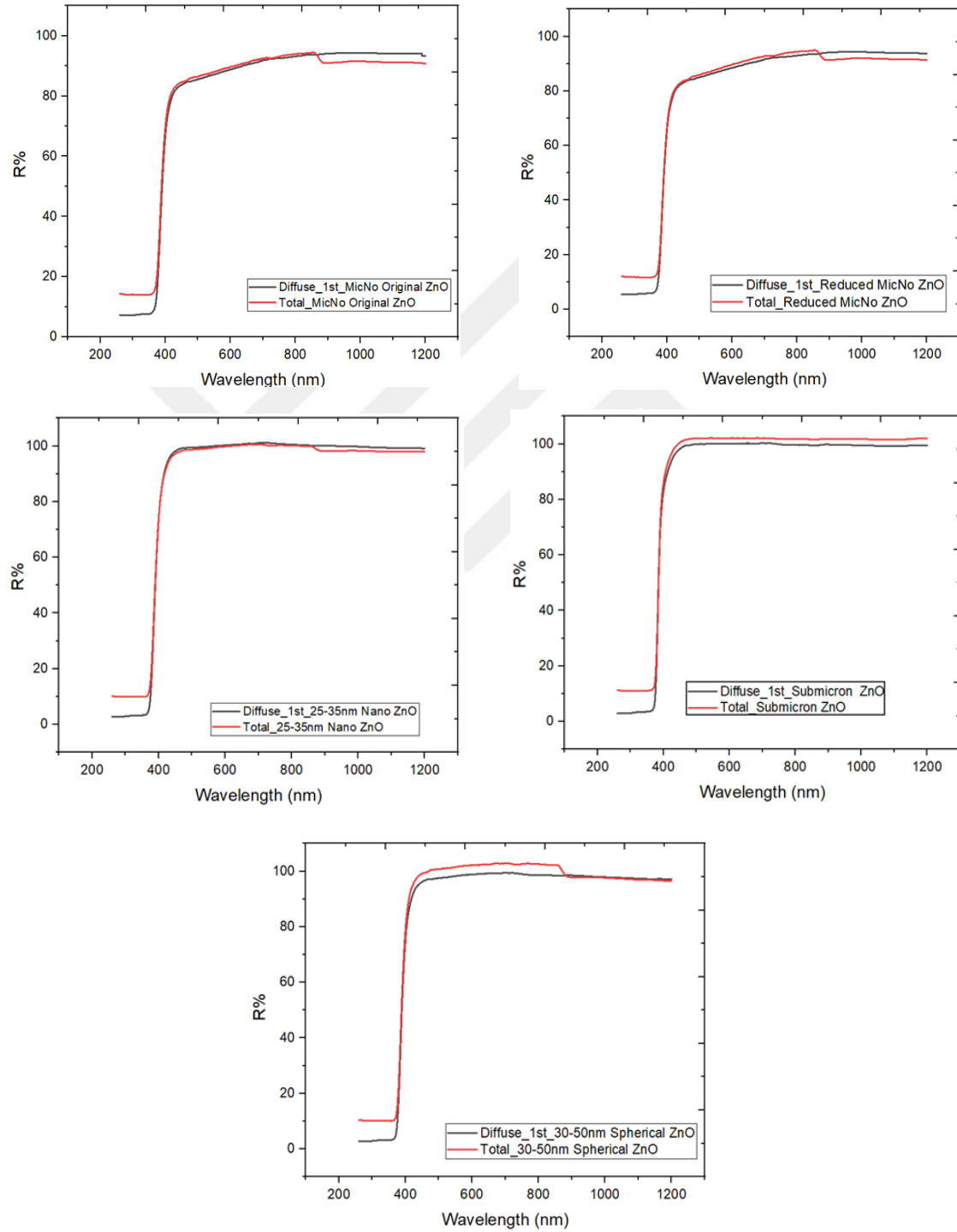


Figure 5.32. Graphs of relative total reflectance and the 1st relative diffuse reflectance data

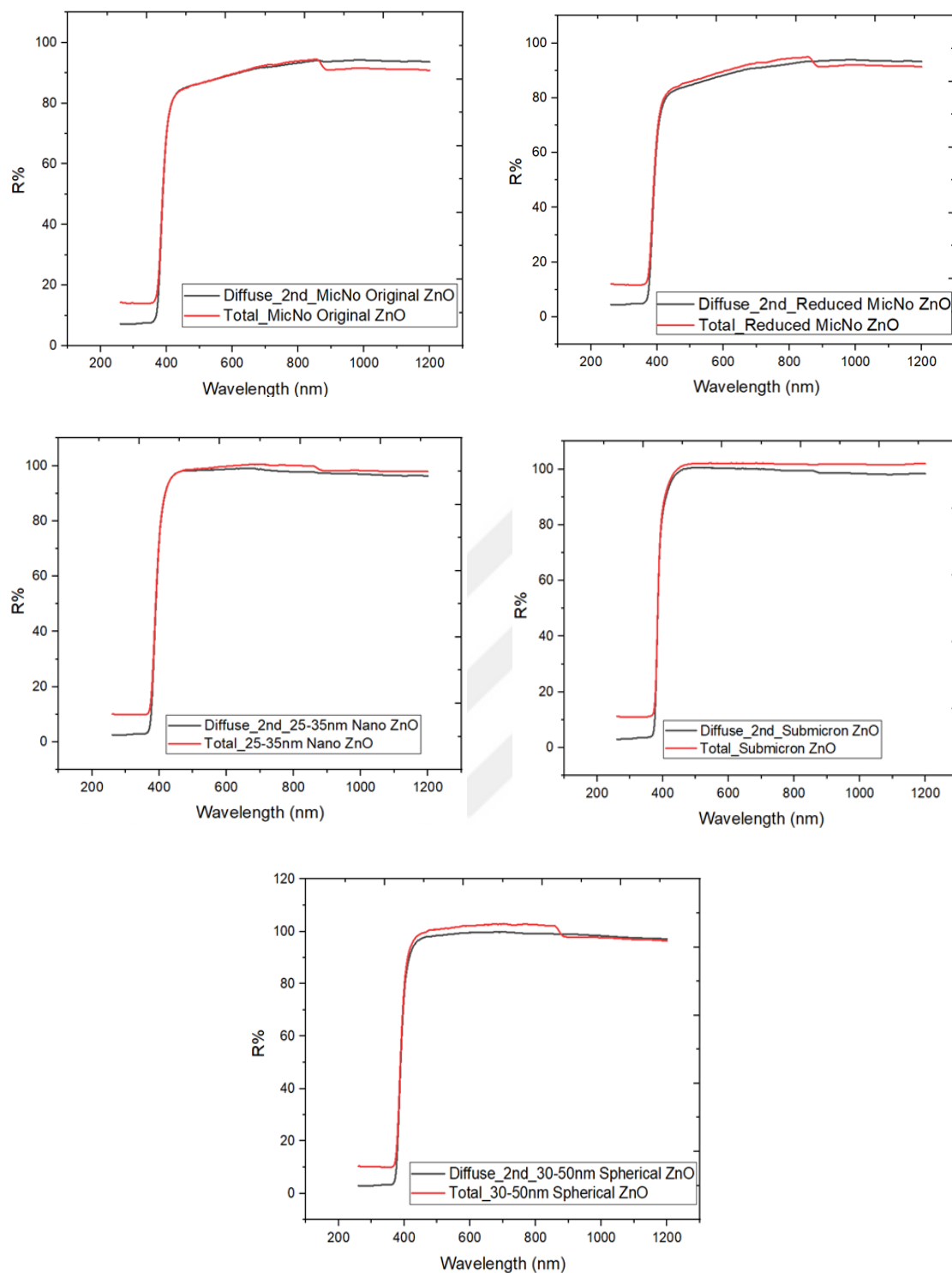


Figure 5.33. Graphs of relative total reflectance and the 2nd relative diffuse reflectance data

In the two diffuse reflectance measurements presented, the highest reflectance value was observed for the original MicNo-ZnO, followed by reduced size MicNo-ZnO, submicron ZnO, 30–50 nm spherical ZnO, and 25–35 nm nano ZnO. The five ZnO samples experienced a shape increase near the UV_A-VIS region. This sharp increase was observed at 380 nm for submicron and original MicNo-ZnO and at 382 nm for 30-50 nm spherical ZnO, 25-35 nm nano ZnO, and reduced size MicNo-ZnO. At around 420 nm (visible light region), it was observed that the five ZnO samples started to experience strong reflective characteristics, which were maintained till 1200 nm in the IR region. In the visible (400-700 nm) and IR (700-1200 nm) regimes, the highest reflectance value was observed for submicron ZnO, followed by 30-50 nm spherical ZnO, 25-35 nm nano ZnO, original MicNo-ZnO, and reduced MicNo-ZnO. The same trend was observed in the total reflectance in terms of highest to the lowest ranking in the UV, visible and the IR regions. The comparisons graphs of the diffused reflectance (first and second measurements) to the total reflectance measurement showed significant difference between diffused and total reflectance spectra in the UV region. This indicates that specular reflectance occurred in each of the five powder samples.

5.3. Results of Formulated Sunscreens

5.3.1 SPF and optical measurement results of formulated sunscreens

Sunscreen formulations made at the initial stage of this research include original and reduced MicNo-ZnO, submicron ZnO, and 30-50 nm spherical ZnO. Due to the late procurement of nano ZnO, its sunscreen was formulated about 10 months after the initial formulations, utilizing the same formulation constituents and procedures. The SPF and optical properties of the initial formulated sunscreens were measured with the aid of a spectrophotometer as discussed in Chapter 4, and the results are as shown in Table 5.15. This table also includes the nano ZnO results obtained. The SPF and optical properties measurements of the initial formulated sunscreens were repeated 10 months after production and the results are shown in Table 5.16.

Table 5.15. *SPF and optical properties measurement results*

	Original MicNo-ZnO	Reduced Size MicNo-ZnO	30-50nm Spherical ZnO	Submicron ZnO	25-35nm Nano ZnO
SPF	38.66	68.22	73.32	14.66	49.39
COV	6.26	10.43	9.92	4.11	9.84
UV _A PF	20.18	29.07	29.93	12.66	20.55
UV _A	32.57	53.77	57.34	14.34	39.12
UV _B	39.83	71.26	76.70	24.71	51.53
UV _A /UV _B	0.82	0.75	0.75	0.97	0.76
Critical Wavelength (nm)	374	374	374	379	372
400 nm %T	59.63	54.99	53.72	44.72	66.30
500 nm %T	67.65	64.27	62.16	49.50	75.60
550 nm %T	72.85	69.47	66.94	53.30	80.45

Table 5.16. *Repeated SPF and optical properties measurement results of initial formulated sunscreens*

	Original MicNo-ZnO	Reduced Size MicNo-ZnO	30-50nm Spherical ZnO	Submicron ZnO	25-35nm Nano ZnO
SPF	24.20	32.74	23.10	12.41	-
COV	11.10	9.05	8.49	13.99	-
UV _A PF	14.94	17.91	14.28	11.65	-
UV _A	21.33	28.18	20.48	12.48	-
UV _B	24.72	33.60	23.58	12.40	-
UV _A /UV _B	0.86	0.84	0.87	1.01	-
Critical Wavelength (nm)	375	374	374	379	-
400 nm T%	60.797	60.385	64.786	43.742	-
500 nm T%	68.913	68.775	73.452	48.555	-
550 nm T%	73.727	73.590	78.129	51.994	-

SPF value obtained for the original MicNo-ZnO powder seemed to be approximately half of the SPF value of its reduced size counterpart. This came surprisingly and unfortunately, there was no sufficient amount of original MicNo-ZnO of the same production LOT number needed to repeat the same formulation. This happened because a larger amount of the specific LOT number of the original MicNo-ZnO powder obtained for this study was utilized during the size reduction experiment (described earlier in Chapter 3), which had several repetitions with varied conditions until the preferred particle size was obtained. The SPF values obtained for the initial and repeated

measurements were compared as shown in Figure 5.34. The percentages of SPF retained for original MicNo-ZnO, reduced size MicNo-ZnO, 30-50 nm spherical ZnO and submicron ZnO are 62.6, 48, 31.5 and 84.7, respectively. ZnO with smaller particle size seemed to have lower SPF value due to agglomeration in the formulation.

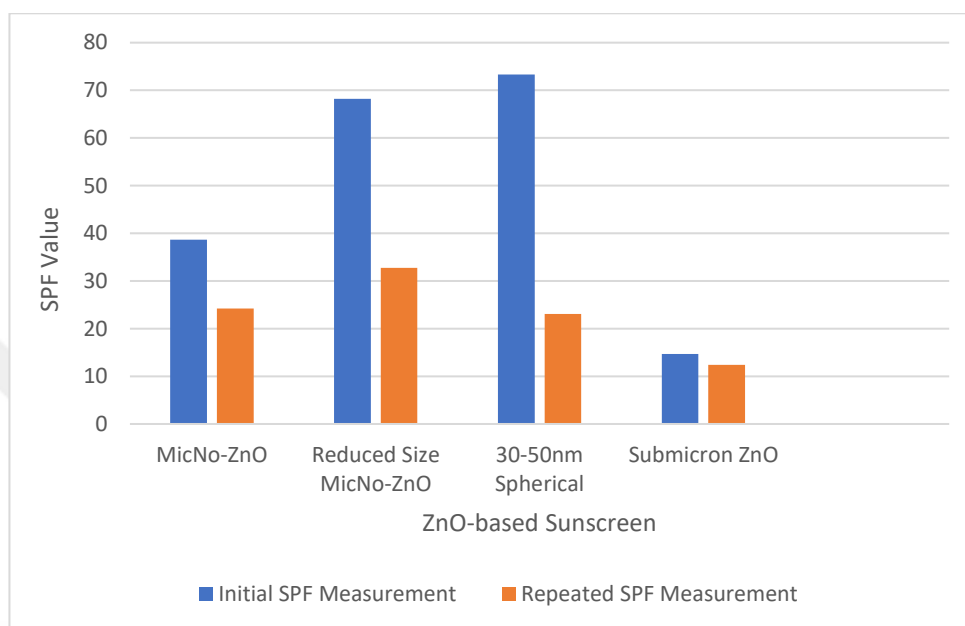


Figure 5.34. Initial vs repeated SPF measurements

With one formulation system utilized in this study, the excellent optical properties observed in the solid powder samples seemed not to have been reflected in two of the formulated sunscreens, although the effects of particle size and shape were observed in the formulations. The original MicNo-ZnO and the submicron ZnO, because of their larger particle size, were observed to retain a significant amount of their SPF values after 10 months of formulation compared to the smaller particles, which agglomerated and led to lower SPF in their formulations.

6. CONCLUSIONS AND RECOMMENDATIONS

This study represents the first investigation of the effects of size and shape on the optical properties of solid ZnO powders using a UV-VIS-NIR spectrophotometer. Unlike the conventional cuvette method, the novel approach employed for absorbance and transmittance measurements enabled fair comparisons between the powder samples of different rates of sedimentation in deionized water. From the five samples of different shapes and sizes that were utilized, it was observed that size and shape have a significant impact on the optical properties of ZnO particles. The MicNo-ZnO powder particles were observed to have excellent UV_A and UV_B absorbance properties, with very good protection at blue light wavelengths. The superior optical properties exhibited are based on their particle sizes and shapes. The formulation system used to make formulated sunscreens, on the other hand, hides these great qualities. This was as a result of the complex relationship that exists between the formulating ingredients and the ZnO particles. In the continuation of this investigation, the relationship that exists between the surface coverage of PMMA plates and the measured optical properties is recommended to be studied. In order to ensure that the excellent optical properties of the solid samples are exhibited in formulations, different types of formulation systems and approaches are recommended.

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http-30: Shimadzu, “UV-VIS Spectrophotometers Accessories”; https://www.shimadzu.co.kr/sites/shimadzu.co.kr/files/pim/pim_document_file/brochures/11008/267_c101e070l.pdf (Date of Access: 16.05.2022)

APPENDIX

APPENDIX-1. Optical Microscopy Images of PMMA Plates

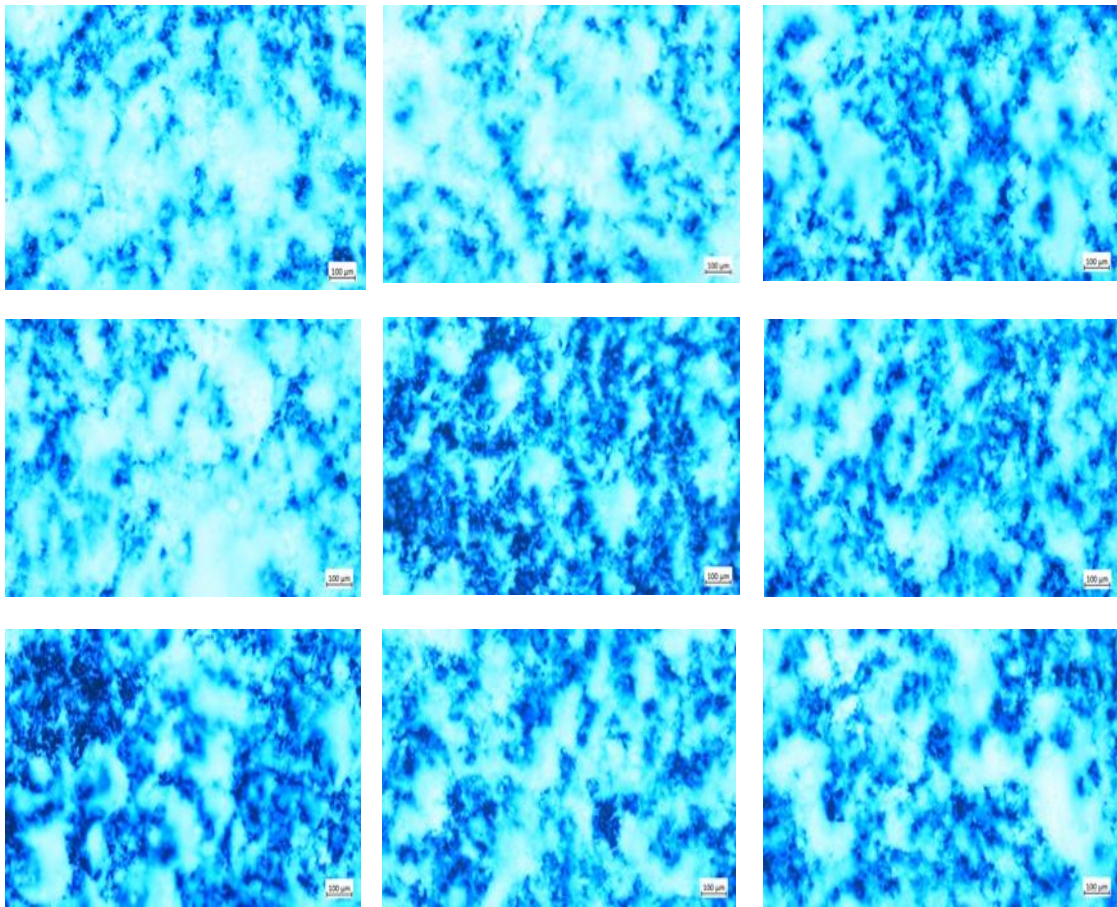


Figure 0.1. *Optical microscopy images of MicNo-ZnO PMMA 1st face*

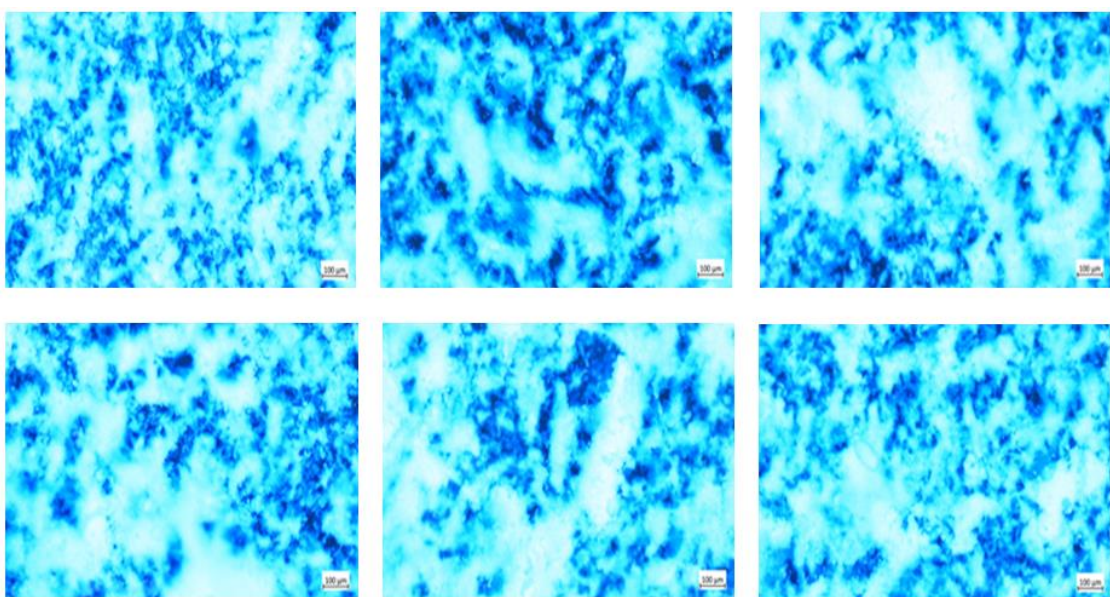


Figure 0.2. *Optical microscopy images of MicNo-ZnO PMMA 2nd face*

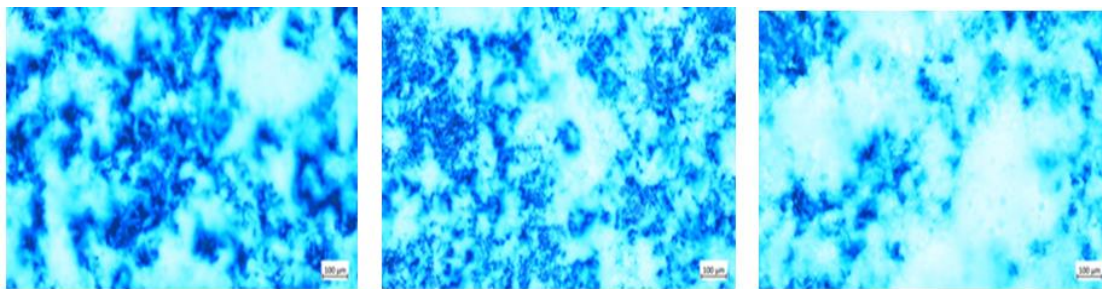


Figure 0.2. (Continued) *Optical microscopy images of MicNo-ZnO PMMA 2nd face*

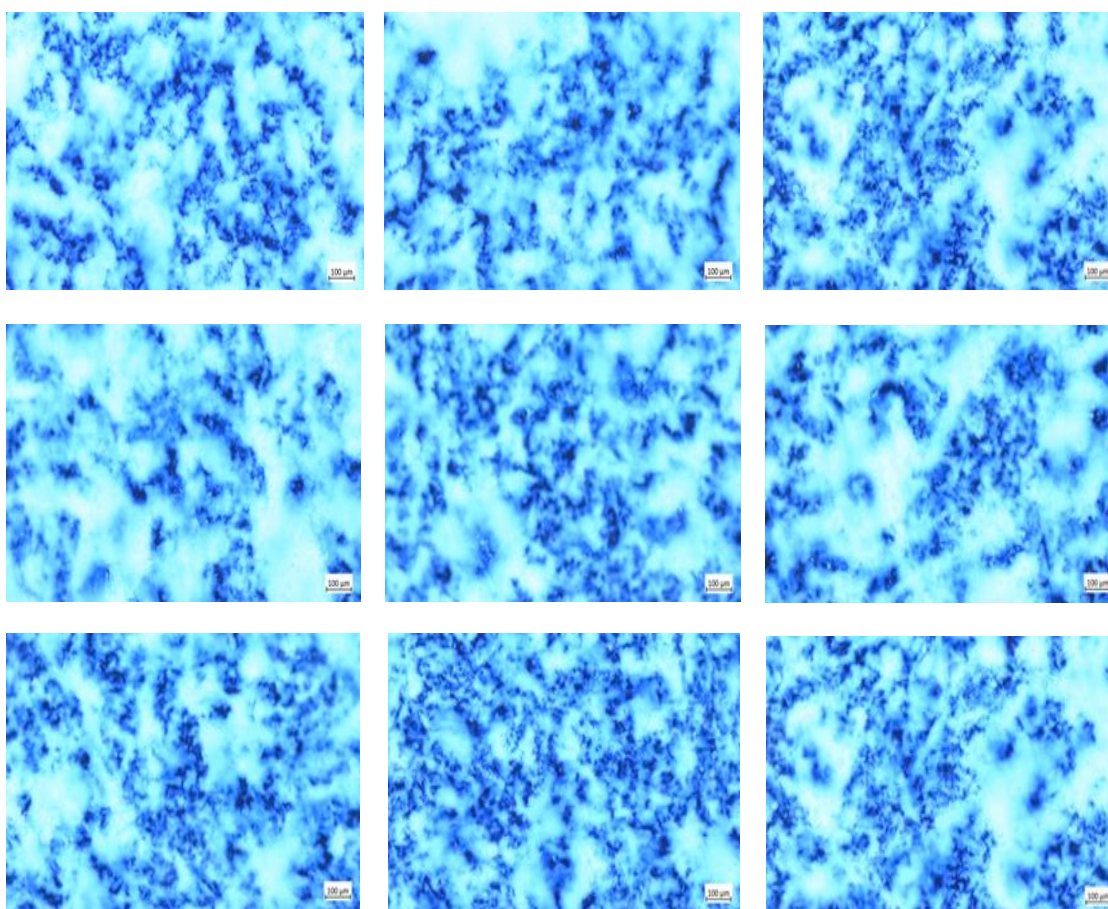


Figure 0.3. *Optical microscopy images of reduced size MicNo-ZnO PMMA 1st face*

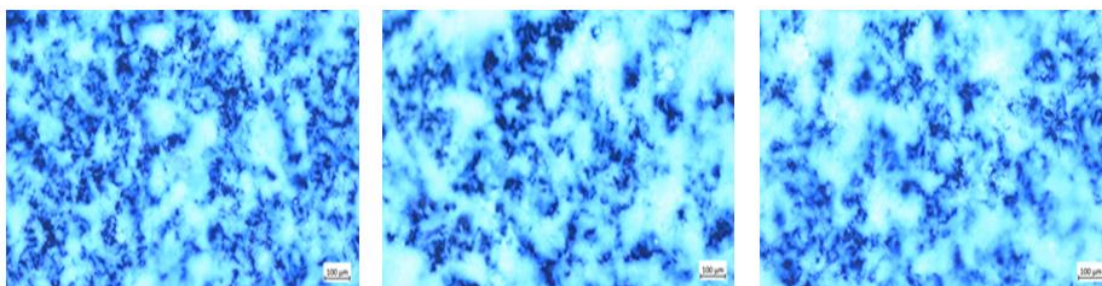


Figure 0.4. *Optical microscopy images of reduced size MicNo-ZnO PMMA 2nd face*

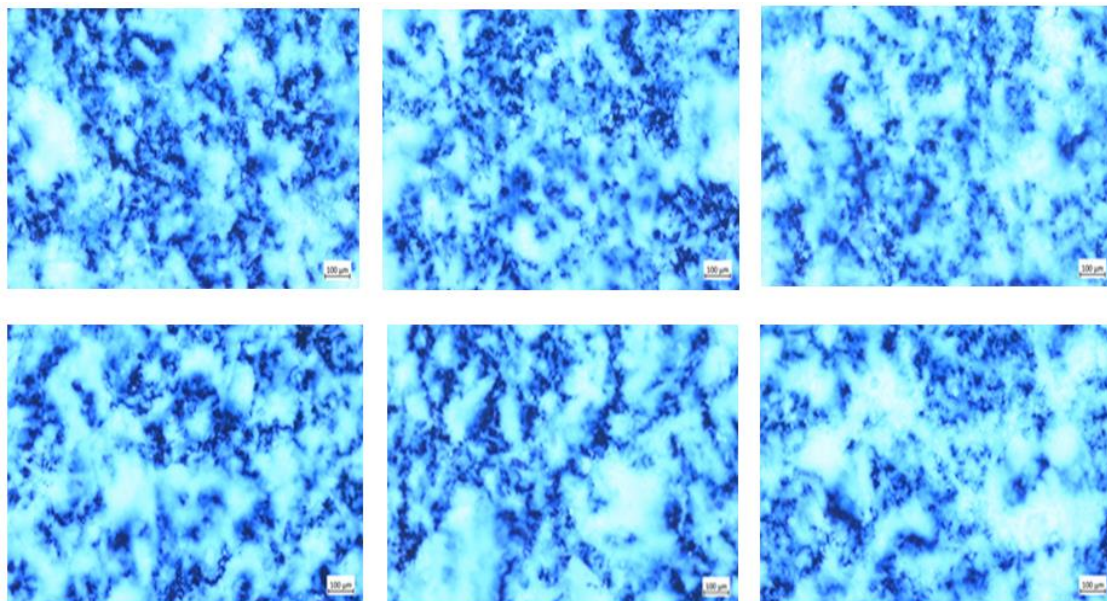


Figure 0.4. (Continued) Optical microscopy images of reduced size MicNo-ZnO PMMA 2nd face

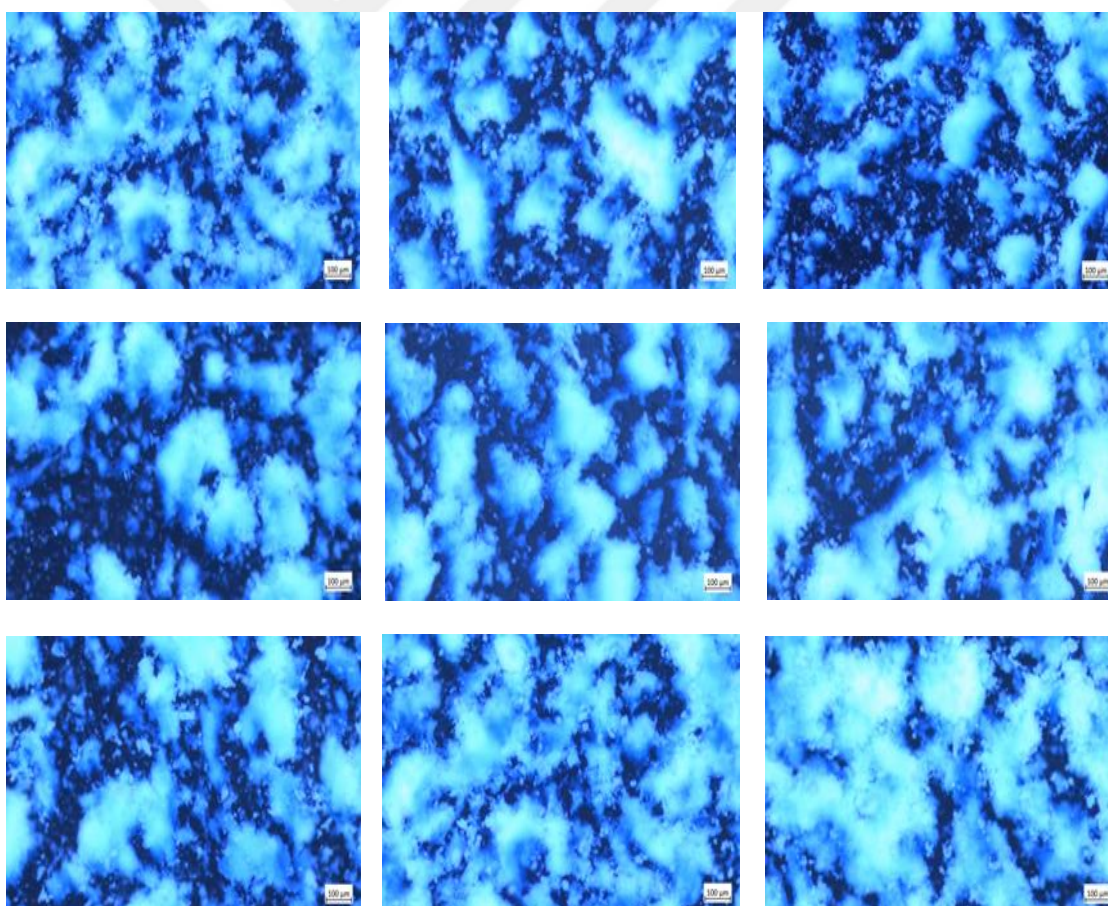


Figure 0.5. Optical microscopy images of 25-35 nano ZnO PMMA 1st face

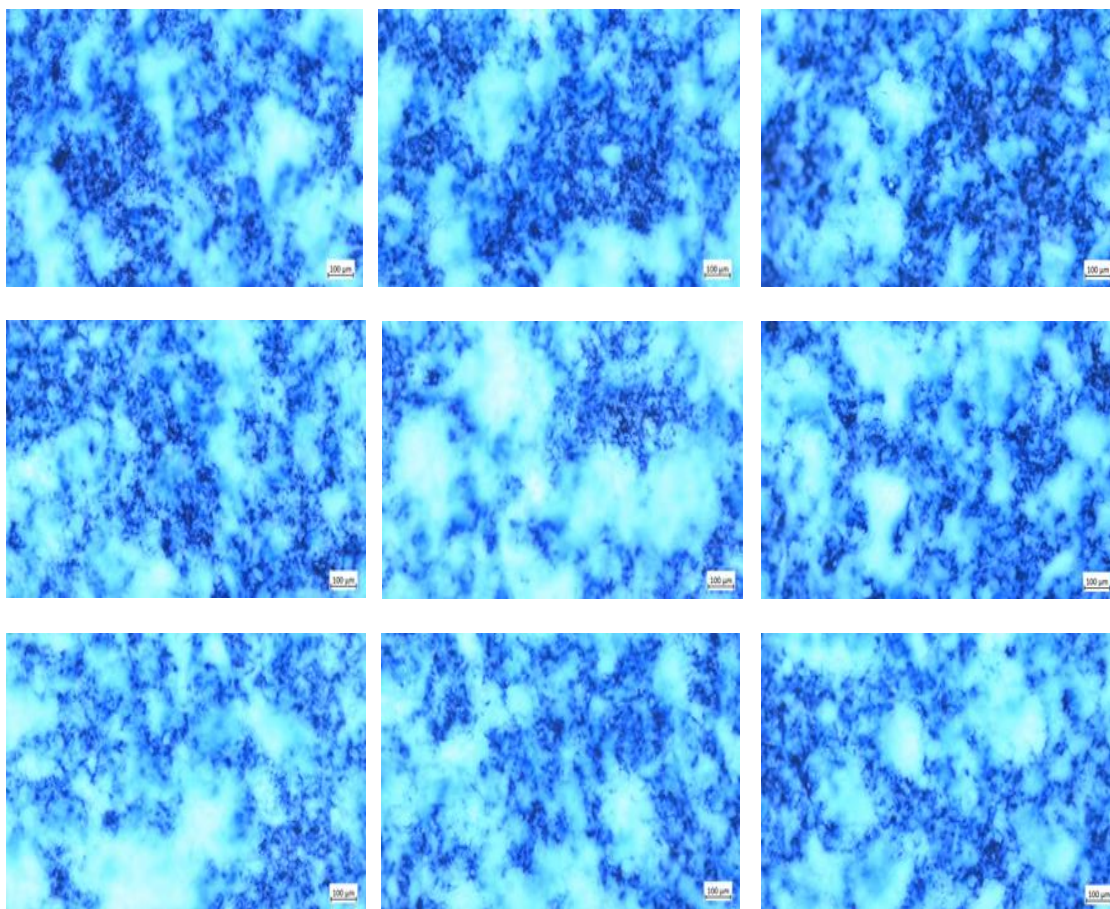


Figure 0.6. Optical microscopy images of 25-35 nano ZnO PMMA 2nd face

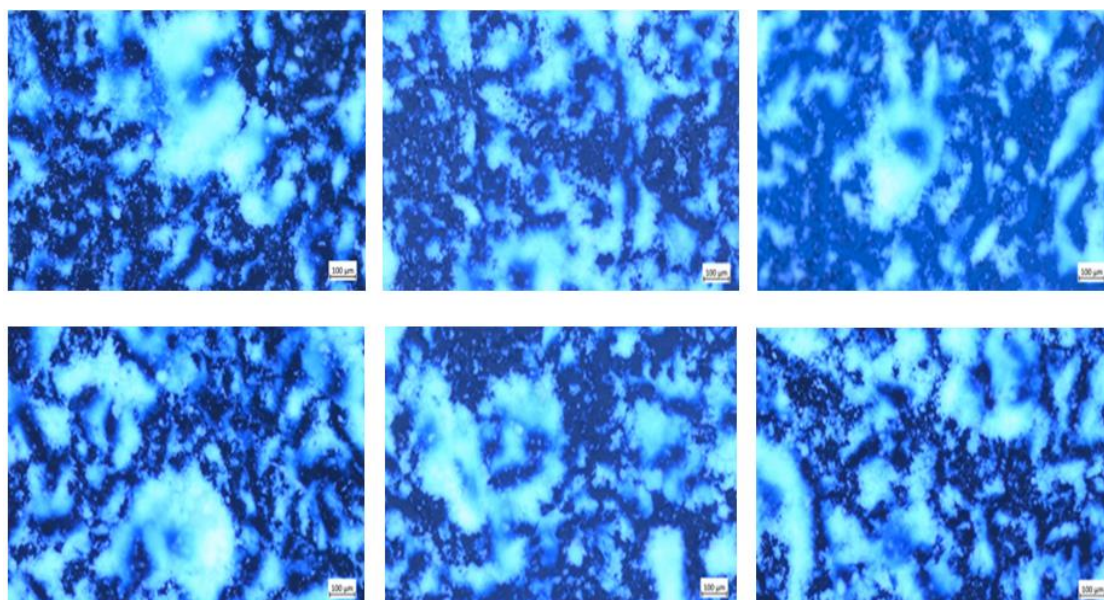


Figure 0.7. Optical microscopy images of 30-50nm spherical ZnO PMMA 1st face

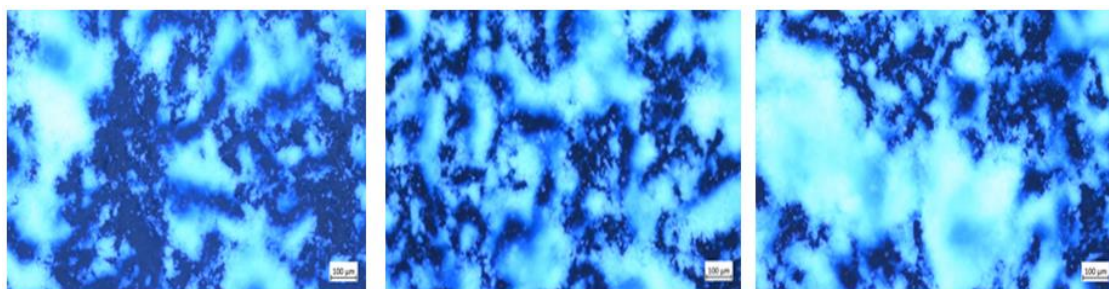


Figure 0.7. (Continued) *Optical microscopy images of 30-50nm spherical ZnO PMMA 1st face*

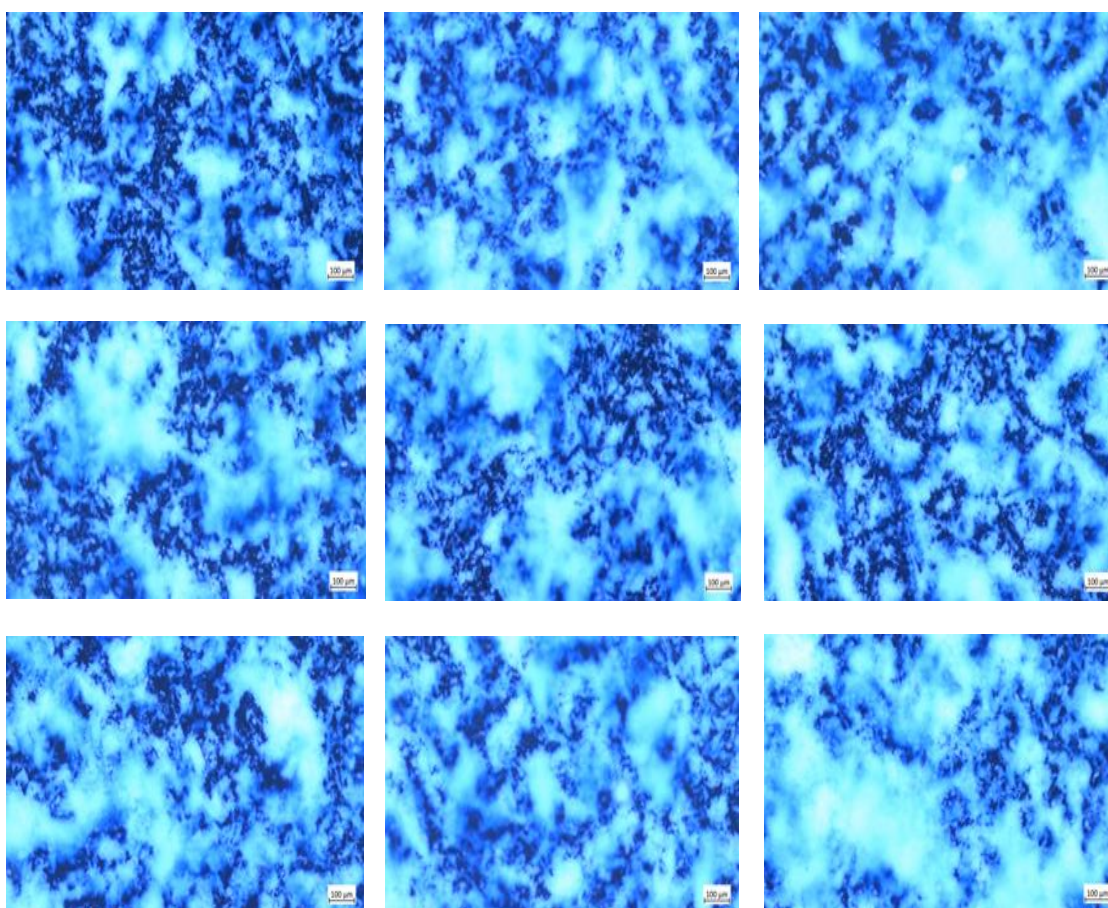


Figure 0.8. *Optical microscopy images of 30-50nm spherical ZnO PMMA 2nd face*

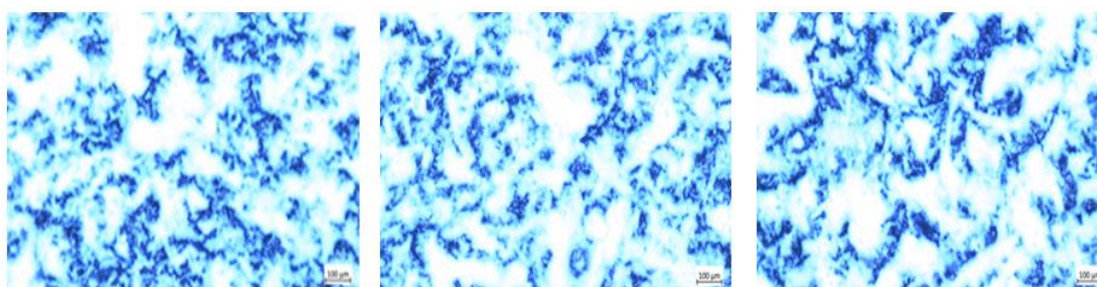


Figure 0.9. *Optical microscopy images of submicron ZnO PMMA 1st face*

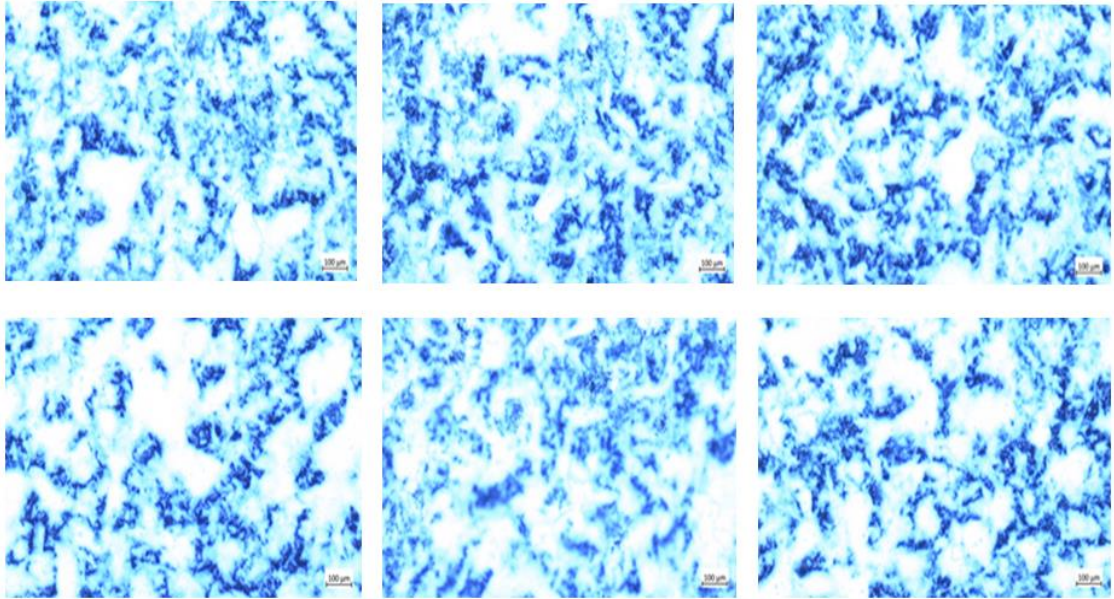


Figure 0.9. (Continued) *Optical microscopy images of submicron ZnO PMMA 1st face*

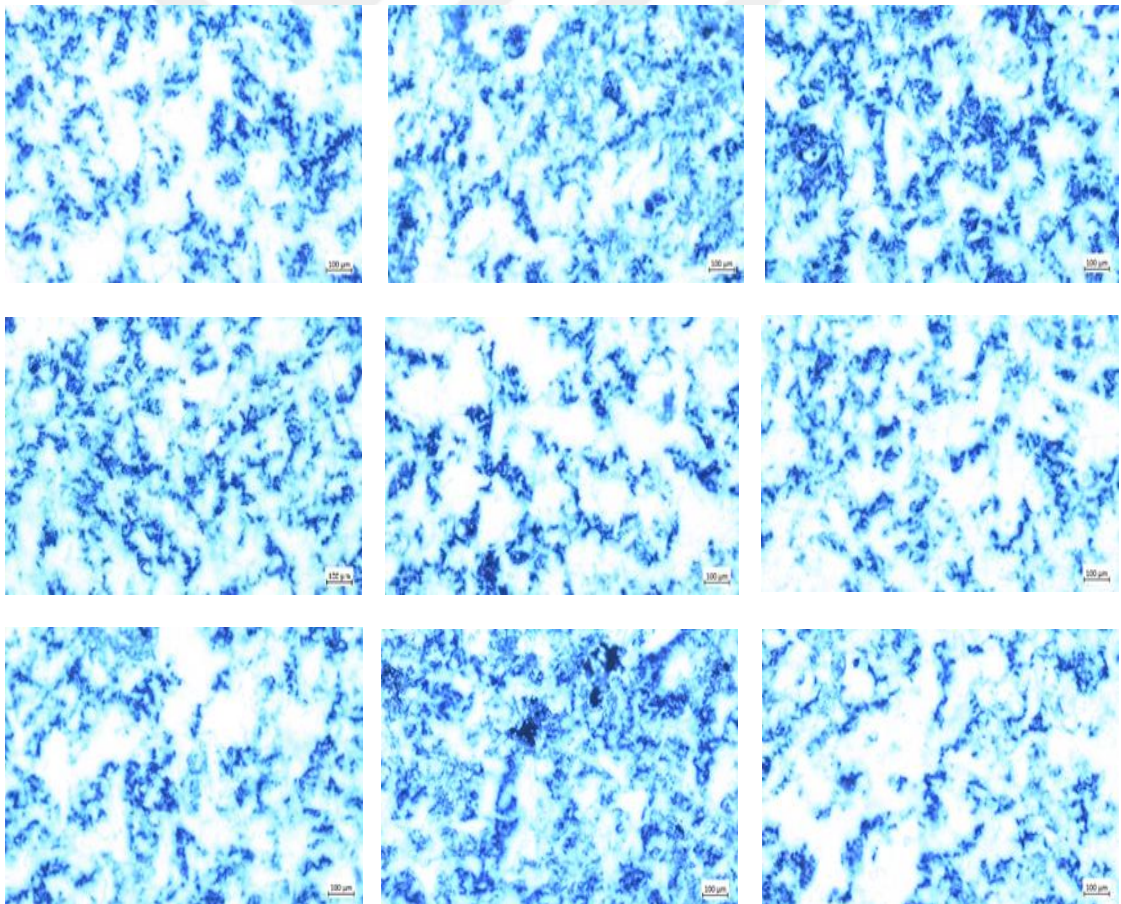


Figure 0.10. *Optical microscopy images of submicron ZnO PMMA 2nd face*

APPENDIX-2. Absorbance Results for the First Set of Data Obtained

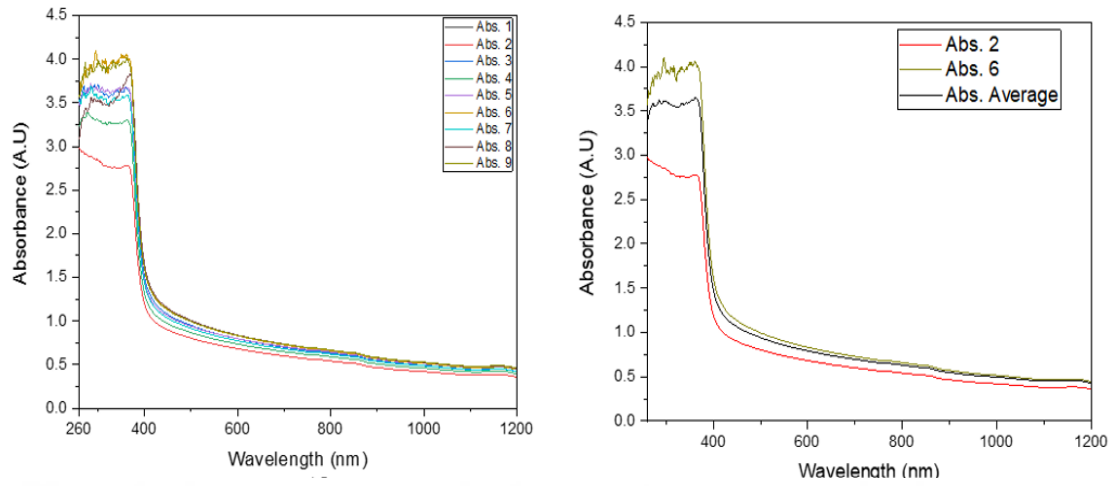


Figure 0.11. Absorbance graphs of original MicNo- ZnO PMMA plate (1st face)

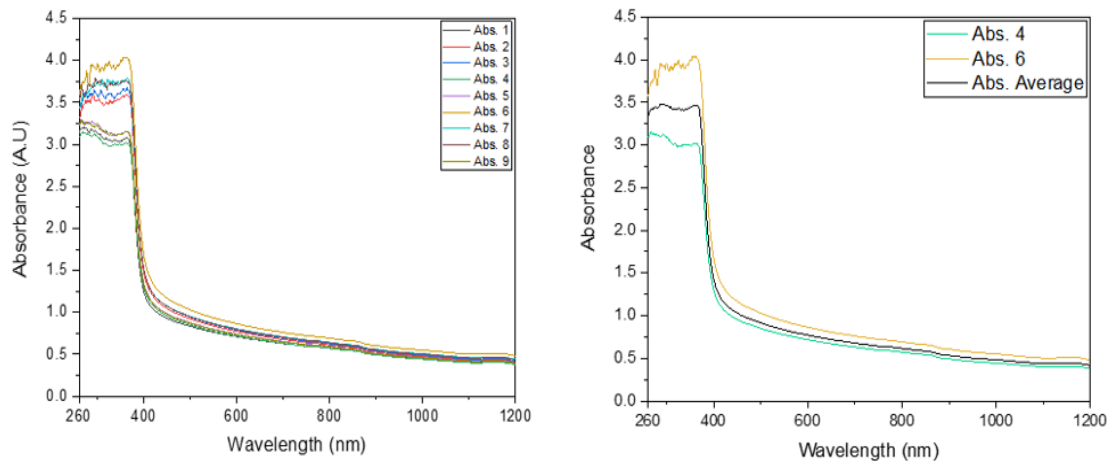


Figure 0.12. Absorbance graphs of original MicNo- ZnO PMMA plate (2nd face)

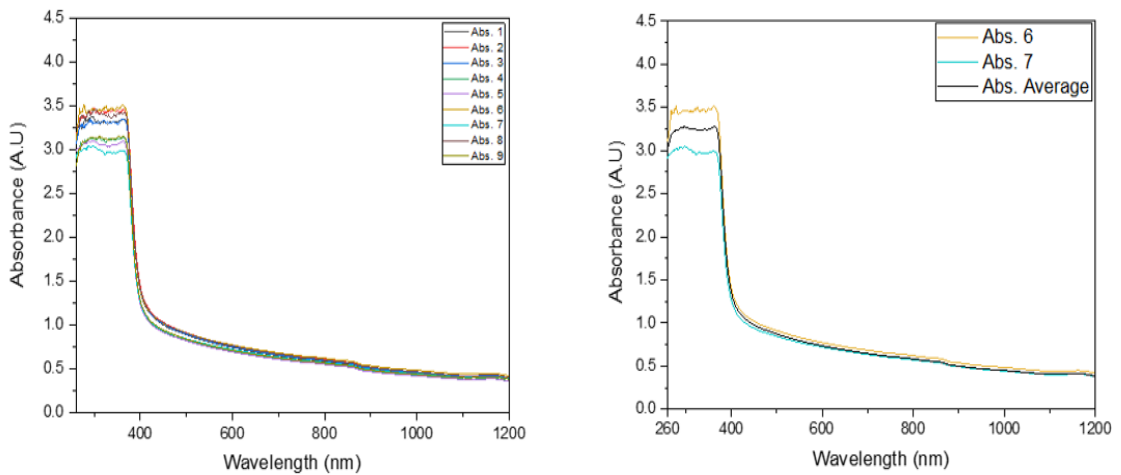


Figure 0.13. Absorbance graphs of reduced size MicNo-ZnO PMMA plate (1st face)

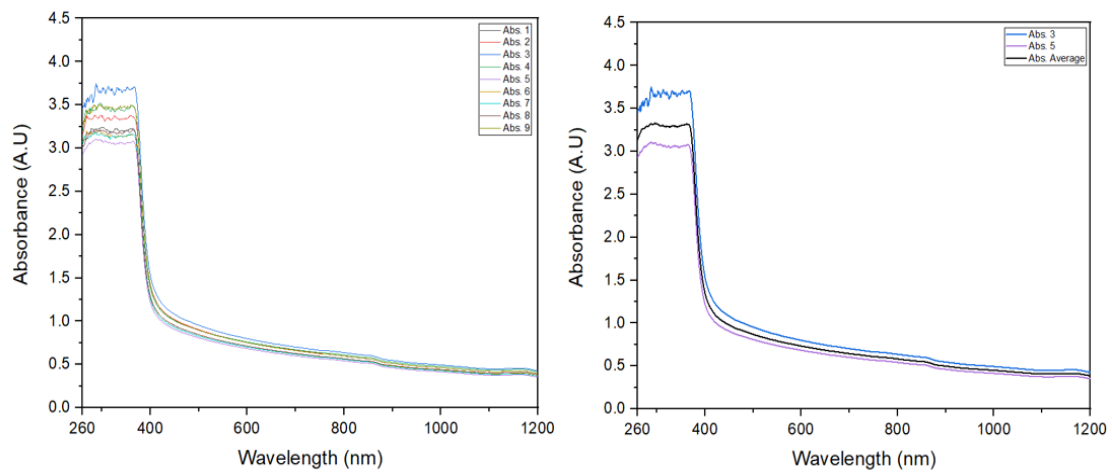


Figure 0.14. Absorbance graphs of reduced size MicNo-ZnO PMMA plate (2nd face)

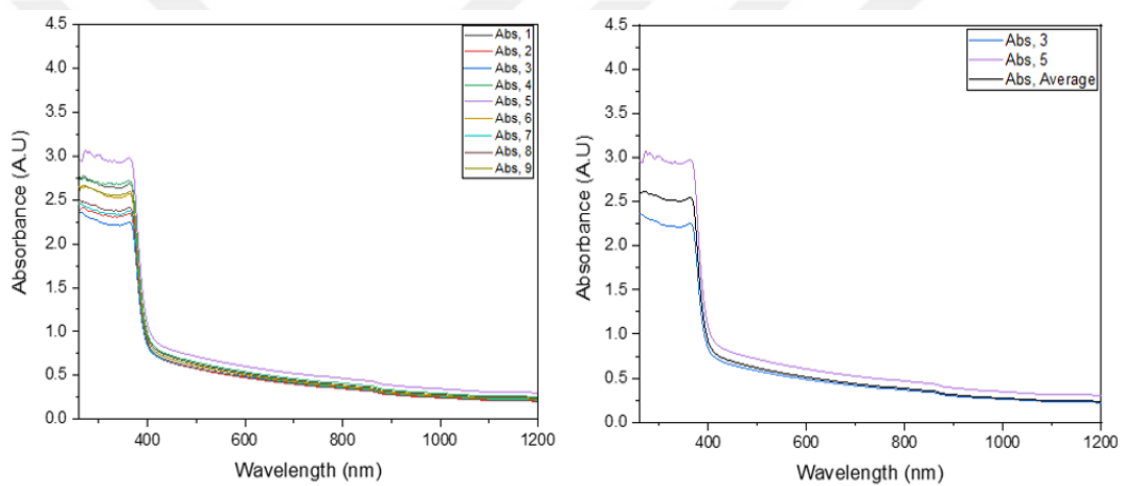


Figure 0.15. Absorbance graphs of 25-35 nm nano ZnO PMMA plate (1st face)

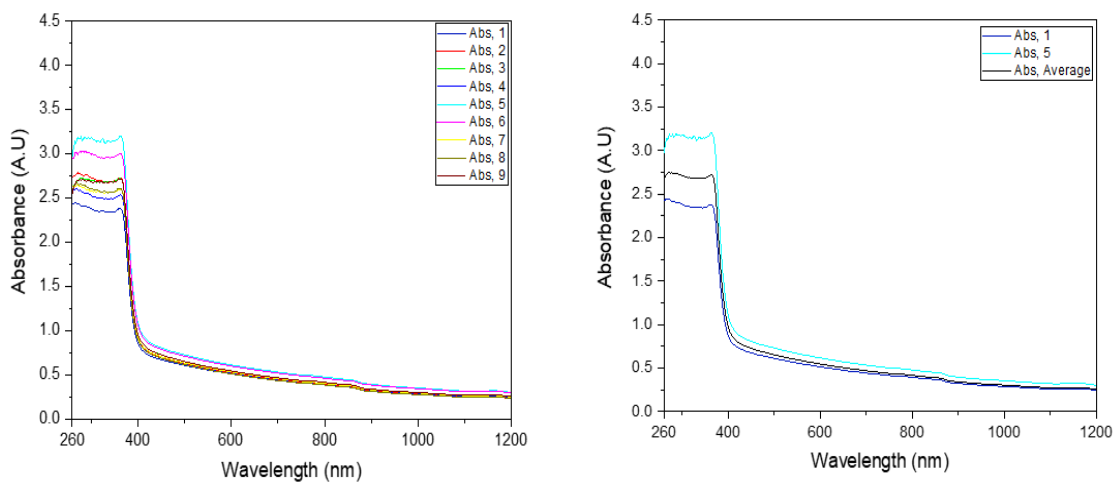


Figure 0.16. Absorbance graphs of 25-35 nm nano ZnO PMMA plate (2nd face)

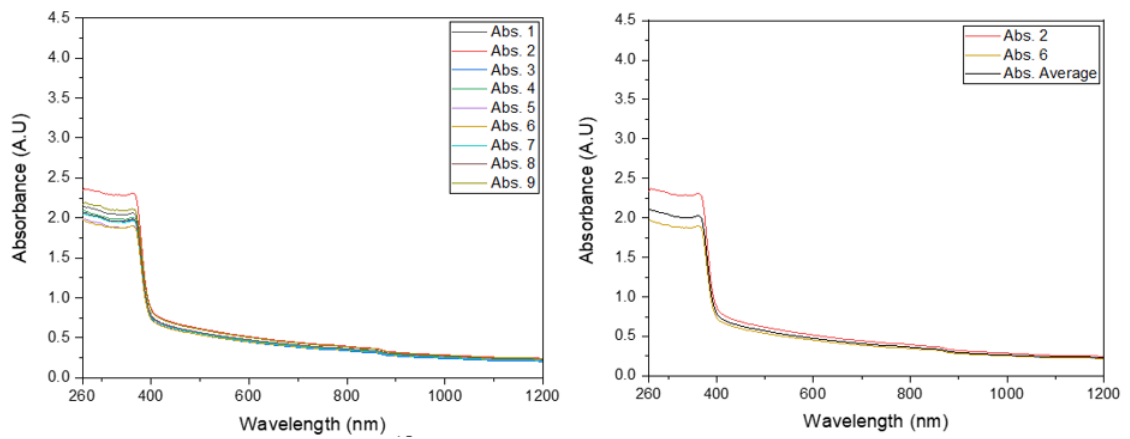


Figure 0.17. Absorbance graphs of 30-50 nm spherical ZnO PMMA plate (1st face)

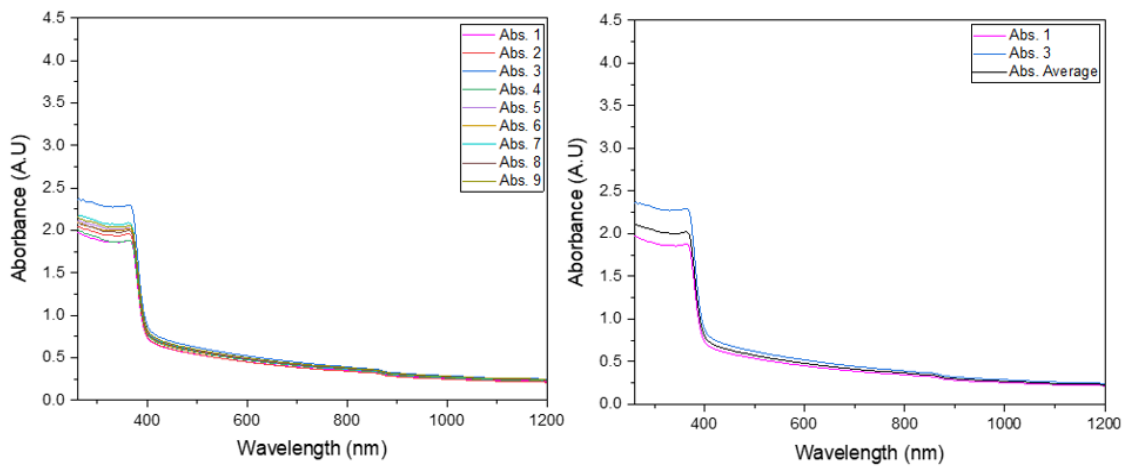


Figure 0.18. Absorbance graphs of 30-50 nm spherical ZnO PMMA plate (2nd face)

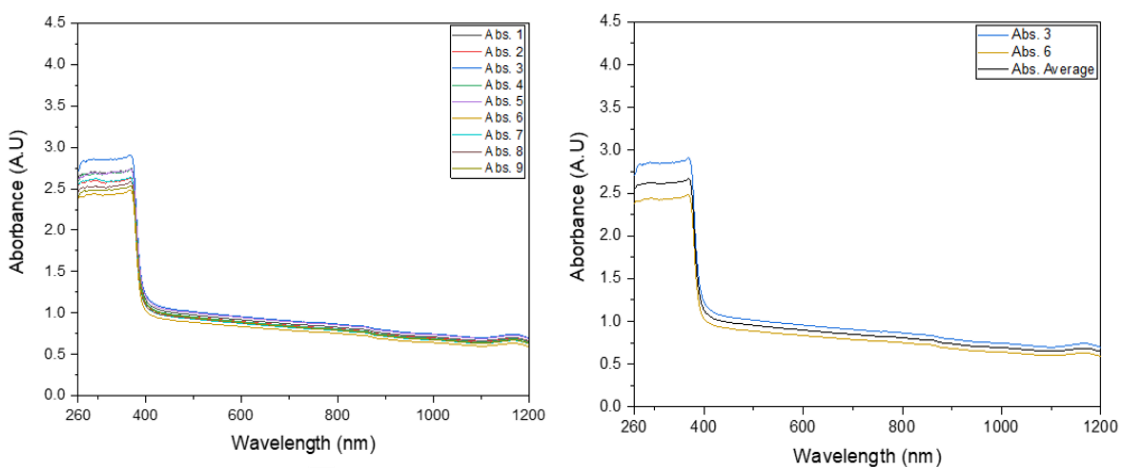


Figure 0.19. Absorbance graphs of submicron ZnO PMMA plate (1st face)

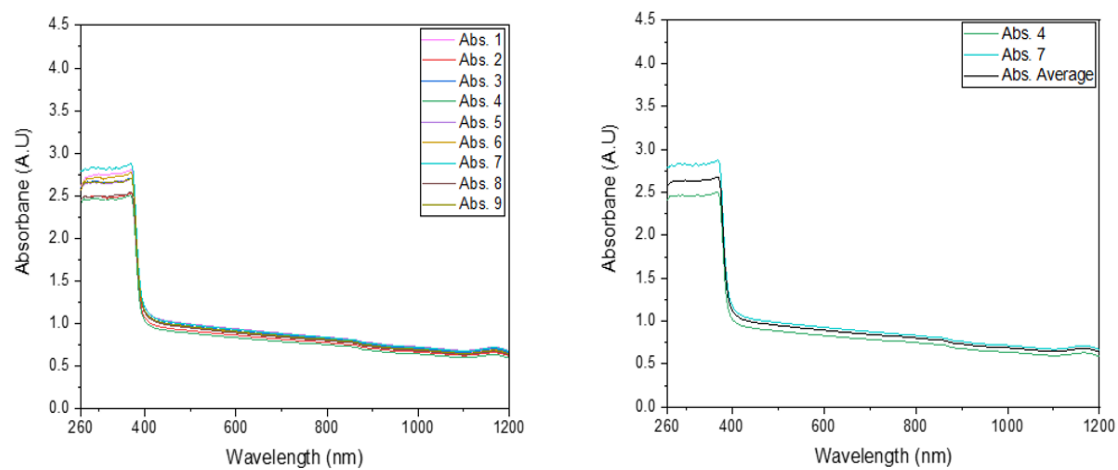


Figure 0.20. Absorbance graphs of submicron ZnO PMMA plate (2nd face)

APPENDIX-3. Absorbance Results for the Second Set of Data Obtained

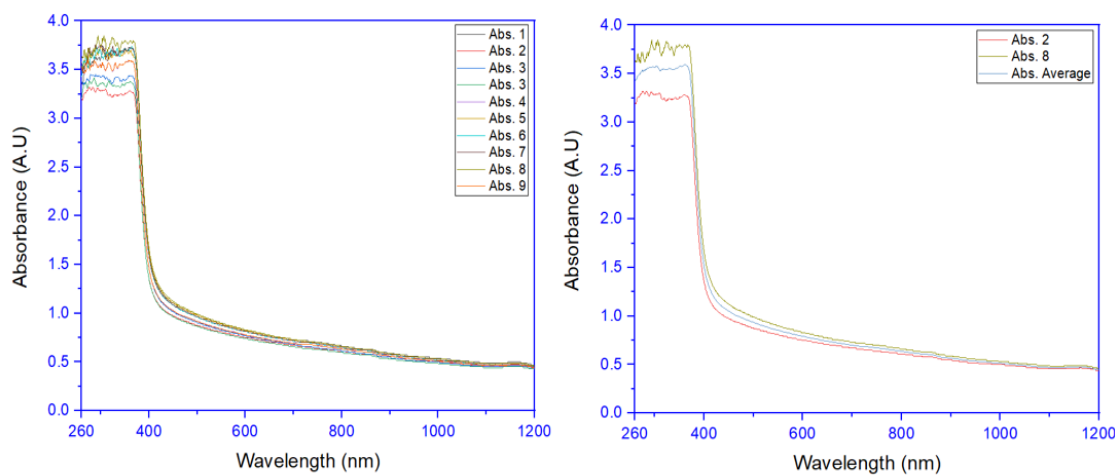


Figure 0.21. Absorbance graphs of original MicNo-ZnO PMMA plate (taken from the two faces)

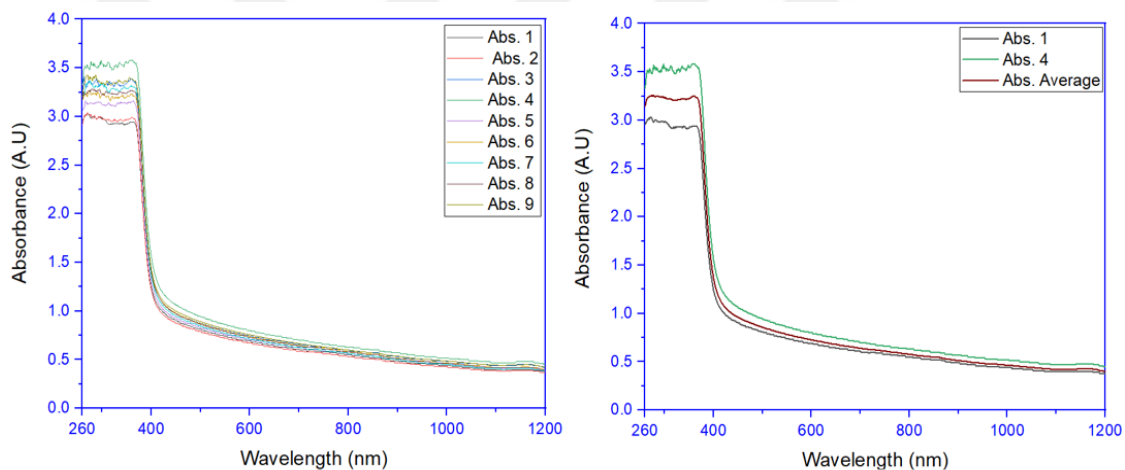


Figure 0.22. Absorbance graphs of reduced size MicNo- ZnO PMMA plate (taken from the two faces)

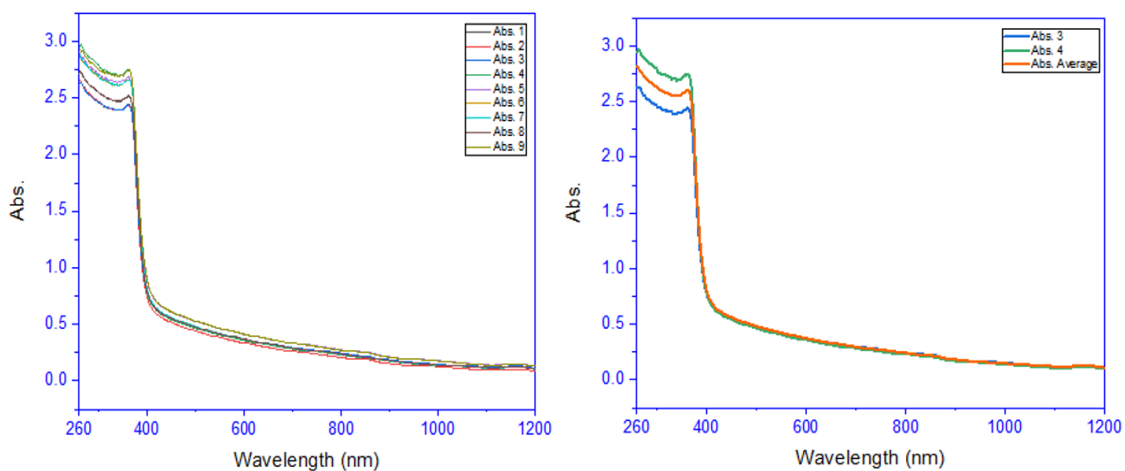


Figure 0.23. Absorbance graphs of 25-35 nm nano ZnO PMMA plate (taken from the two faces)

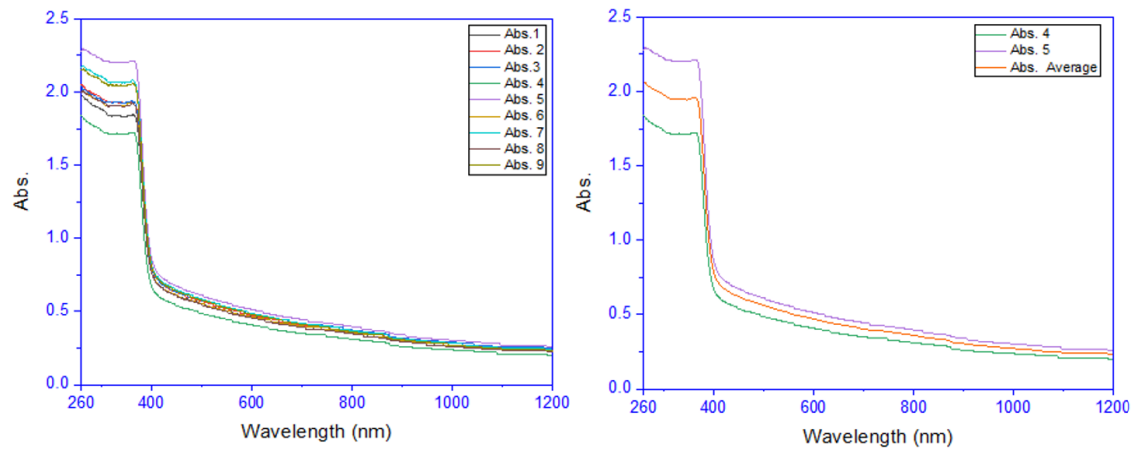


Figure 0.24. Absorbance graphs of 30-50 nm spherical ZnO PMMA plate (taken from the two faces)

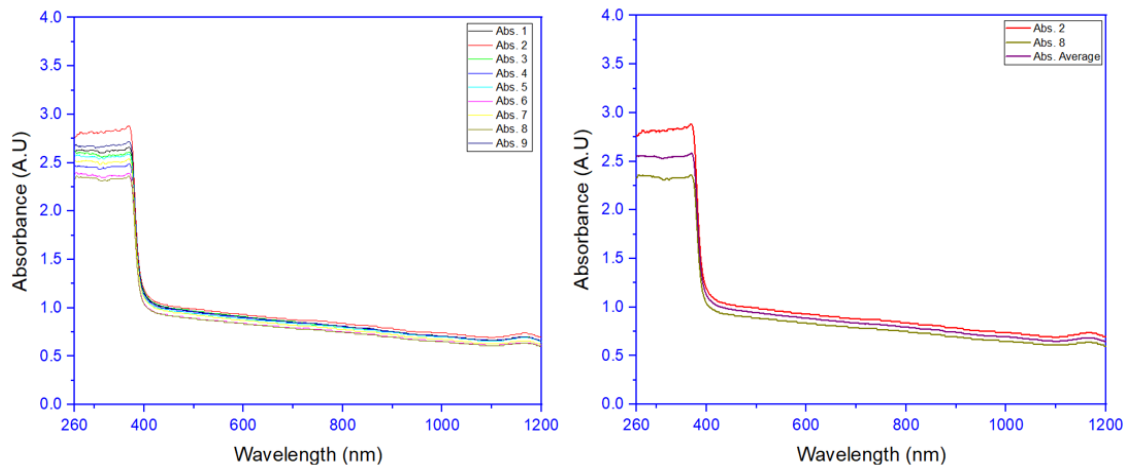


Figure 0.25. Absorbance graphs of submicron ZnO PMMA plate (taken from the two faces)

APPENDIX-4. Transmittance Results Obtained for the First data set

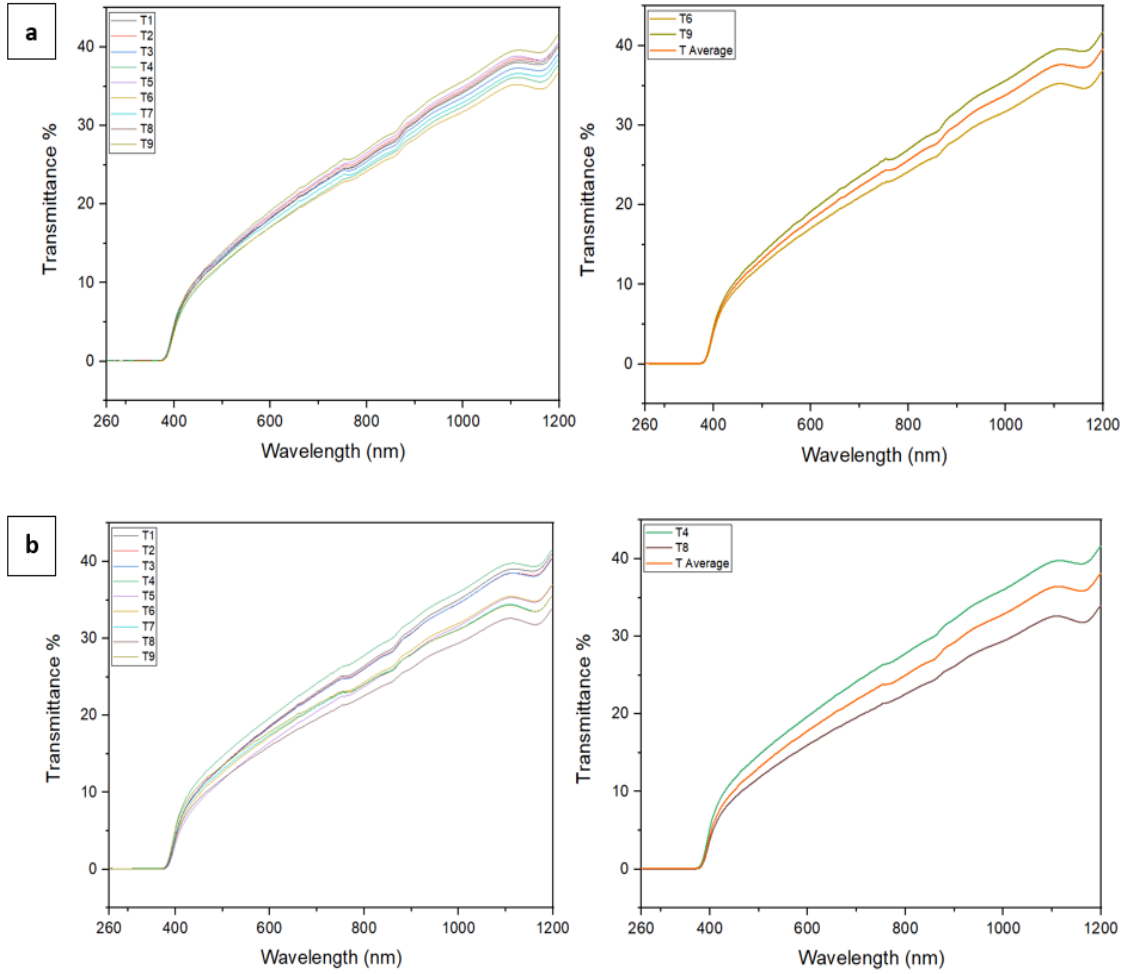


Figure 0.26. Transmittance graphs of original MicNo PMMA for first data set (a) 1st face (b) 2nd face

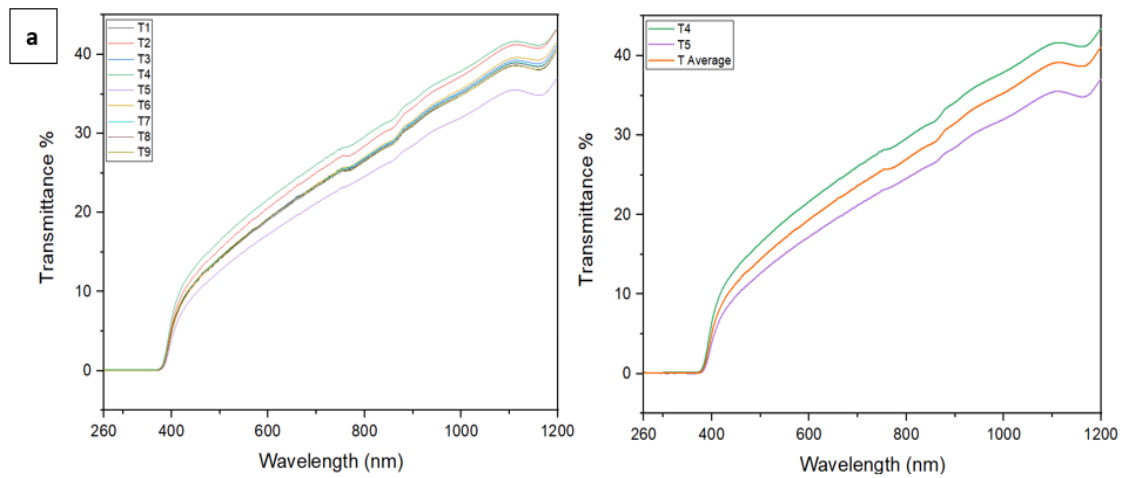


Figure 0.27. Transmittance graphs of reduced MicNo PMMA for first data set (a) 1st face, (b) 2nd face

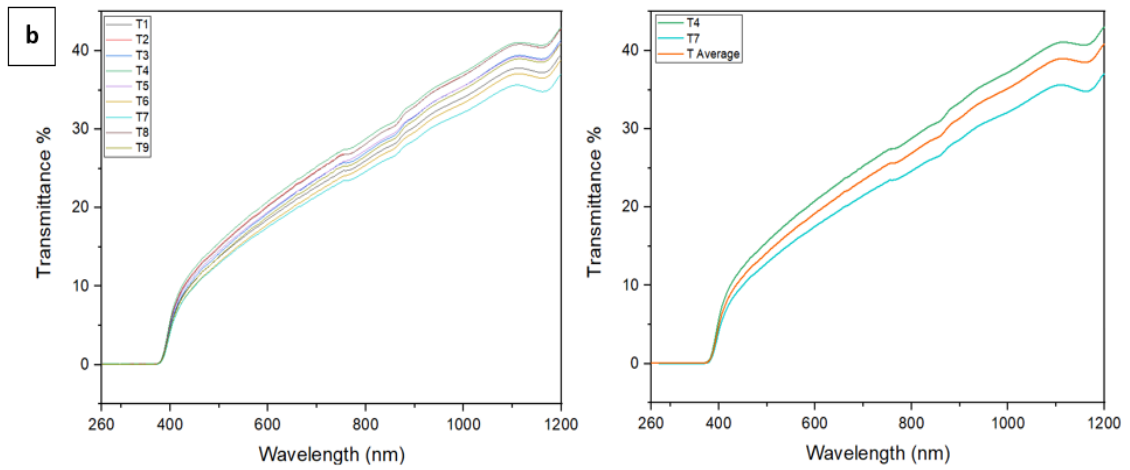


Figure 0.27. (Continued) Transmittance graphs of reduced MicNo PMMA for first data set (a) 1st face, (b) 2nd face

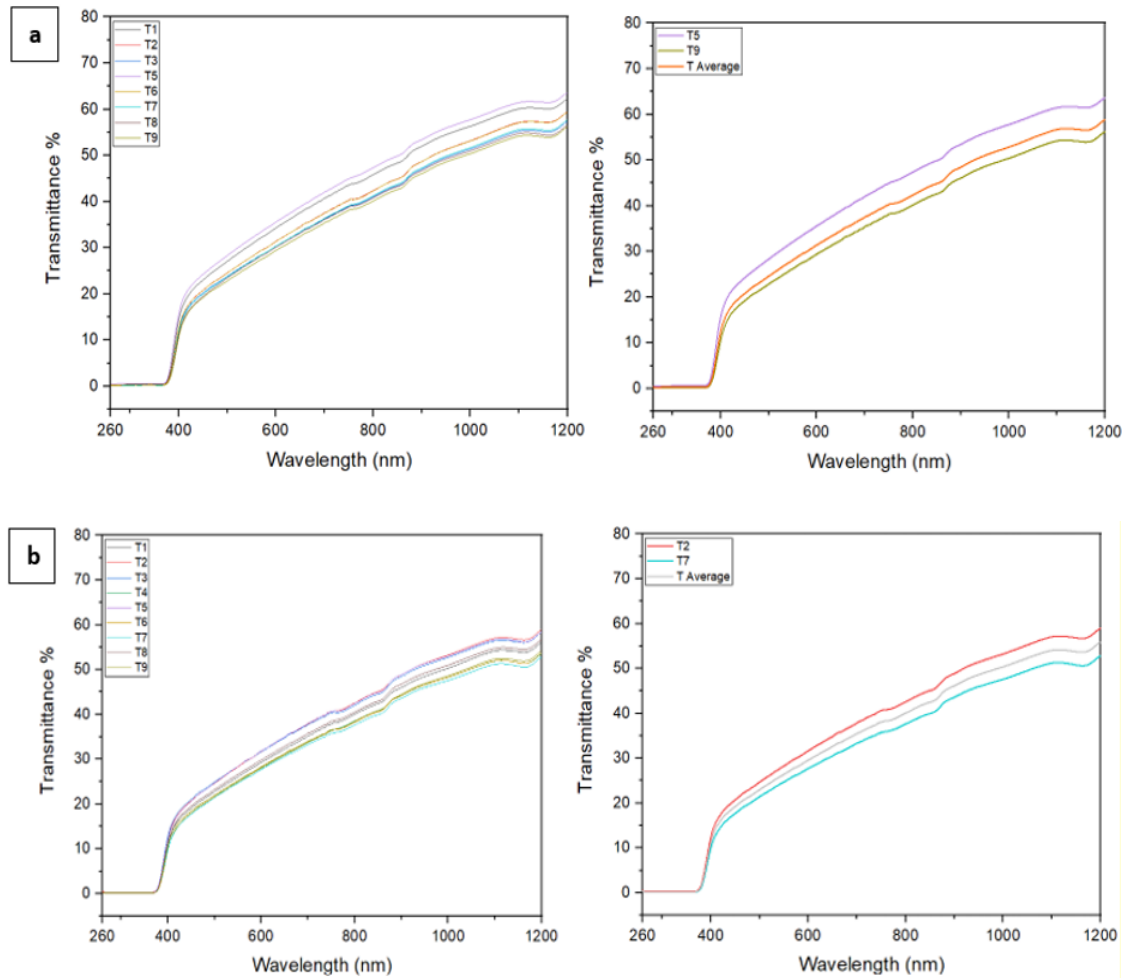


Figure 0.28. Transmittance graphs of nano ZnO PMMA for first data set (a) 1st face, (b) 2nd face

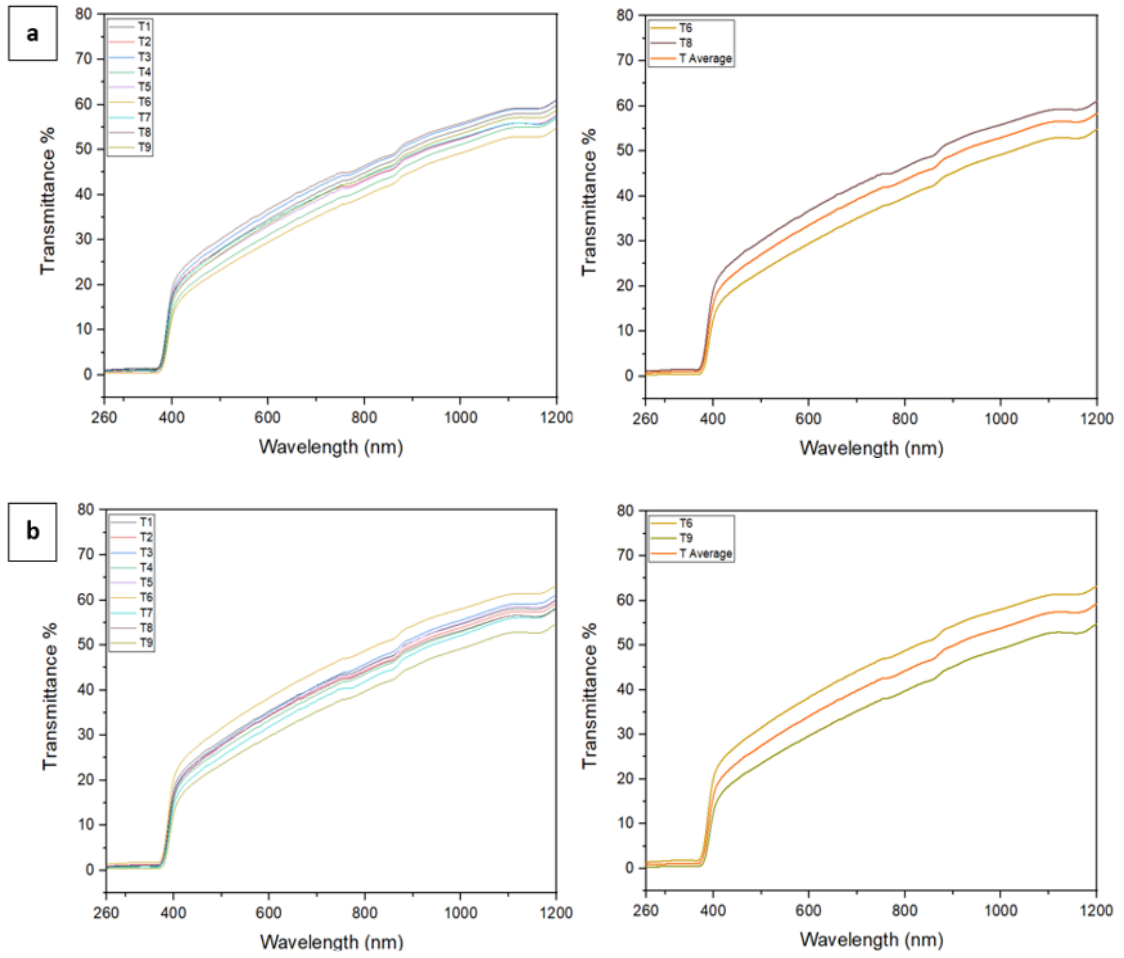


Figure 0.29. Transmittance graphs of 30-50m spherical ZnO PMMA for first data set (a) 1^s face, (b) 2nd face

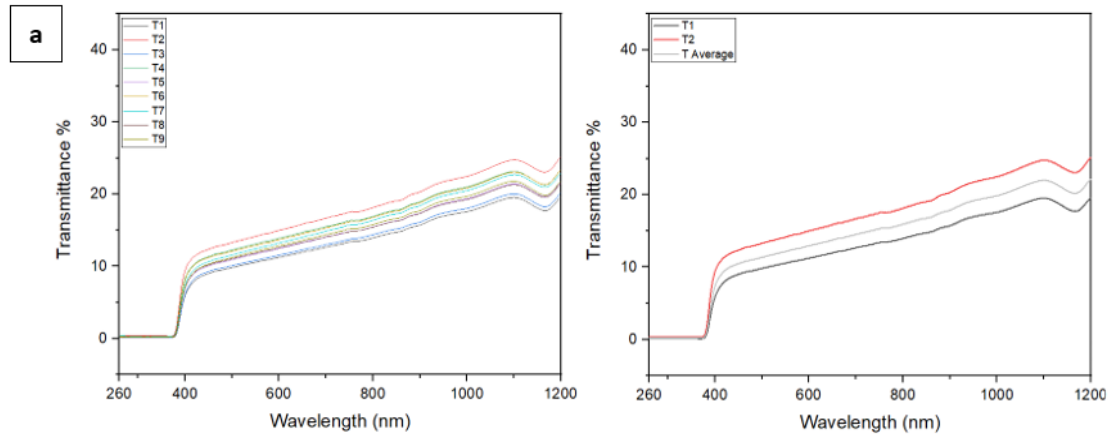


Figure 0.30. Transmittance graphs of submicron ZnO PMMA for first data set (a) 1^s face, (b) 2nd face

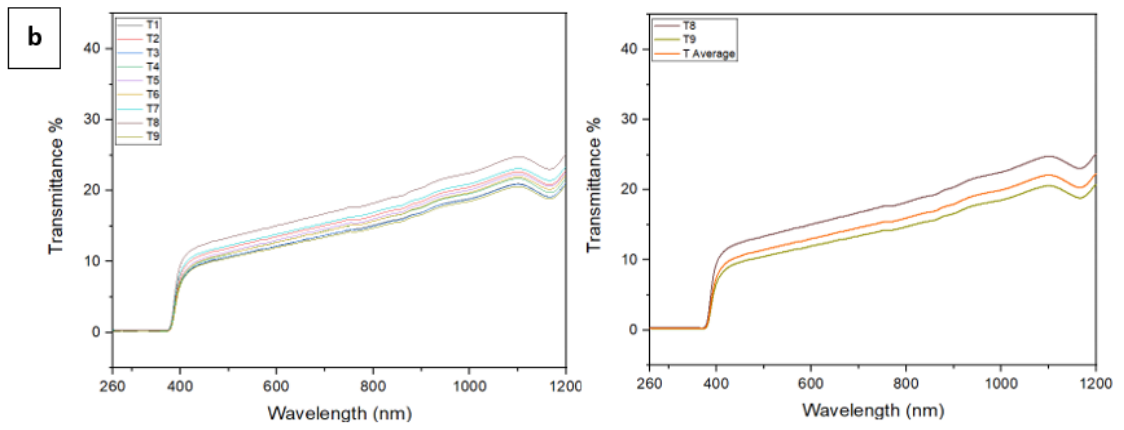


Figure 0.30. (Continued) Transmittance graphs of submicron ZnO PMMA for first data set (a) 1st face, (b) 2nd face

APPENDIX-5. Transmittance Results Obtained for the Second data set

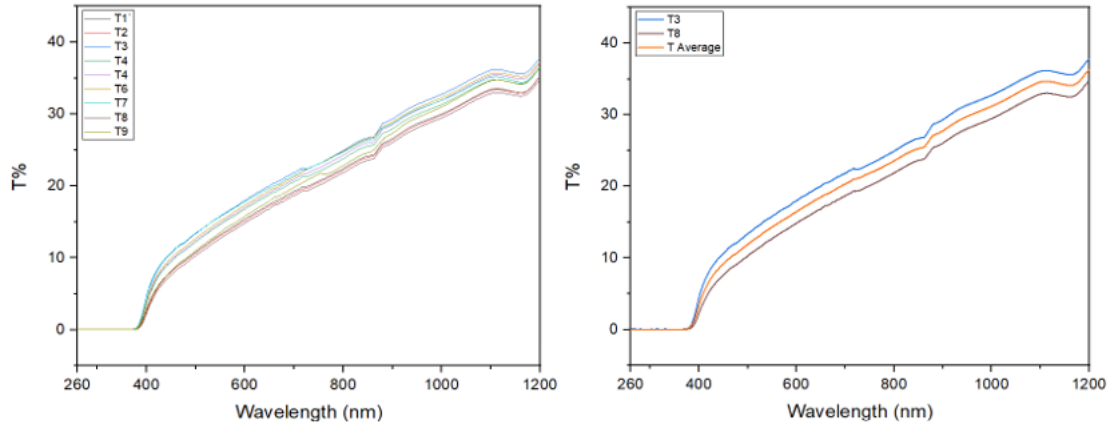


Figure 0.31. Transmittance graphs of original MicNo- ZnO PMMA plate (taken from the two faces)

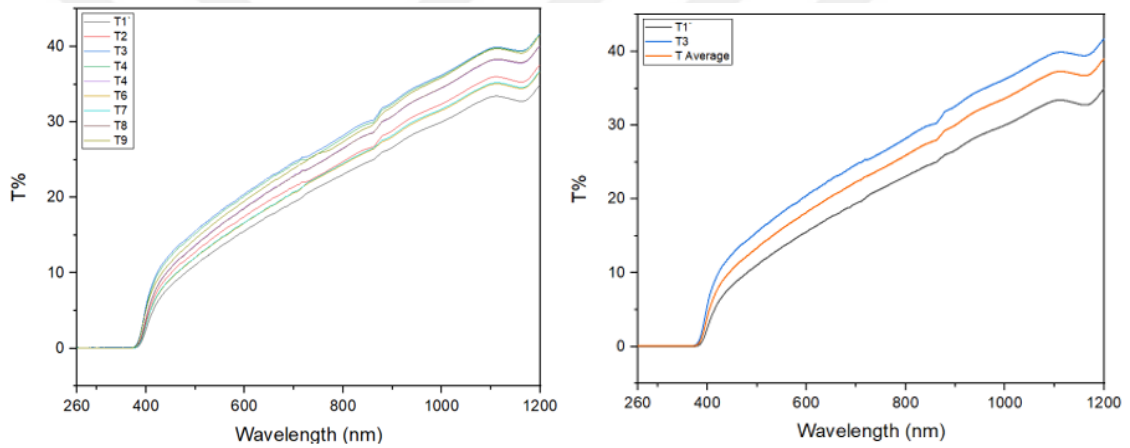


Figure 0.32. Transmittance graphs of reduced size MicNo- ZnO PMMA plate (taken from the two faces)

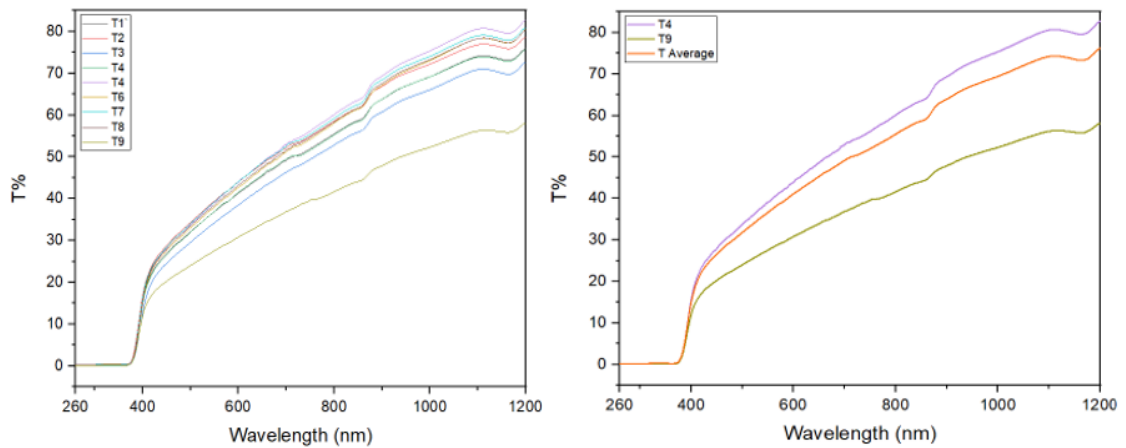


Figure 0.33. Transmittance graphs of nano ZnO PMMA plate (taken from the two faces)

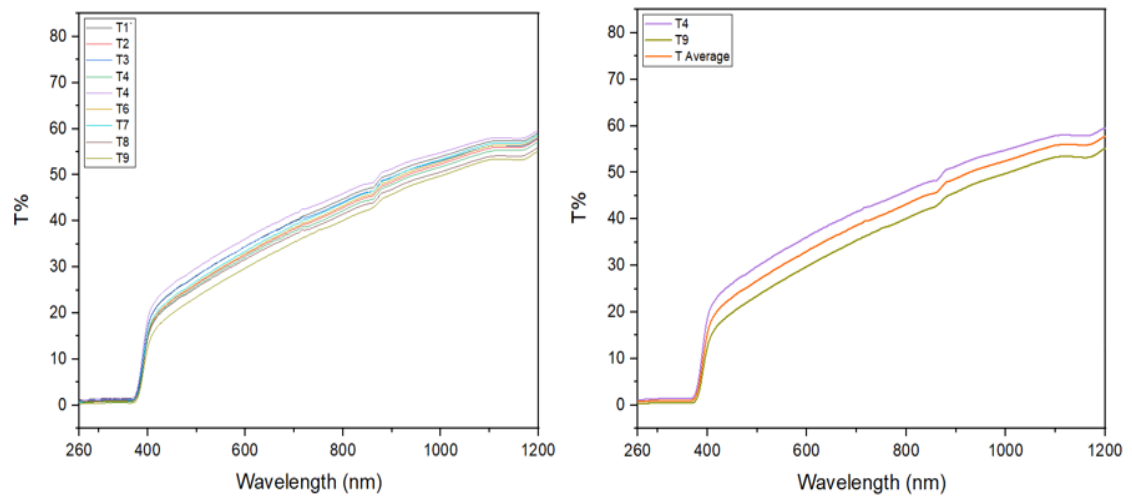


Figure 0.34. Transmittance graphs of 30-50nm spherical ZnO PMMA plate (taken from the two faces)

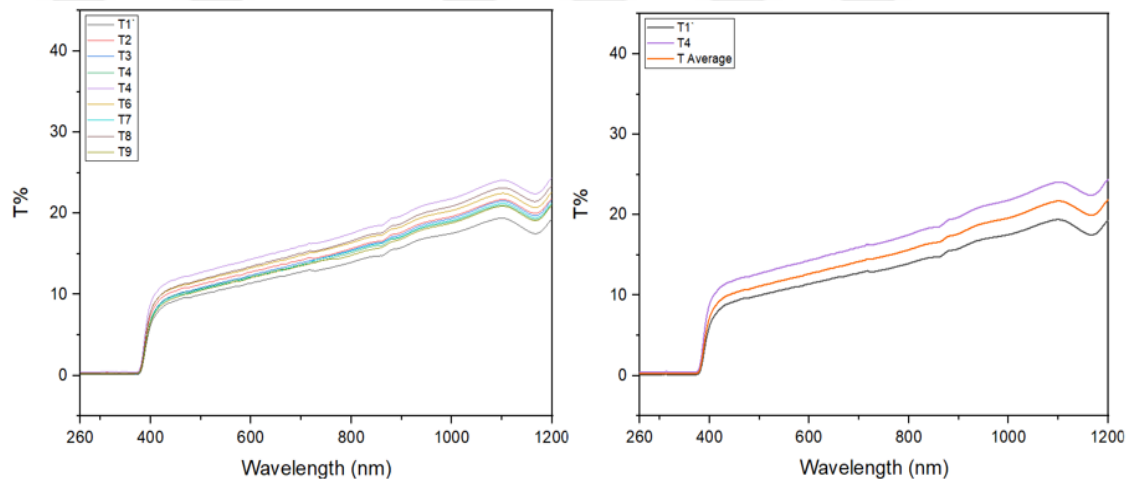


Figure 0.35. Transmittance graphs of submicron ZnO PMMA plate (taken from the two faces)

APPENDIX-6. Relative Diffuse Reflectance (First Measurement)

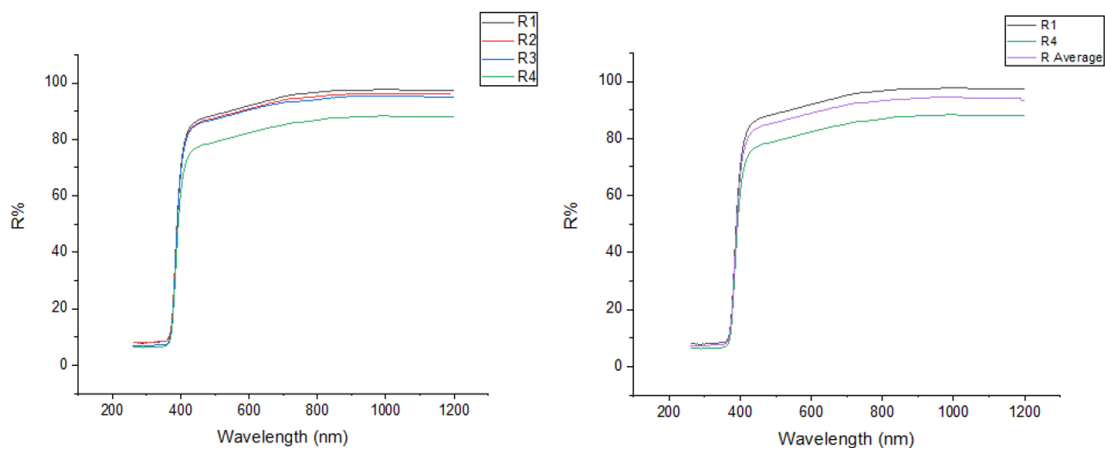


Figure 0.36. Relative diffuse reflectance graphs of MicNo ZnO (first measurement)

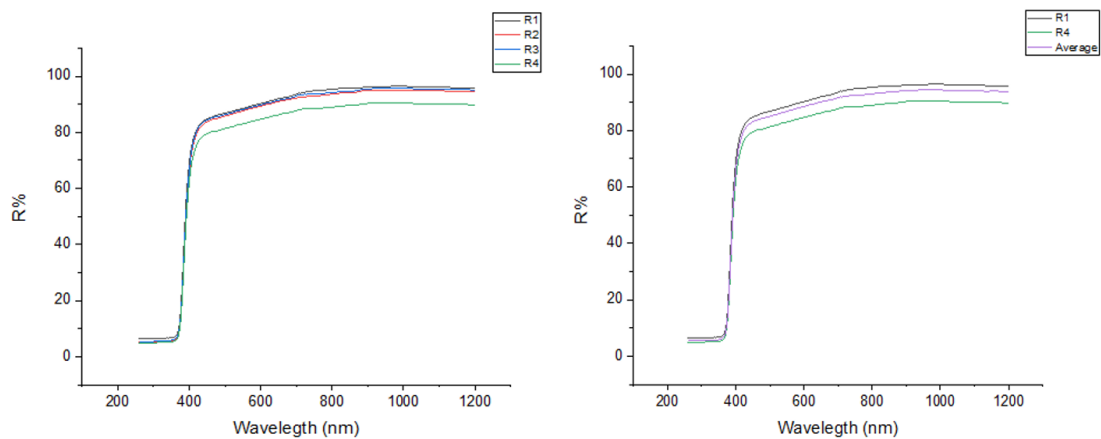


Figure 0.37. Relative diffuse reflectance graphs of reduced size MicNo ZnO (first measurement)

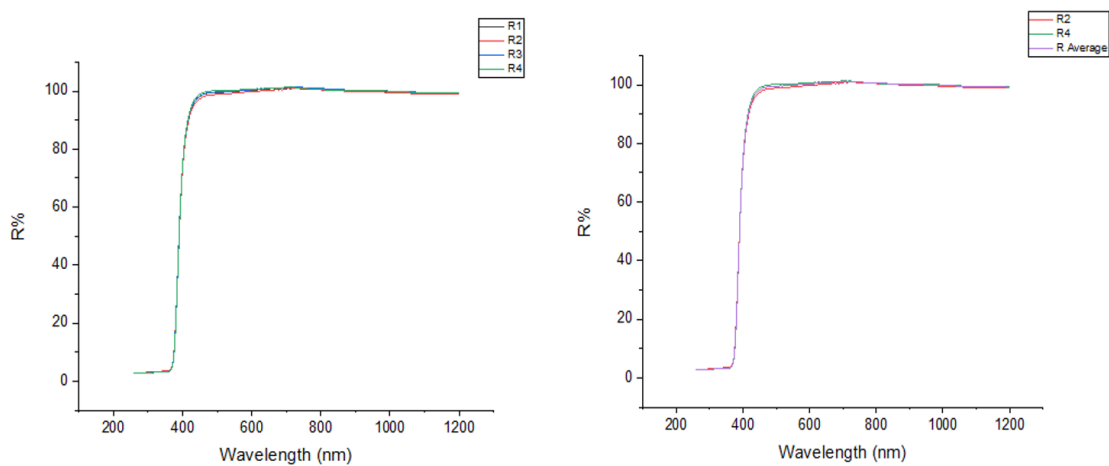


Figure 0.38. Relative diffuse reflectance graphs of nano ZnO (first measurement)

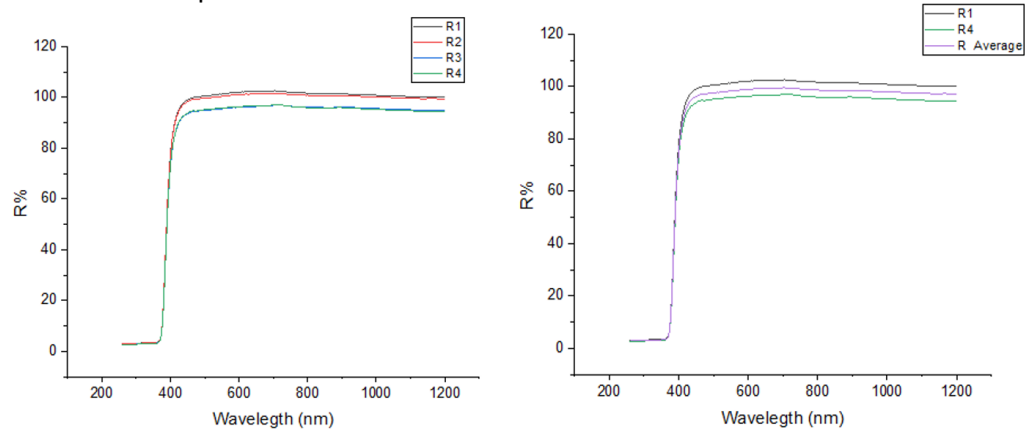


Figure 0.39. Relative diffuse reflectance graphs of 30-50 nm spherical ZnO (first measurement)

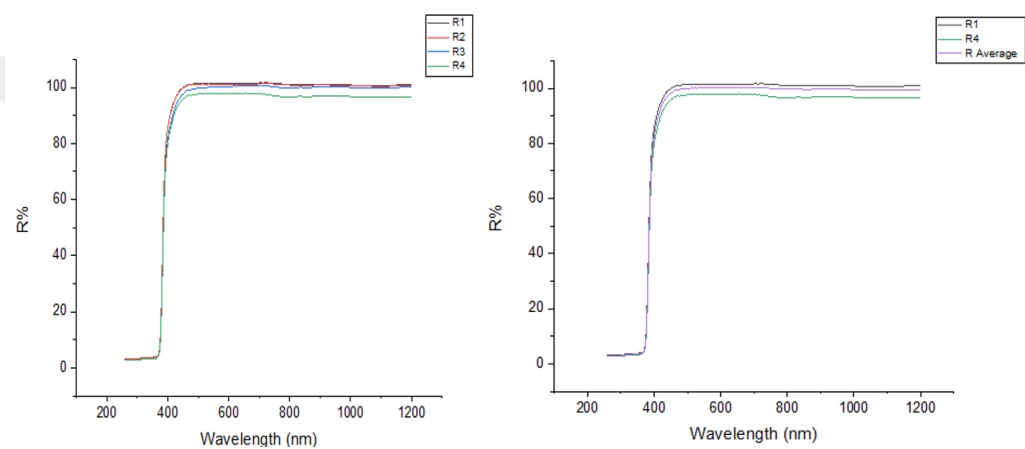


Figure 0.40. Relative diffuse reflectance graphs of submicron ZnO (first measurement)

APPENDIX-7. Relative Diffuse Reflectance (Second Measurement)

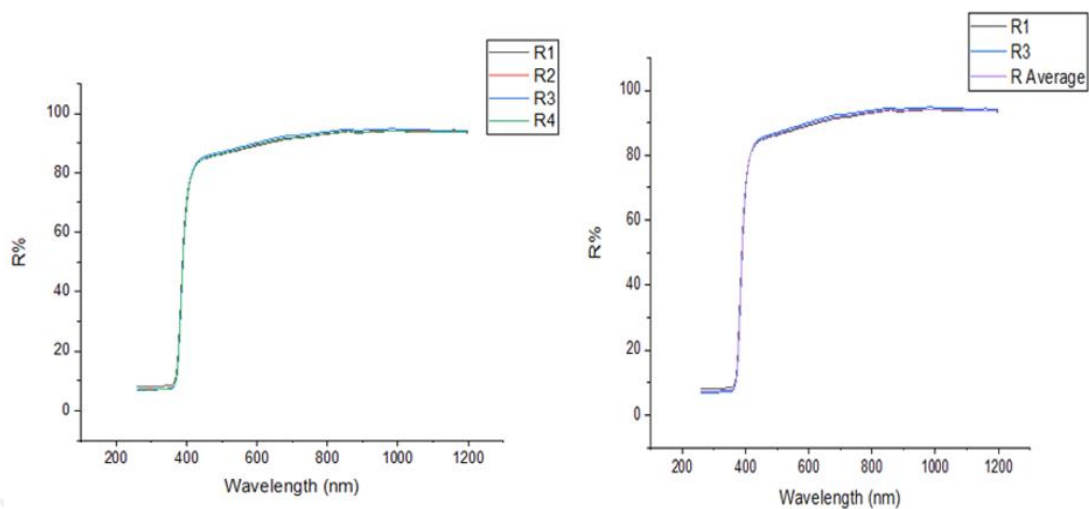


Figure 0.41. Relative diffuse reflectance graphs of MicNo ZnO (second measurement)

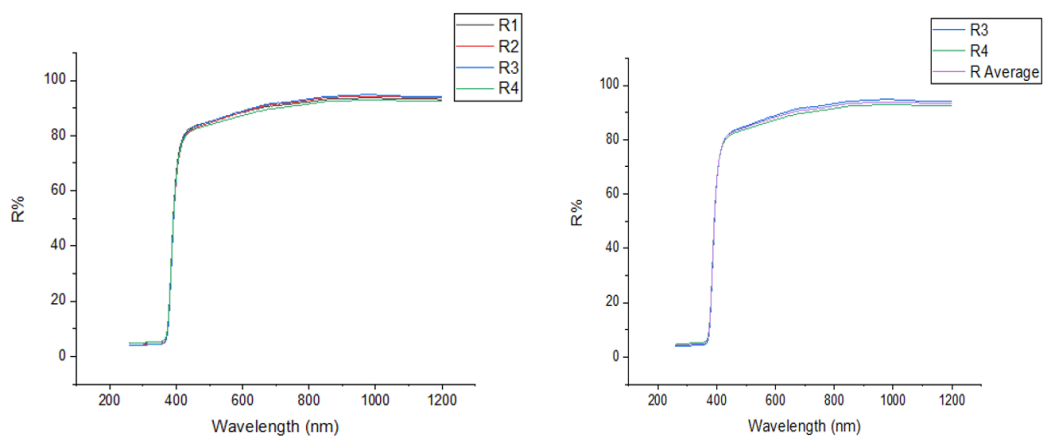


Figure 0.42. Relative diffuse reflectance graphs of reduced size MicNo ZnO (second measurement)

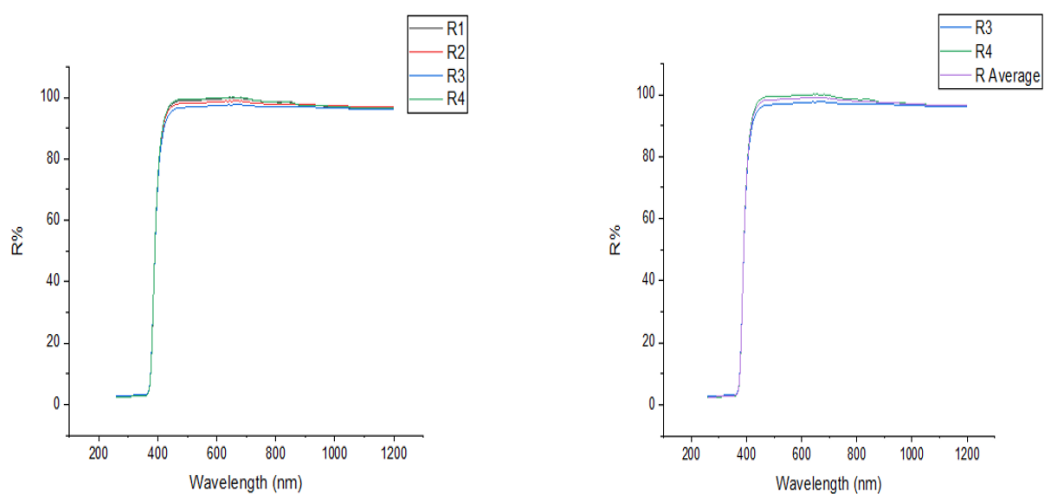


Figure 0.43. Relative diffuse reflectance graphs of nano ZnO (second measurement)

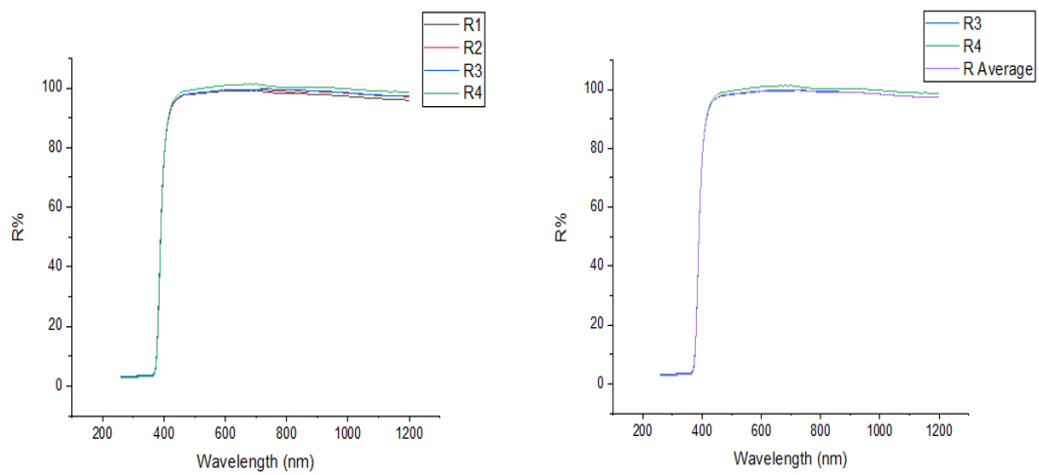


Figure 0.44. Relative diffuse reflectance graphs of 30-50 nm spherical ZnO (second measurement)

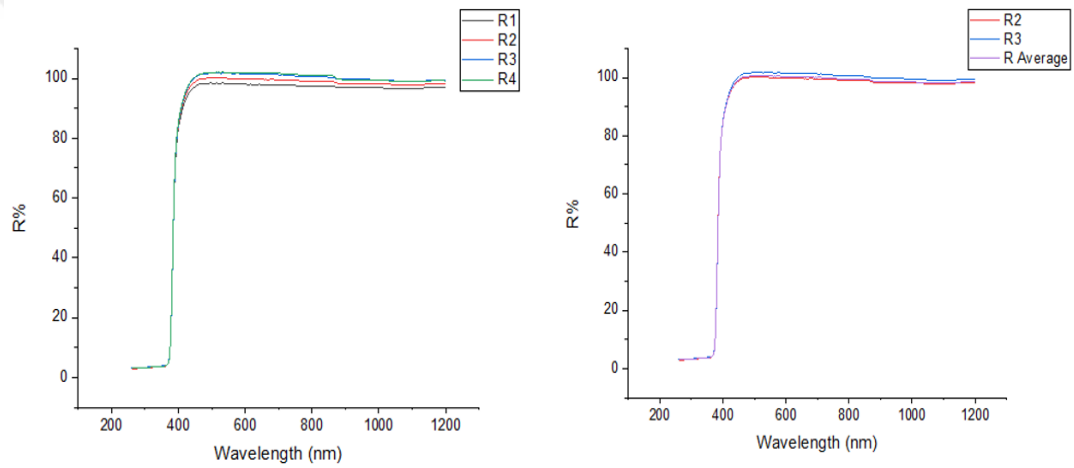


Figure 0.45. Relative diffuse reflectance graphs of submicron ZnO (second measurement)

APPENDIX-8. Relative Total Reflectance

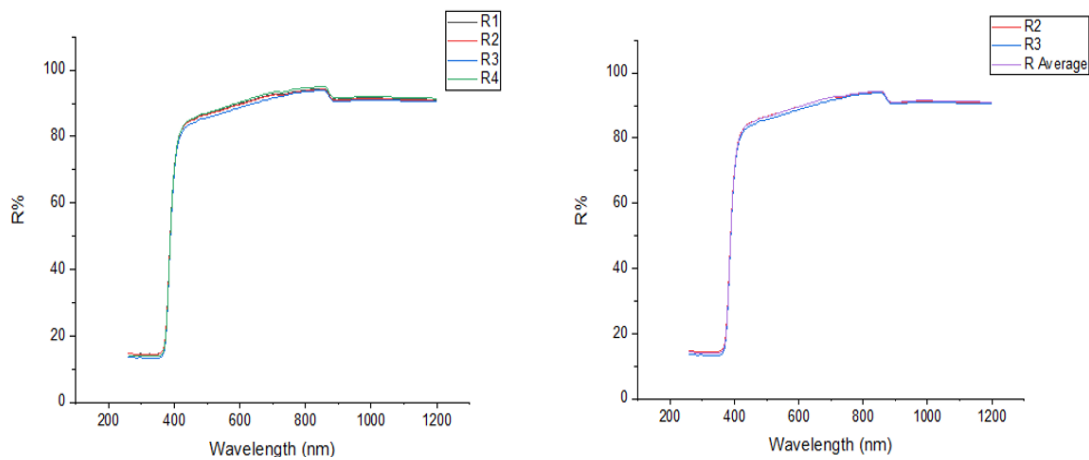


Figure 0.46. Relative total reflectance graphs of MicNo ZnO

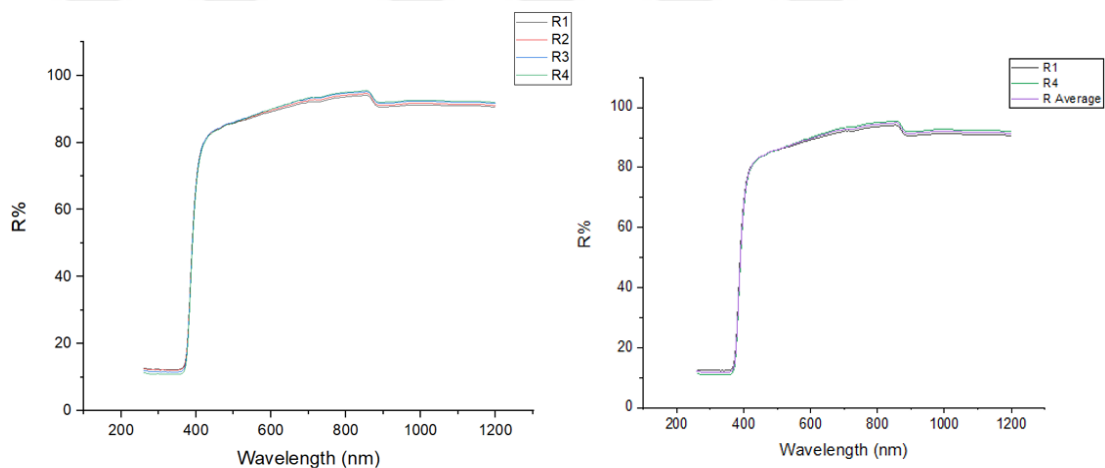


Figure 0.47. Relative total reflectance graphs of reduced size MicNo ZnO

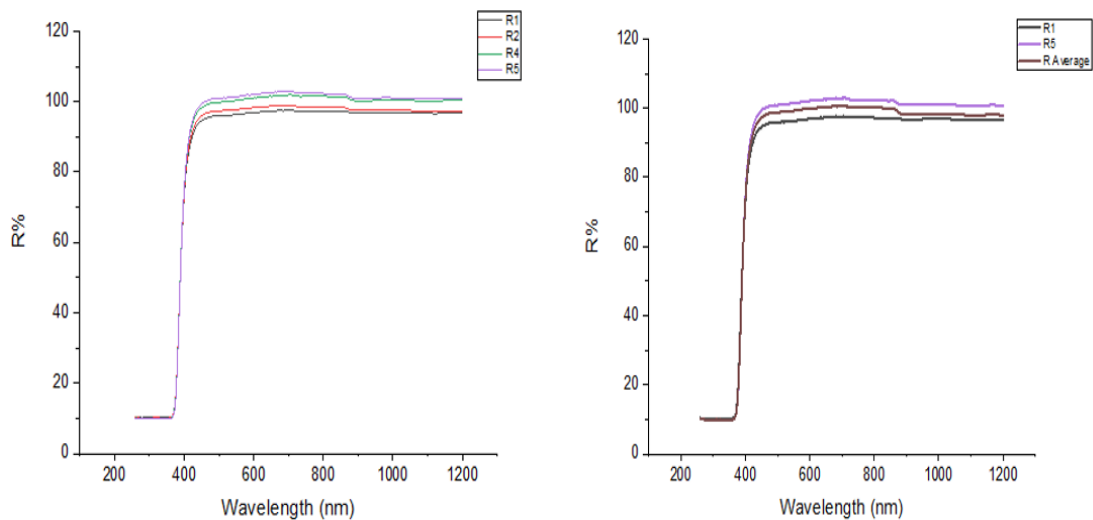


Figure 0.48. Relative total reflectance graphs of nano ZnO

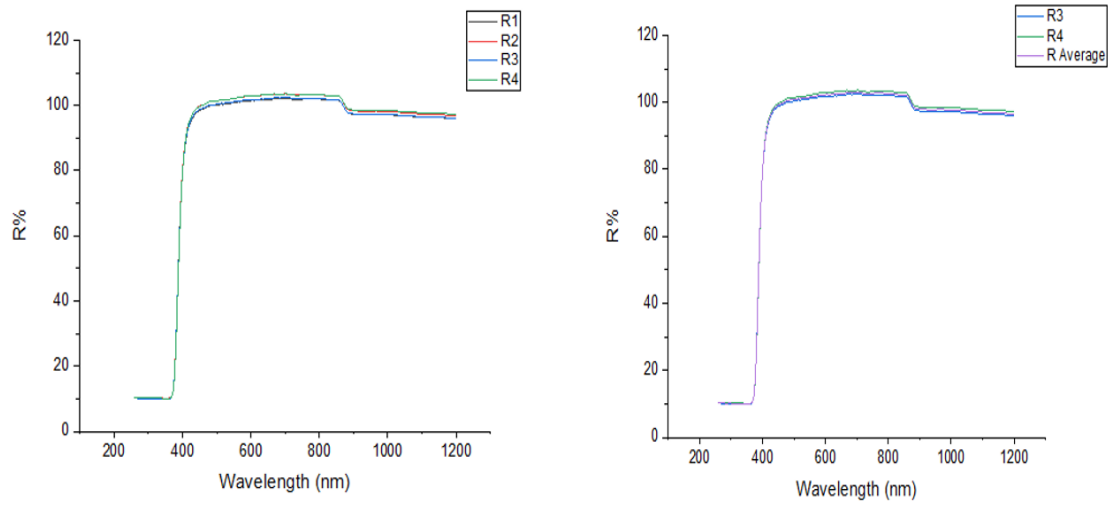


Figure 0.49. Relative total reflectance graphs of 30-50 nm spherical ZnO

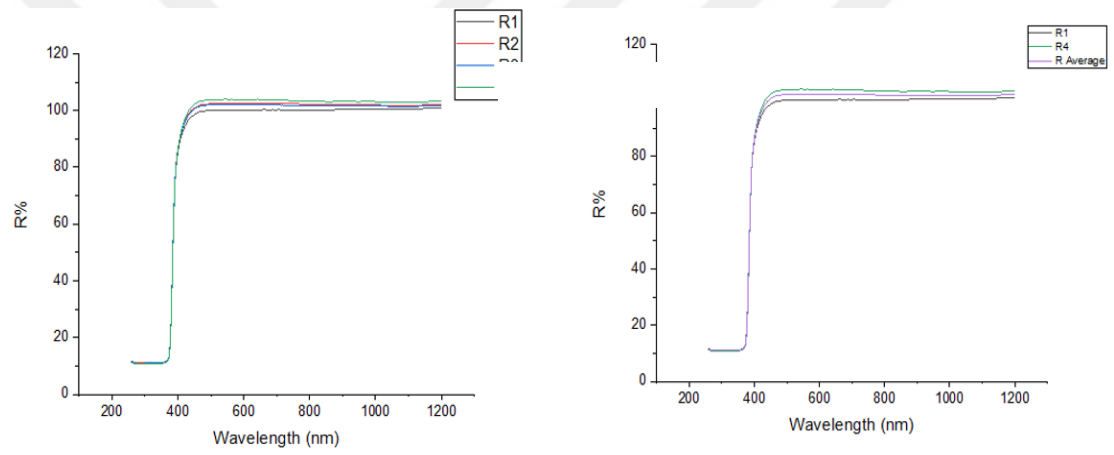


Figure 0.50. Relative total reflectance graphs of submicron ZnO

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- **Anadolu University (Turkey):** Turkish Language Course (2018-2019)
- **University of Lagos (UNILAG) (Nigeria):** Metallurgical and Materials Engineering (September 2011- November 2016)

WORK EXPERIENCE

- **China Civil Engineering Construction Corporation (CCECC Nigeria Limited):** Materials & Geotechnical Engineer (January 2017- May 2018)
- **Nigeria Gas and Steel Limited (Engineering Ιντερνσηιπ):** Mechanical Engineer (July 2015- Jan 2016)

OTHER CERTIFICATIONS:

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Prime International Risk and Safety Management (PIRSM) (2018)
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Federal University of Technology, Akure, Nigeria (FUTA) (2018)

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- Minitab and OriginLab