

A
DISSERTATION REPORT ON
**SYNTHESIS OF POLYMER NANOPARTICLES FOR
STRUCTURAL COLOR APPLICATIONS**

INDIAN INSTITUTE OF TECHNOLOGY ROORKEE

AKZONOBEL AUTOMOTIVE AND AEROSPACE COATINGS



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Polymer Science & Technology

**Department of Polymer and Process Engineering
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2013-14

Work carried out at

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Declaration

I, **Nallapaneni Asritha** (Enrolment Number – 09412010), hereby, declare that the work which is being presented in this Dissertation report entitled “**Synthesis of polymer nanoparticles for structural color applications**” in partial fulfilment of the requirements for the award of the degree of Integrated Master of Technology in Polymer Science and Technology, Department of Polymer and Process Engineering, Indian Institute of Technology Roorkee for the academic year 2013-14 is an authentic record of my work carried out under the supervision of **Prof Yuvraj Singh Negi**, Professor-In charge, IIT Roorkee and **Dr M J Yanjarappa**, Senior Group Leader, AkzoNobel International Research Center, Bangalore.

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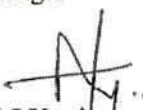
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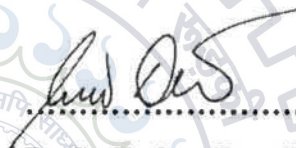
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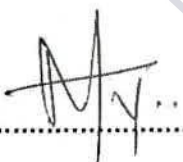
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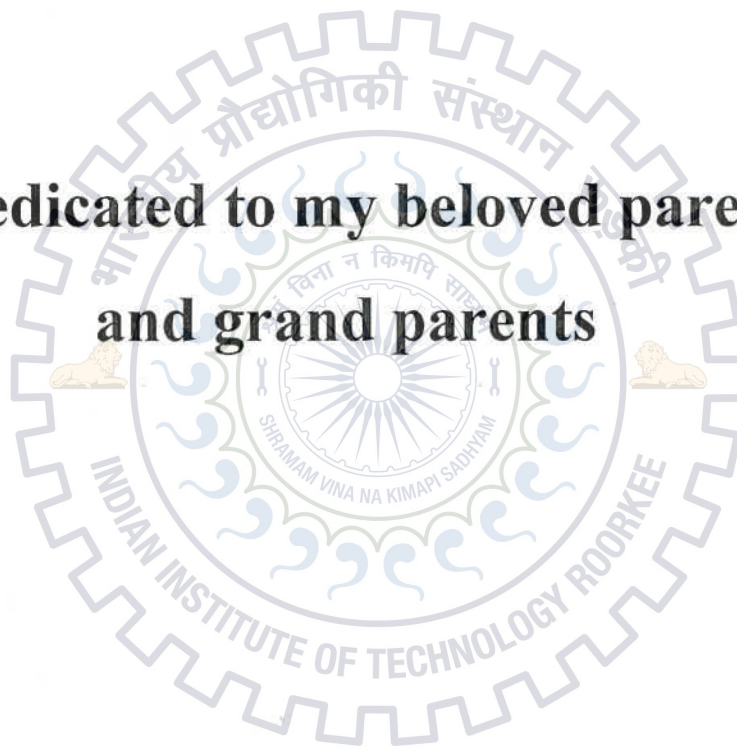
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**Dedicated to my beloved parents
and grand parents**



Acknowledgement

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Date: 4th June, 2014

NALLAPANENI ASRITHA

Abstract

Colors are the evolution's most beautiful accident. The color of the paint in general is attributed to the pigments present in it. Pigments exhibit color by absorbing defined portion of the wavelength of light, leaving the reflected portion of light which is being perceived by human as color. However, nature offers us with various examples such as butterfly wings, peacock feathers, beetle shells which exhibit color based on physical interaction of light with biological structures rather than pigments. Research focus has been shifted from pigment based colors to structural based colors in the recent years. The color of the *Morpho* butterfly wings originates from the Bragg diffraction and scattering of light in the visible spectrum which is termed as structural color. Many researchers have laid focus on the bio-mimicry of the biological structures to obtain structural color. Mimicking the structural color through synthetic means has been partially successful. The concept of structural color through bio-mimicking has motivated us to explore the feasibility of achieving color of the paint without pigments. Herein, we report a preliminary method to obtain color from the proper alignment of synthetic polymer nanoparticles. We have synthesised polystyrene, poly(styrene-*co*-methyl methacrylate-*co*-acrylic acid), poly(styrene-*co*-methyl methacrylate-*co*-2-hydroxy ethyl methacrylate) and poly(styrene-*co*-methyl methacrylate-*co*-EDM) nanoparticles with particle size varying from 200-350 nm *via* emulsion polymerization. The resultant nanoparticles exhibited different colors like violet, blue and green depending on the particle size, refractive index of the particles and spacing between the particles, when coated upon an aluminium substrate. The color of the films obtained from nanoparticle coated panels was further confirmed by UV-Vis-NIR spectroscopy measurements. An increase in adhesion of nanoparticles on aluminium substrate was observed with films obtained from poly(styrene-*co*-methyl methacrylate-*co*-EDM) nanoparticles compared to acrylic acid and HEMA based nanoparticles. Overall the concept of structural color was established and made efforts to

achieve good adhesion over aluminium substrate. Finally, proposed few routes to improve the adhesion of polymer nanoparticles on aluminium substrate.



List of Notations

St/Sty: Styrene

MMA: Methyl methacrylate

AA: Acrylic acid

HEMA/2-HEMA: 2-hydroxy ethyl methacrylate

SDS: Sodium dodecyl benzene sulfonate

APS: Ammonium persulphate

EDM: Electron deficient monomer

PS-MMA-AA: Copolymer of styrene, methyl methacrylate and acrylic acid

PS-MMA-HEMA: Copolymer of styrene, methyl methacrylate and 2-hydroxy ethyl methacrylate

PS-MMA-HEMA-AA: Copolymer of styrene, methyl methacrylate, 2-hydroxy ethyl methacrylate and acrylic acid

PS-EDM: Copolymer of styrene and electron deficient monomer

PS-MMA-EDM: Copolymer of styrene, methyl methacrylate and electron deficient monomer

P(MMA-AA): Copolymer of methyl methacrylate and acrylic acid

P(MMA-HEMA): Copolymer of methyl methacrylate and 2-hydroxy ethyl methacrylate

P(MMA-EDM): Copolymer of methyl methacrylate and electron deficient monomer

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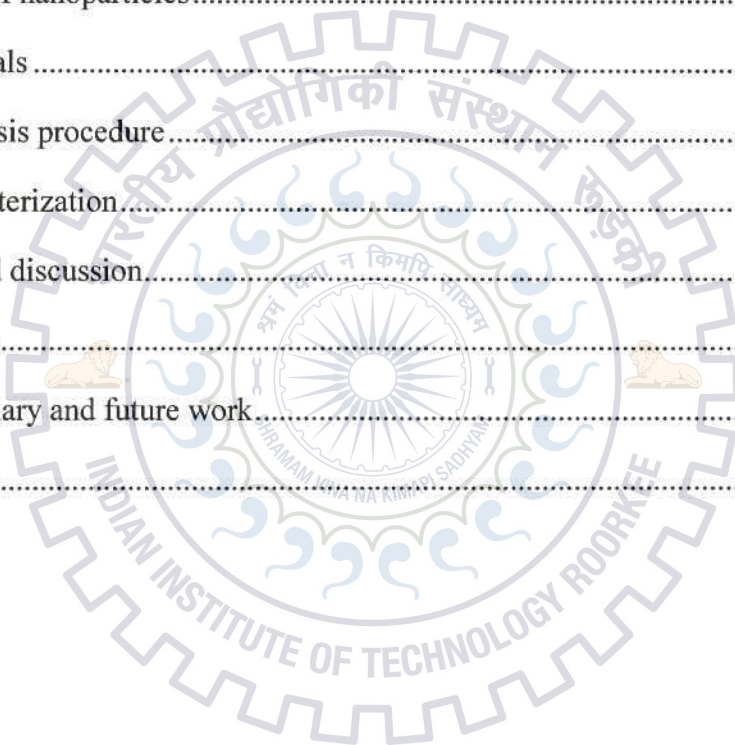
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Chapter 1: Introduction

Paint is either liquid or solid or liquefiable or mastic composition that, after application to a substrate in a thin layer, converts to a solid film. It is most commonly used to protect, color or provide texture to objects. Paint can be manufactured in many colors—and in many different types, such as water color, artificial. Paint is typically stored, sold and applied as a liquid, but dries into a solid. Paint essentially comprises of three major ingredients – binder, solvent and pigments. The primary function of the binder is to form the film. Solvent assists in maintaining the viscosity of the paint system as well as application of paint on to substrates. Pigments impart color, toughness and texture to the paint. Certain special additives help to modify surface tension, improve flow properties, pigment stability & finished appearance, increase wet edge, impart antifreeze properties and control foaming & skinning.

The substrate is coated with three to four layers of paint before final use as shown in Figure 1 in order to obtain the desirable properties as explained below.

- Primer – It's the first coat and protects the substrate from corrosion.
- Surfacer – It's the second coat and compensates unevenness of the substrate body in order to have a smooth under coat and to have the neat coats fixed. In some special cases, only one coat is used which simultaneously serves as primer and surfacer.
- Base Coat – It's the third coat and it is either an effect coat or a unicoat, giving the substrate its color.
- Clear Coat – It's the last coat and improves the resistance against weathering, sun, stone projections, and scratches. This coat is not always necessary when unicoat is used, because unicoat can combine the functions of basecoat and the clear coat.

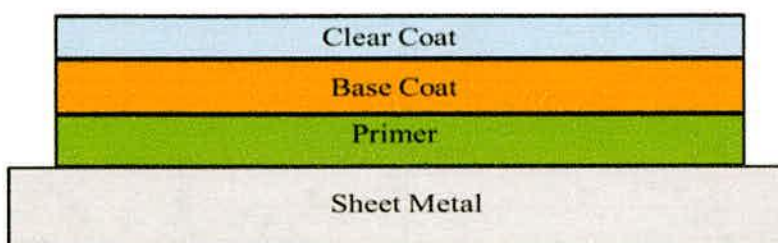
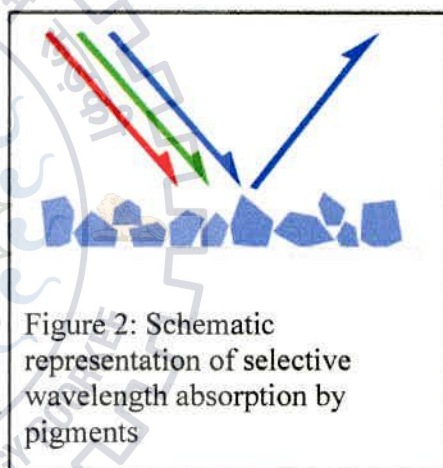


Figure 1: Different layers of paint applied onto a metal substrate

1.1 Pigment based colors

A pigment is a material that imparts color to the object by changing the color of reflected or transmitted light as a result of wavelength-selective absorption as shown in Figure 2. This physical process differs from fluorescence, phosphorescence and other forms of luminescence in which a material emits light. Pigments have special properties that make them ideal for coloring other materials. It must be stable in solid form at ambient temperature. Permanence and stability are desirable properties for industrial applications. Pigments that are not permanent are called fugitive, which fade over time or with exposure to light, while some eventually blacken. Most pigments used in paint manufacturing are ground into a fine powder and added to the binder solution to suspend the pigment in the liquid media.

The visual colors of the pigment arise due to their selective reflection and absorption of certain wavelengths of visible light. White light is a roughly equal mixture of the entire spectrum of visible light with a wavelength range from 390 - 760 nm. When the visible light encounters a pigment, portion of the spectrum is absorbed by the chemical bonds of conjugated systems of the pigment leaving the other portion (wavelengths) of the spectrum as reflected or scattered. Most pigments are charge-transfer complexes. For example, transition metal compounds, with broad absorption bands that subtract most of the colors of the incident white light. Ultramarine



reflects blue light and absorbs other colors. Pigments, unlike fluorescent or phosphorescent substances, can only subtract wavelengths from the source light, never add new ones. The appearance of pigments is intimately connected to the color of the source of light. Sunlight has a high color temperature and a fairly uniform spectrum and is considered a standard for white light. Artificial light sources tend to have great peaks in some parts of their spectrum, and deep valleys in others. Viewed under these conditions, pigments will appear as different colors. Other properties of color such as its saturation or lightness may be determined by the other substances that accompany pigments. Binders and fillers added to pure pigment chemicals also have their own reflection and absorption patterns, which can affect the final spectrum. Likewise, in pigment/binder mixtures, individual rays of light may not encounter pigment molecules and may be reflected as it is. These stray rays of source of light contribute to a slightly less saturated color. Pure pigment allows very little white light to escape,

producing a highly saturated color. A small quantity of pigment mixed with a high volume of binder, however, will appear de-saturated and pale, due to the high quantity of escaping white light.

The global pigments and dyes market is projected to grow at a compound annual growth rate of 3.6% from 2013 to 2018 and is expected to reach 11 million metric tons by 2018. The major driving factors of pigments market are rising demand for high performance pigments (HPP) and rising preference towards environment-friendly products. The paints & coatings industry is the major consumption of pigments (~56%). The addition of pigments to paint formulations results in the increase in cost of the final product apart from health and environmental issues. Some of the pigments have already been banned due to their toxic nature. For example, paint manufacturers began replacing white lead pigments with titanium white (TiO_2) before lead was banned in paint for residential use in 1978 by US Consumer Product Safety Commission.

1.2 Bio-inspired colors

Nature offers us a wide variety of examples such as peacock feathers, butterfly wings whose color depends on the physical interaction of light with the biological structures irrespective of the pigments. Such colors are obtained by the Bragg diffraction and scattering of light in the visible region. Many morpho butterflies are colored in metallic, shimmering shades of blues and greens. The microscopic scales covering the Morpho's wings reflect incident light repeatedly at successive layers, leading to interference effects that depend on both wavelength and angle of incidence/observance. The color of the light can be intensified by increasing the number of stacking layers. The structure of the wings of the *Morpho* butterfly is shown in Figure 3.

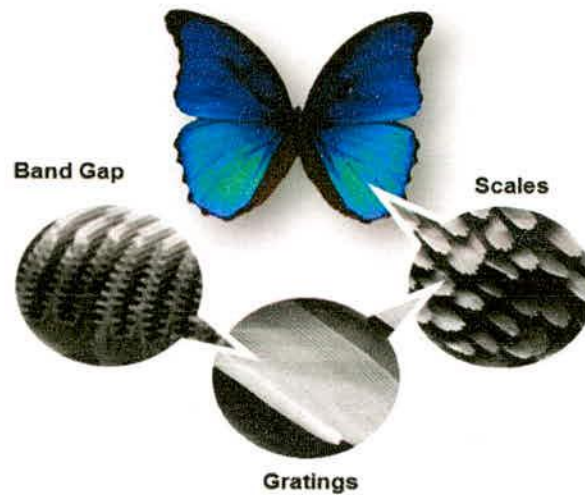


Figure 3: Color in *Morpho* butterfly

When the Pollia fruits (Figure 4) were examined by transmission and scanning electron microscopes, the researchers found that the fruit's long-lasting blue iridescence was generated by the outermost layers of thick-walled cells. Specifically, within the walls of those cells are layers of cellulose microfibrils, stacked in a manner resembling a helix—each layer slightly rotated with respect to the next. Within each cell wall is many such helicoids stacked one on top of another. The distance between two similar points in a given helix—a value known as the helical pitch—is about the same as the wavelength of blue light. As a result, blue light is selectively reflected while other color wavelengths pass through or get cancelled out through a property called constructive interference. However, the spacing of the cellulose layers varies slightly from cell to cell, with a minority of cells giving off red, purple, and green hues, thus giving the fruit a pixelated appearance when viewed under a certain type of illumination.

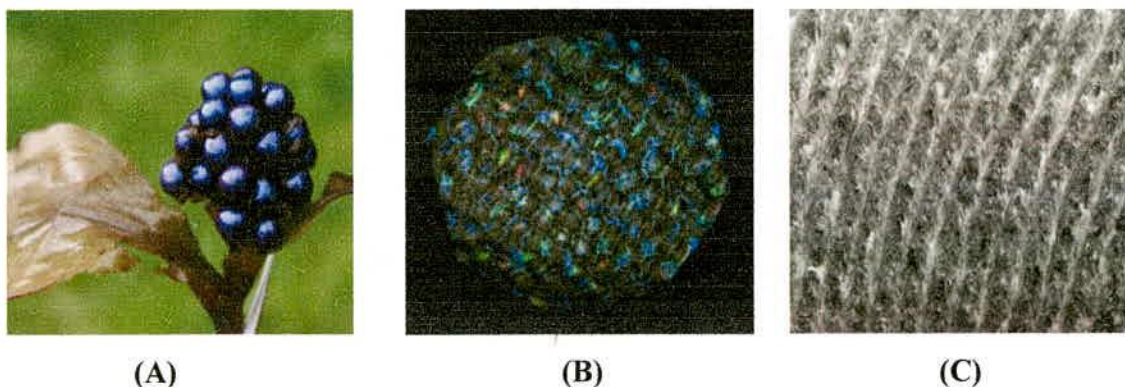


Figure 4: (A) Photographic image (B) Optical microscopic image under epi-illumination (C) Transmission Electron Microscopic image of Pollia Condensata

The vivid colors of a peacock feather do not arise entirely from pigments - in fact, the role of pigments may be minimal. The structure of the feather plays a role in the color according to investigations by Jian Zi et al¹. The structural arrays in the barbules of the peacock feather are measurably different for the different colored regions. The barbules are described as straplike "twigs" which come off the branches of the peacock feather. The structures which produce the colors are described as arrays of melanin cylinders which in a green region were measured to have an array spacing of about 150 nm (Figure 5, (B)). The surface of the barbule is made of keratin, containing about 10 rows of the melanin cylinders in the green region. The blue regions in the barbules were found to have a melanin cylinder spacing of about 140 nm (Figure 5, (C)). Variations in the spacing and numbers of layers were distinctive for the different colors with yellow barbules having spacing of about 165 nm in a square lattice of about six periods. Brown barbules exhibited a rectangular lattice with about four periods.

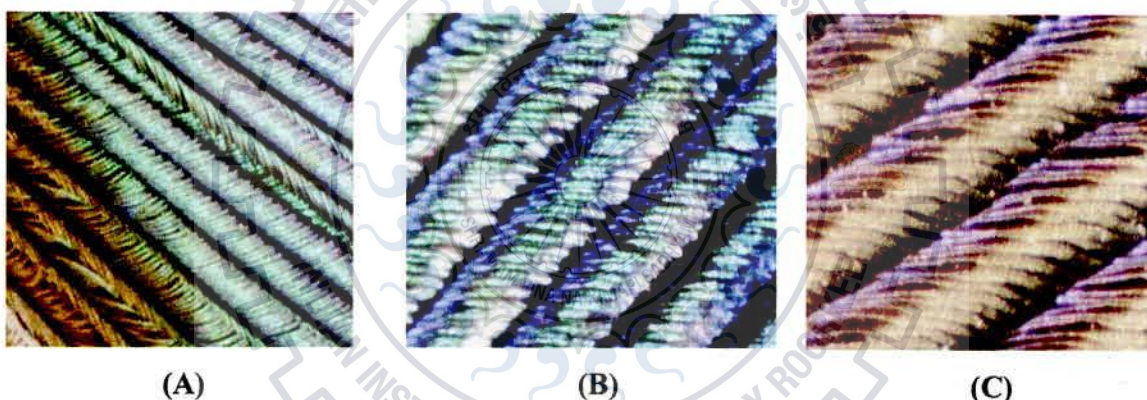


Figure 5: Photographic images of peacock's feather at (A) 50x (B) 100x (C) 200x magnification

Dynamic iridescence is most strikingly exemplified by cephalopods, such as some species of

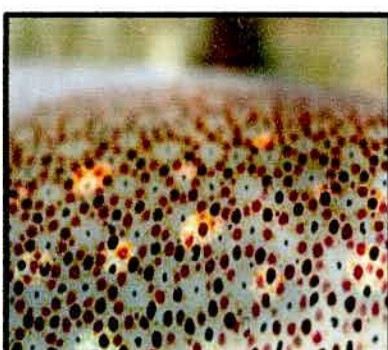


Figure 6: Atlantic longfin squid (Cephalopod)

squid (Figure 6), that can undergo dramatic and lightning-quick transformations in both their structural and pigmented coloration at will. In 2004, a team of researchers led by Margaret McFall-Ngai discovered that the reflective material responsible for structural iridescence in cephalopods is a novel and unusual family of proteins, which they aptly named reflectins. Instead of the plates of purine crystals found in the reflective structures of many fish, the cephalopod iridophores contain multiple layers of membrane-enclosed reflectin proteins. The nervous systems of certain species, such as the

longfin inshore squid (*Loligo pealei*), can control the reflective properties of the reflectin structures by releasing neurotransmitters that modulate the phosphorylation of reflectin. The phosphorylation is thought to affect reflectin's solubility and thus fine-tune the spacing of the protein layers—ultimately changing the color reflected by the iridophores.

The color obtained from structural arrangement irrespective of the pigments is termed as structural color.

1.3 Structural color

Structural color is the color caused by interference effects rather than pigments. Color effects are produced when a material is scored with fine parallel lines formed of one or more parallel thin layers, or otherwise composed of microstructures on the scale of the color's wavelength. If the microstructures are spaced randomly, light of shorter wavelengths will be scattered preferentially to produce Tyndall effect colors: the blue of the sky (Rayleigh scattering, caused by structures much smaller than the wavelength of light, in this case air molecules), the luster of opals and the blue of human irises. If the microstructures are aligned in arrays, for example the array of pits in a CD, they behave as a diffraction grating: the grating reflects different wavelengths in different directions due to interference phenomena, separating mixed "white" light into light of different wavelengths. If the structure is one or more thin layers then it will reflect some wavelengths and transmit others, depending on the layers' thickness.

Structural color is responsible for the blues and greens of the feathers of many birds (the blue jay, for example), as well as certain butterfly wings and beetle shells (Figure 7). Variations in the pattern's spacing often give rise to an iridescent effect, as seen in peacock feathers, soap bubbles, films of oil and mother of pearl, because the reflected color depends upon the viewing angle.



Figure 7: Structural color in beetle

Nature provides us with many examples in this regard. Many researchers have investigated the butterfly wings, beetles, etc. for their color. They found that such color is obtained from the structure and sometimes from both the color and pigments present in them. Several articles have been published on structural color^{2,3}. For example, Hein et al reported on refractive index and dispersion of butterfly chitin and bird keratin measured by polarizing interference

microscopy⁴. Luke et al. published an article on structural optimization for broadband scattering in several ultra-thin white beetle scales⁵.

Structural coloration is responsible for the blues and greens of the feathers of many birds (the bee-eater, kingfisher and roller, for example), as well as many butterfly wings and beetle wing-cases (elytra). These are often iridescent, as in peacock feathers and nacreous shells such as of pearl oysters (Pteriidae) and Nautilus. This is because the reflected color depends on the viewing angle, which in turn governs the apparent spacing of the structures responsible. Structural colors can be combined with pigment colors: peacock feathers are pigmented brown with melanin.

A layman's term that describes particularly the most ordered or the most changeable structural colors are iridescence. Iridescence is a direct consequence of structural colour. It says that the perceived color of an object depends on the viewing angle, like CDs or natural opals. Because the distance light travels when reflecting from the top and bottom of a layer depends on the angle it hits at, the constructive interference condition (and thus the colour) changes.

1.3.1 Principle of structural color

Structural color is based on the principle of Bragg diffraction of light (Figure 8). When light falls on a material, defined portion of the light gets diffracted while the rest gets transmitted depending on the nature of the substance. The diffracted light interferes either constructively or destructively. For materials which result in constructive interference of light, the color of the light corresponding to the wavelength of the light is perceived by humans as the material's respective color. Bragg's law can be expressed in the following equation:

$$\lambda = 2 n * d \sin \theta$$

where n is the effective refractive index of the material, λ is the wavelength of reflected light, d is the spacing between the planes in the atomic lattice, and θ is the angle between the incident ray and the scattering planes.

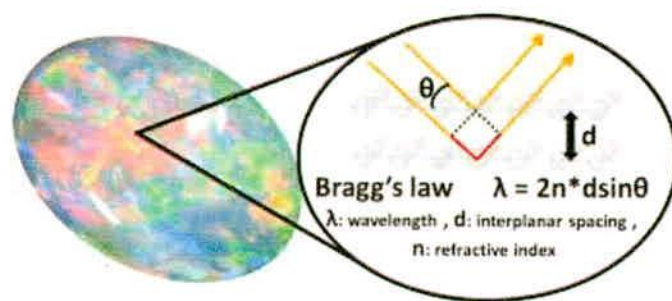


Figure 8: Schematic representation of Bragg diffraction of light

Researchers have successfully explored the ways to mimic structural colors in nature. This particular area opened new doors in the field of photonics and colloids.

1.4 Photonic crystals

Photonic crystals are periodic optical nanostructures that affect the motion of photons similar to that of ionic lattices which affect electrons in solids. Photonic crystals occur in nature in the form of structural coloration and promise to be useful in different forms in a wide range of applications. Photonic crystals can be fabricated for one, two or three dimensions. One-dimensional photonic crystals can be made of layers deposited or stuck together; two-dimensional ones can be made by drilling holes in a suitable substrate, and three-dimensional ones by, for example, stacking spheres in a matrix and dissolving the spheres (Figure 9).



Figure 9: 1D, 2D, 3D photonic crystal

Photonic crystals are attractive optical materials for controlling and manipulating the flow of light. Many researchers have adopted the idea of aligning nanoparticles in a regular lattice structure in order to obtain color. Various groups have reported on Photonic colloidal crystals^{6,7,8}. For example, Pursiainen et al.⁹ reported an article on nanoparticle-tuned structural color from polymer opals. They used nanoparticles with core-shell architecture consisting of a hard cross-linked polystyrene (PS) sphere coated with a thin poly (methyl-methacrylate) (PMMA) inter-layer which anchors the outer shell composed of soft poly (ethyl acrylate) (PEA). Additional carbon sub-50 nm nanoparticle dopants were introduced into the interstices of the photonic crystal lattice without disrupting the lattice quality which resulted in intensification of the color. A hyper spectral imaging setup was used to map a wider angular scattering cone. *Castañeda-Uribe et al.*¹⁰ studied the Fabrication and optical characterization of a high-quality FCC-opal-based photonic crystal grown by the vertical convective self-assembly method. A review article has

been published on From Opals to Optics: Colloidal Photonic Crystals by Colvin¹¹. Foulger et al.¹² investigated on Robust polymer colloidal crystal photonic band-gap structures. Ruhl et al.¹³ reported an article on Artificial opals prepared by melt compression.

Colloidal systems can be used to fabricate photonic crystals. Colloids are small objects dispersed in a medium having at least one dimension in the range of 1nm to 1 μ m and often the upper limit can be extended to hundreds of microns. Brownian motion - resulting from the random bombardment of solvent molecules, is the characteristic feature of the colloidal particles. Colloidal particles are important in a broad range of technologies and in the processing of various materials including foods, inks, paints, coatings, cosmetics and photographic films, and thus are intensely studied in materials science, chemistry and biology.

Colloidal crystals are three-dimensional periodic lattices assembled from mono-dispersed spherical colloidal particles. For example, the natural opals, which show attractive iridescence are polycrystalline colloidal crystals composed of the silica colloids and surrounding medium and the iridescence is due to the diffraction of visible or near infrared light as a consequence of the periodic modulation of the refractive index between the silica particles and the surrounding medium.

Most importantly, in recent years colloidal crystals have fully demonstrated the potential to obtain interesting and useful functionality not only from the constituent materials of the colloidal particles but also from the long-range order of the crystalline lattice (meta-materials). The effect of temperature on the wettability of the colloidal crystal assembly has been reported¹⁴.

Emulsion polymerization is one of effective ways to produce polymer colloids. Emulsion polymerization has gained prominence in the recent years and stands out among various other polymerization techniques due to colloidal stability, excellent heat removal etc.

1.5 Emulsion polymerisation

Emulsion polymerization is a type of radical polymerization that usually starts with an emulsion incorporating water, monomer and surfactant. The most common type of emulsion polymerization is an oil-in-water emulsion, in which droplets of monomer (the oil) are emulsified (with surfactants) in a continuous phase of water. Water-soluble polymers such as polyvinyl alcohols or hydroxyethyl celluloses can be used as emulsifiers/stabilizers. Polymerization takes place in the latex particles that form spontaneously in the first few

minutes of the process. These latex particles are typically 10 nm to 10 μm in size and are made of many individual polymer chains. The particles are stopped from coagulating with each other because each particle is surrounded by the surfactant ('soap'); the charge on the surfactant repels other particles electrostatically. Emulsion polymerization is used to manufacture several commercially important polymers. Many of these polymers are used as solid materials and must be isolated from the aqueous dispersion after polymerization. In other cases the dispersion itself is the end product. They are often preferred over solvent-based products in these applications due to the absence of VOCs (Volatile Organic Compounds) in them. A review article has been published by Rao et al.¹⁵ which covered the general description of the preparation of polymer nanoparticles and the detailed description of the crucial parameters involved in techniques designed to obtain the desired properties. A review article by Chern¹⁶ described mechanism and kinetics of emulsion polymerization.

1.6 Motivation

The concept of structural color through bio-inspiration has motivated us to obtain the color of the paint through structural alignment of the nanoparticles obtained through emulsion polymerization. Subsequent interaction of the light with well aligned nanoparticles of paint enable to produce different colors based on the particle size, refractive index and spacing between the nanoparticles. Such colors can also be called “**Green Colors**” as they are environment friendly, free of pigments and desirable properties can also be attained. The structural colors look metallic although they don't contain any metals, doesn't contain UV sensitive dyes and have low toxicity. Structural colors also exhibit iridescence.

1.7 Scope

Structural coloration has potential for industrial, commercial and military application, with biomimetic surfaces that could provide brilliant colors, adaptive camouflage, efficient optical switches and low-reflectance glass. Photonic band gap structures find wide applications in the field of optics.

1.8 Aim

The aim of this project is to formulate paint for a base coat using synthetic polymer nanoparticles obtained through emulsion polymerization and then obtain color from the physical interaction of light with the structural arrangement of the respective nanoparticles which is typically a 3D photonic crystal. The nanoparticles with core-shell morphology were

given importance in this study as the color obtained can be controlled by having control over the refractive index gradient, particle size, spacing between the nanoparticles.



Chapter 2: Synthesis of poly (styrene-co-MMA-co-acrylic acid) nanoparticles

2.1 Introduction

Polymeric nanoparticles with uniform particle size obtained through various techniques have found numerous applications. Recently application of nanoparticles to obtain structural color has attracted considerable interest^{2,3,4}. Emulsion polymerisation is the most suitable technique to prepare polymeric nanoparticles due to its advantages over other polymerisation techniques. It has matured as a preferred production method for adhesives, paints, additives in paper and textiles¹⁷. It has gained popularity because of the low viscosity of the final dispersion, high colloidal stability, excellent heat removal as water is usually the continuous medium, good temperature control and high polymerization rates. In general, the polymerization is quantitative and unreacted monomers are removed without difficulty.

In the present study, we prepared model polystyrene nanoparticles with well-defined particle size to get the color upon application on a polyurethane coated black aluminium metal substrate. Subsequently we prepared styrene copolymers with methyl methacrylate and acrylic acid to improve the adhesion on metal substrates as pure polystyrene nanoparticles are known to have poor adhesion due to lack of polar groups. The nanoparticles of styrene, methyl methacrylate, acrylic acid copolymers were presumed to have core-shell morphology¹⁸. We reasoned to have better control over the refractive index gradient of the material as well as the nature of surface groups. As per literature, the presence of anionic groups due to acrylic acid provides better adhesion over substrates. Additionally styrene forms the core and provides the strength to the particle. MMA and AA will form the shell. MMA helps to improve the mechanical strength and flexibility to the nanoparticles. The general mechanism for emulsion polymerisation is shown below in Figure 10.

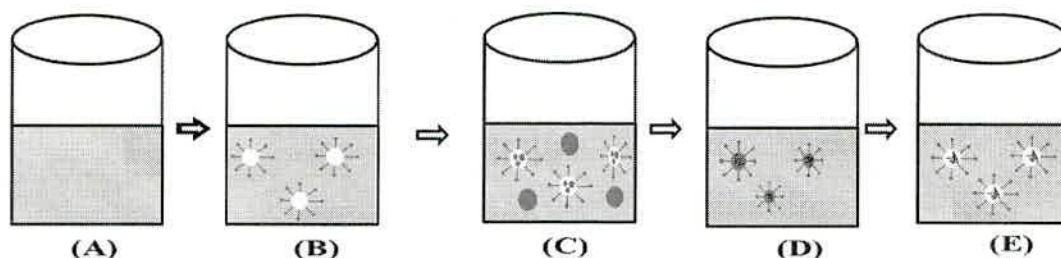


Figure 10: Mechanism of Emulsion Polymerisation

The formation of polymeric nanoparticles involves five different phases as shown in Figure 10. Water was used as dispersing medium in the Emulsion. As the concentration of micelles is above critical micelle concentration (CMC), the surfactants form micelles at the temperature of 50°C (Stage B in Figure 10). When the monomer is added to the water, it forms oil-in-water emulsion. Part of the monomer is present in aqueous phase whereas the remaining portion of monomer is present inside the micelles. After the monomer addition is complete, the emulsion is allowed to stabilise for 30 minutes at a temperature of 70°C (Stage C in Figure 10). The initiator which was then added to the emulsion to initiate the free radical polymerisation of monomer in aqueous phase; which propagates in the micelles at a temperature of 80°C (the temperature at which APS decomposes to give free radicals) (Stage D in Figure 10). At the end of the polymerisation, the polymer is present in the micelles. However, there could be traces of oligomer/monomer present outside the micelles (Stage E in Figure 10). The stirring speed of the propeller was maintained at 350 rpm in order to ensure the uniform distribution of heat inside the reaction vessel.

2.2 Synthesis of polymer nanoparticles

2.2.1 Materials

Styrene was purchased from Avra Synthesis. Methyl methacrylate and acrylic acid were obtained from Rolex Chemical Industries and Loba Chemie respectively. All the three monomers were purified by passing through neutral active alumina column. Ammonium bicarbonate and ammonium per sulphate were obtained from Finar Chemicals. Emulsifier sodium dodecyl benzene sulfonate was procured from Sigma Aldrich.

2.2.2 Synthesis procedure

A typical polymerisation procedure used in synthesis of Emulsion 3 is described here. The three necked 500 ml round bottomed glass vessel was charged with 200 ml of deionised water containing 1 g of ammonium bicarbonate. A nitrogen blanket and a stirring rate of 350 rpm of the propeller were maintained throughout the reaction. The water solution was deoxygenated by bubbling with nitrogen for 40 minutes followed by addition of 0.008 g of sodium dodecyl benzene sulfonate dissolved in 5 ml water. The temperature was increased to 50°C. Previously de-inhibited and de-oxygenated methyl methacrylate, acrylic acid and styrene were mixed together and added to the reaction vessel in a drop wise manner. The reaction mixture was kept at 70°C for 0.5 h followed by the addition of an aqueous solution of 0.96 g of ammonium persulfate. The polymerization was then carried out at 80°C for 10 h

with continuous stirring. The emulsions were collected after the polymerisation and stored for 24 h to observe any settling of particles. However, no settling of particles was observed. The emulsions were centrifuged at 12,000 rpm for 15 minutes to remove any coagulum (~10%) and the supernatant was collected and used for further color applications. Similar experimental protocol has been used for synthesis of emulsions 4-6 and the detailed ingredients are tabulated in Table 1.

2.2.3 Characterization

Particle Size Analysis

The emulsions have been characterised for the particle size of the nanoparticles using Particle Size Analyser procured from Microtrac, USA (M3551-1B-BUTO-0000-00000-000-2M). The software used for this purpose is Microtrac Flex. The refractive index of the material was kept as 1.59 while using the software and the dispersing medium used was water. The particle size measurements observed in Microtrac doesn't reflect the actual size and shape of the particles as the particle size corresponds to the hydrodynamic diameter of the particle irrespective of the shape of the particle whether it is spherical or non-spherical. However, the results help in better understanding of the size of the particles. The results obtained from Microtrac coupled with Scanning Electron Microscopy will give better information related to true size and shape of nanoparticles.

Refractive Index Measurements

The refractive index measurements of the emulsions have been done using Automatic Digital Refractometer (RX – 5000I) (SL # 120543N). A small amount (~1-2 drops) of the emulsion has been placed on the sample holder using a dropper and the measurements have been noted.

Fourier Transform –Infrared Spectroscopy

At the end of the polymerisation, FT-IR measurements of emulsion sample were conducted using PerkinElmer L10000A Spectrum to check for the presence of the free monomer. An emulsion sample of volume ~10ml should be placed uniformly on the trough made of Zinc Selenoid crystal using a dropper.

Color

The Emulsions synthesised were sprayed onto the (6 X 4 size) polyurethane coated aluminium black panel using spray gun followed by visual observation of color immediately after spraying. The panels were rubbed with emery paper prior to spraying in order to impart

hardness. Emulsion sample of approximately 50 ml was used for spraying. The panels were coated to achieve high dry film thickness of around 30-40 μm .

UV-Vis-NIR Spectroscopy

The emulsions were sprayed onto the black Akzo panels and then reflectance spectra of the films were observed. The wavelength of the peak observed should correspond to the color that is observed on the panel. The measurements were conducted using PerkinElmer UV-Vis-NIR Spectrometer Lambda 950.

Adhesion Test

The adherence of nanoparticles to the polyurethane coated aluminium black panel was checked by Automatic Cross Hatch Cutter (S/N NO 12001, TYPE CHC MK3) using program 3 (6 X 2) at regular intervals after spraying. Adhesion test was performed on panels on the following day (Day 1) after spraying. In order to study the effect of temperature upon heating, the emulsion sprayed panel was placed in the oven on Day 1, the temperature of which was maintained at 110°C for 5-7 minutes and then adhesion test was performed on the corresponding panel.

2.3 Results and discussion

The polymeric nanoparticles synthesized in the present work were presumed to have core-shell morphology as shown in Figure 11 based on the literature. As the dispersing medium is hydrophilic, the hydrophobic polystyrene was expected to form the core and covalently attached by poly(methyl methacrylate-*co*-acrylic acid) to form the shell.

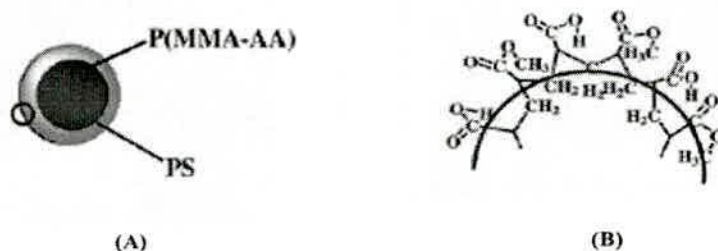


Figure 11: Schematic illustration of the phase inversion of the latex sphere during the assembly procedure. A) The morphology of the latex sphere and B) the conformation mode of the circled part in (A)

The results of the particle size, Refractive Index measurements and the resultant color observed are shown in the following Table 1.

Table 1: Particle Size and Refractive Index measurements

Emulsion	Concentration St/MMA/AA (g)	Particle Diameter (nm)	d_{50} (nm)	Refractive Index	Color
1	38/0/0	232-399	294	1.3634	GREEN
3	38/2/2	237-357	280	1.3616	VIOLET
4	38/2/4	267-437	331	1.3544	BLUE-GREEN
5	38/4/2	268-355	308	1.3584	GREEN
6	38/6/2	221-301	259	1.3508	VIOLET-GREEN

It is evident from the above data that an average particle size remained in the range of 230-350 nm. Due to the limited methods available to measure the refractive index of solids, the refractive index of polymeric nanoparticles in powder form couldn't be measured. It can be seen from Table 1 that reduction in refractive index of emulsions was observed as the concentration of the styrene decreased.

The emulsions were checked for the presence of free monomer using FT-IR Spectroscopy. The results of the FT-IR spectra of the emulsions are shown below in Figure 12.

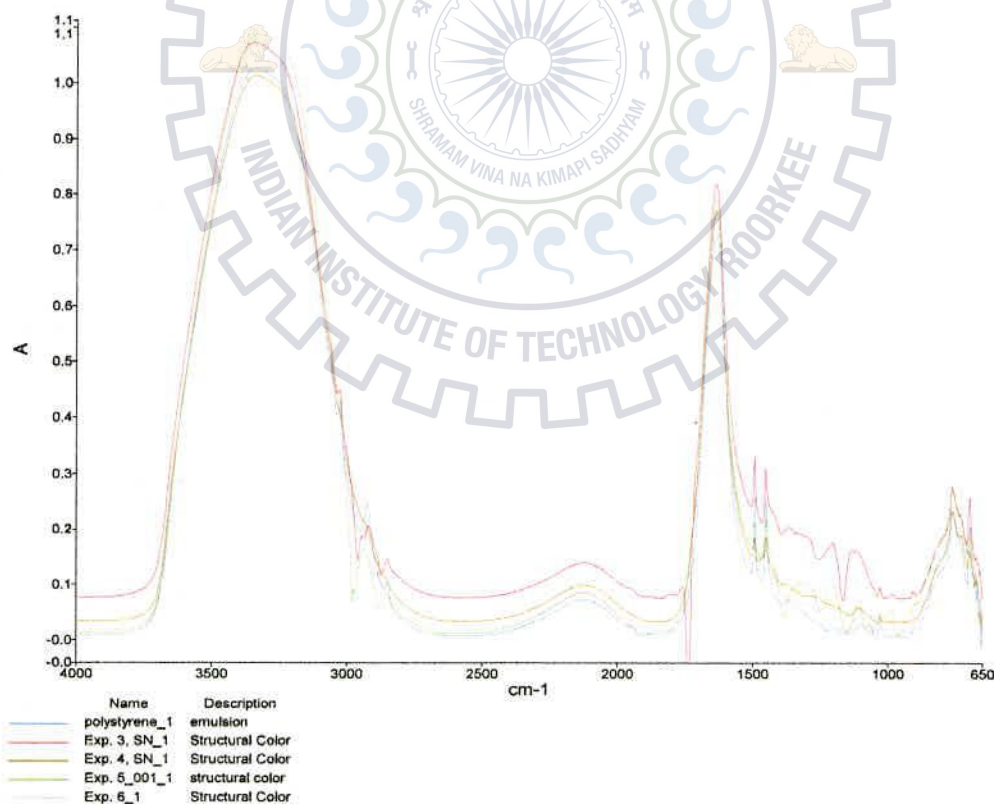
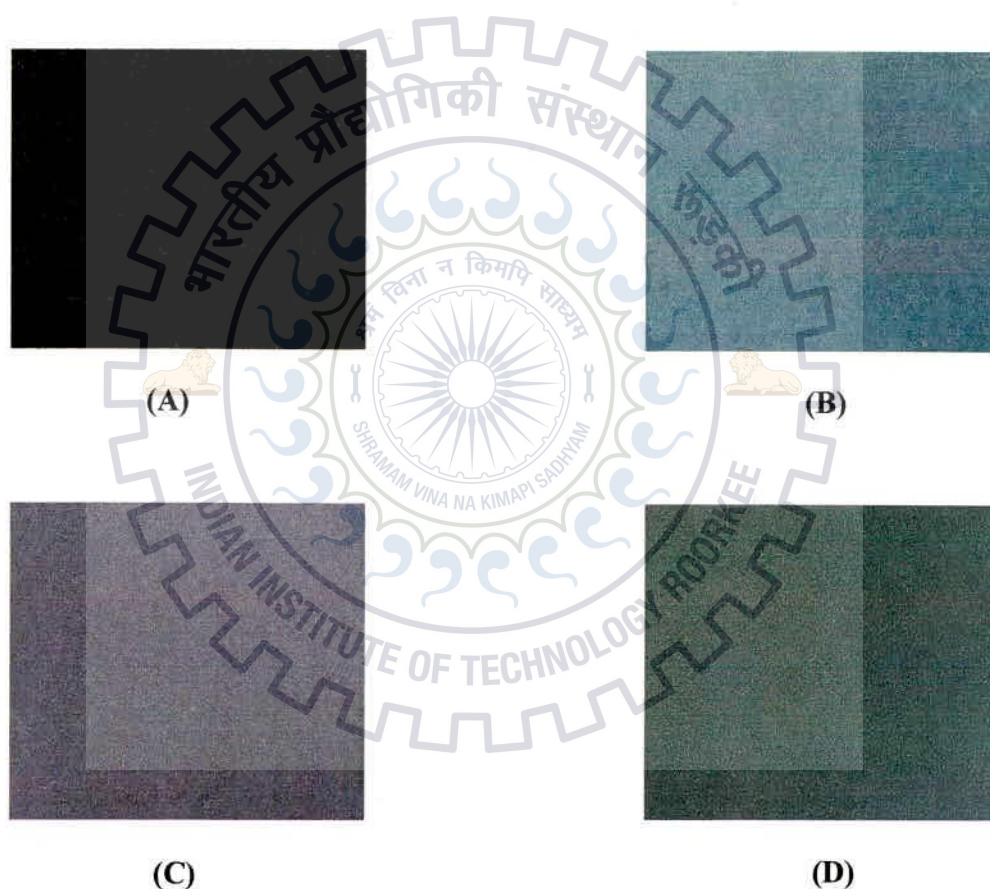


Figure 12: FT-IR absorbance spectra of Emulsions 1, 3-6

It can be analysed from the FT-IR spectra that the presence of peaks at 1452 cm^{-1} (aromatic alkene) and 2927 cm^{-1} (C-H stretch) confirms the presence of polystyrene. The presence of peaks at 3340 cm^{-1} (O-H group) and 1638 cm^{-1} (ester carbonyl) confirms the presence of MMA and AA. The absence of peak corresponding to $>\text{C}=\text{C}<$ indicates the absence of free monomer. The notation of Exp. 3, 4, 5, 6 in Figure 12 correspond to Emulsion 3, 4, 5, 6 respectively whereas polystyrene correspond to Emulsion 1.

The emulsions were sprayed onto the aluminium panels to check for color. The photographic images of the emulsions that were sprayed onto the panels were shown below in Figure 13.





(E)



(F)

Figure 13: Photographic images of the panels sprayed with emulsions (A) Reference – Metal panel (B) Emulsion 1 (C) Emulsion 3 (D) Emulsion 4 (E) Emulsion 5 (F) Emulsion 6

When the emulsions were sprayed on to the aluminium panel, colors were observed which were dependent on the particle size and the respective refractive index of the emulsions. With increase in particle size of emulsions, a considerable shift in color was observed from violet to green.

The colors obtained on the panels were identified with the help of UV-Vis-NIR spectroscopy. The results of the UV-Vis-NIR spectroscopy are shown below in Figure 14.

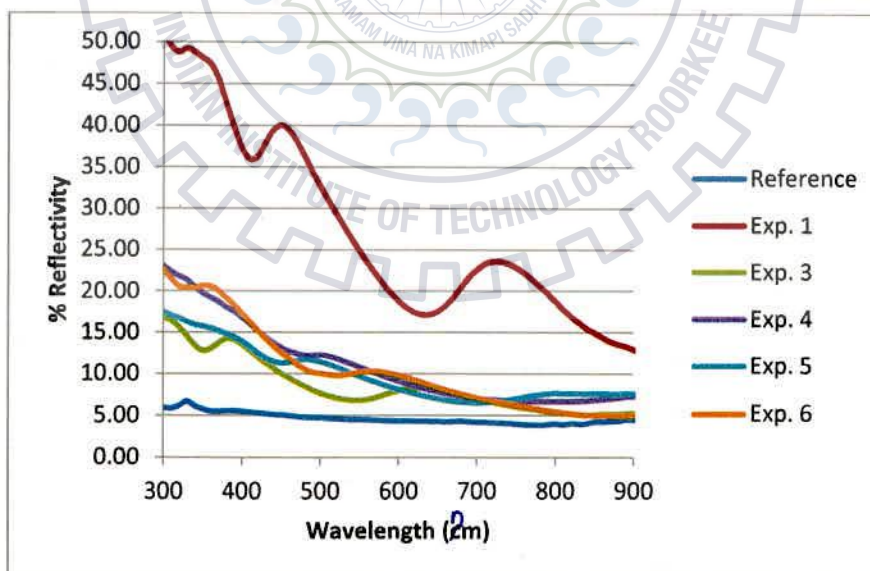
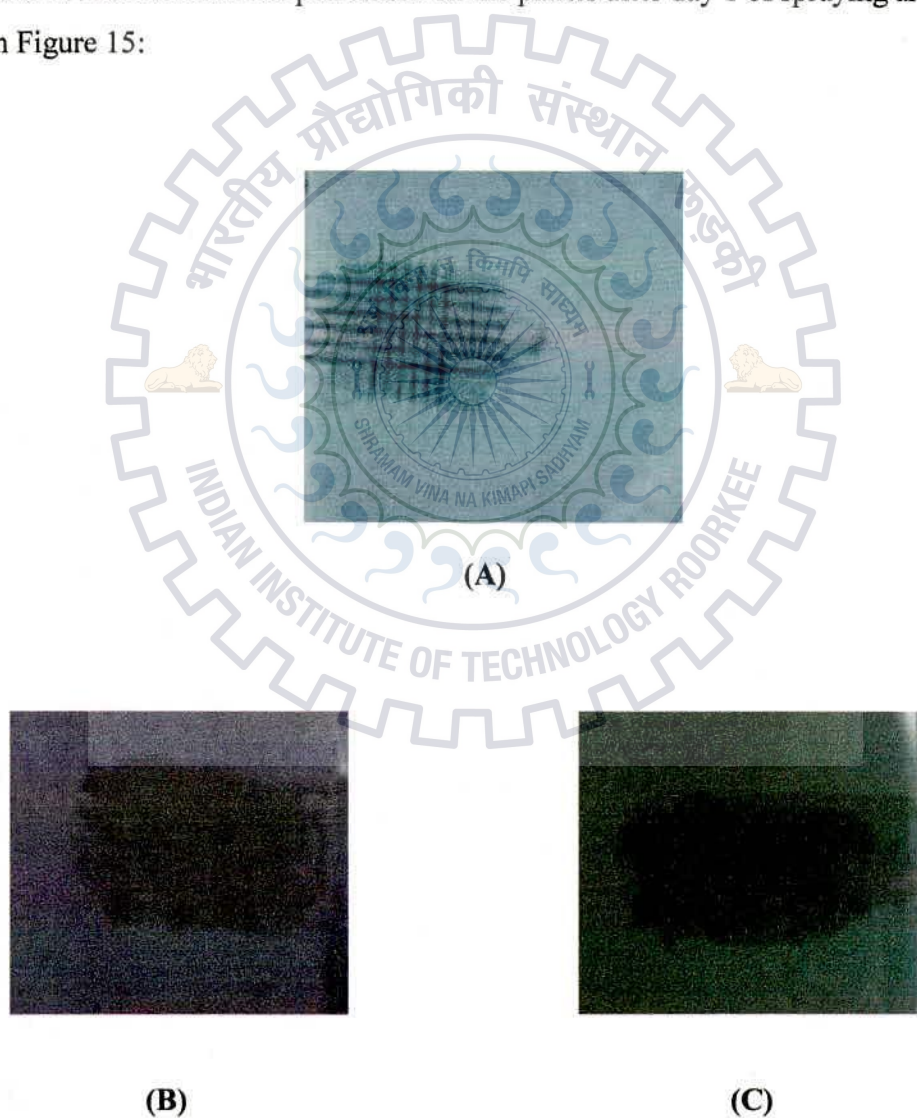


Figure 14: UV-Vis-NIR Spectra of films obtained from Emulsions 1, 3, 4, 5 & 6

From Figure 14, it can be observed that the peaks in the graph for data pertaining to Emulsion 3 correspond to the wavelength of 380 nm and 600 nm. The reflected light consisted of a major portion of violet and a minor portion of red color. It can be seen from data relating to

Emulsion 4 that the peak value corresponds to the wavelength of 490 nm which represents blue-green color. Similarly, the data corresponding to Emulsions 5 and 6 showed that the colors observed were green for Emulsion 5 and mixture of violet (maximum) and green (minimum) for Emulsion 6. From Figure 11, it can be observed that the % reflectance value is low which might be due to the low thickness of the film as well as due to absorption of light by the black panel. From the UV-Vis-NIR spectroscopy data of the reference black panel, it can be observed that most of the light is absorbed; hence the percentage of light reflected is very less. Overall the data obtained in UV-Vis-NIR spectroscopy is in close agreement with the colors obtained upon spraying the emulsions onto the substrate (Figure 13).

The results of the adhesion test performed on the panels after day 1 of spraying are shown below in Figure 15:





(D)



(E)

Figure 15: Results of the adhesion test performed on Day 1 (A) Emulsion 1 (B) Emulsion 3 (C) Emulsion 4 (D) Emulsion 5 (E) Emulsion 6

It can be seen from Figure 15 that fraction of nanoparticles were removed from the surface (which got adhered to the tape) while fraction of them were still anchored to the aluminium panel. The anchoring of the nanoparticles to the substrate indicates that a few fractions of particles have adherence to the substrate. As more water is removed from the substrate (hardening) the adhesion improves. Care should be taken to improve the curing time in order to get better results in adhesion test. However, the adhesion observed is still below the normal adhesion expected for any coatings. The partial adhesion characteristics in nanoparticles with core-shell morphology in Emulsions 3-6 were attributed to the presence of carboxylic groups in acrylic acid. Increasing the concentration of carboxylate moieties did not help in improving adhesion.

Alternatively, we made an attempt to increase the adhesion *via* increasing the curing time of emulsions after application on a substrate as showed below in Figure 16.



(A)



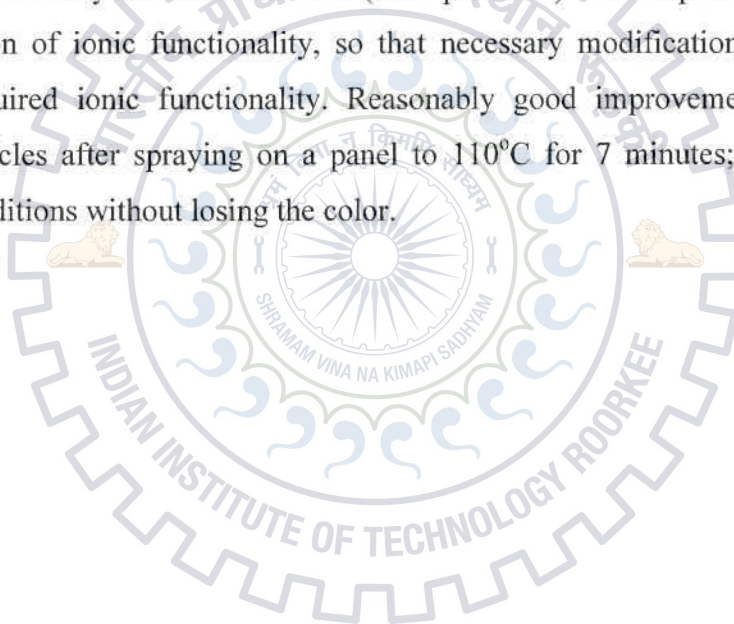
(B)

Figure 16: Adhesion test for Emulsion 3 (A) before & (B) after heating

The adhesion of nanoparticles towards the substrate improved upon heating, while retaining the color. However, if heated up to 110 ° C for more than 7 minutes, the color on the panels was lost. It indicated that there is a need to optimise the temperature and time of heating without losing color so that the nanoparticles get hardened against the substrate. The adhesion of the nanoparticles onto the substrate also improved on long standing time (approximately 1 week to 10 days) which can be attributed to the hardening of the nanoparticles against the substrate due to loss of water molecules without losing color.

2.4 Conclusion

The concept of structural color has been successfully proved using synthetic nanoparticles of polystyrene, poly(styrene-*co*-methyl methacrylate-*co*-acrylic acid). Carboxylate ionic groups acted as adhesion promoters and helped to improve the adhesion marginally. Surface concentration of carboxylate measurements (Zeta potential) will help us to understand the true concentration of ionic functionality, so that necessary modifications can be made to achieve the required ionic functionality. Reasonably good improvement achieved upon heating the particles after spraying on a panel to 110°C for 7 minutes; however, need to optimise the conditions without losing the color.



Chapter 3: Synthesis of poly (styrene-co-MMA-co-2-HEMA) nanoparticles

3.1 Introduction

Several materials have been explored to obtain nanoparticles that give rise to photonic colloidal crystals. The refractive index of the material and the size of the particles greatly affect the color of the colloidal crystals. The adhesion of the nanoparticles to the substrate mainly depends on the nature of surface chemical groups and contact surface area. Here we used a hydroxyl co-monomer like 2-hydroxy ethyl methacrylate (HEMA) in place of acrylic acid to improve the adhesion on metal substrate. We reasoned HEMA will act as a better adhering group than acrylic acid. The polymer nanoparticles based on poly(styrene-co-MMA-co-HEMA) were successfully synthesized and have been characterized further. The emulsion polymerisation adopted is the same mechanism as shown in Figure 10.

3.2 Synthesis of nanoparticles

3.2.1 Materials

All the materials were purchased and used as described in Section 2.2 of Chapter 2 except AA is replaced with HEMA. We reasoned to have better adhesion with HEMA than AA. HEMA was obtained from AkzoNobel, Bangalore. The monomers styrene, methyl methacrylate and HEMA were purified using neutral active alumina.

3.2.2 Synthesis procedure

A typical polymerisation procedure used for synthesis of Emulsion 7 is described here. The three necked 500 ml round bottomed glass vessel was charged with 200 ml of deionised water containing 1 g of ammonium bicarbonate. A nitrogen blanket and a stirring rate of 350 rpm were maintained throughout the reaction. The water solution was deoxygenated by bubbling with nitrogen for 40 minutes. After thorough de-oxygenation, 0.008 g of sodium dodecyl benzene sulfonate dissolved in 5 ml water was added and the temperature was increased to 50°C. Previously de-inhibited and deoxygenated methyl methacrylate, acrylic acid/HEMA and styrene were mixed together and added to the reaction vessel in a drop wise manner. The reaction mixture was kept at 70°C for 0.5 h followed by the addition of an aqueous solution of 0.96 g of ammonium persulfate. The polymerization was then carried out at 80°C for 10 h with continuous stirring. The emulsions were collected after the polymerisation and stored for 24 h to observe any settling of particles. However, no settling of particles was observed. The emulsions were centrifuged at 12,000 rpm for 15 minutes and

supernatant was collected and stored for further color applications. Similar protocol has been used for Emulsions obtained from 8, 9 and the detailed ingredients are tabulated in Table 2.

3.2.3 Characterization

The procedure for particle size analysis, refractive index measurements, FT-IR, color testing, adhesion test and UV-Vis-NIR spectroscopy were followed as per the protocol mentioned in Section 2.2 of Chapter 2.

3.3 Results and discussion

The polymeric nanoparticles synthesized in the present work were presumed to have core-shell morphology as shown in Figure 17. The hydrophobic styrene was expected to form the core due to hydrophilic nature of dispersing medium (water). The covalently attached poly(methyl methacrylate-*co*-2-hydroxy ethyl methacrylate) form the shell. Perhaps, some of the sulphate radicals of the initiator oxidised some of the hydroxyl groups of HEMA to carboxylic groups.

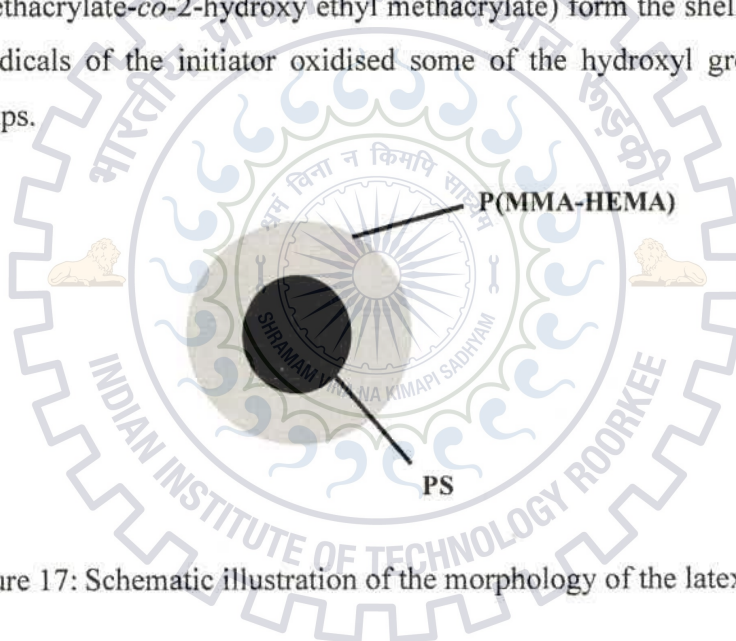


Figure 17: Schematic illustration of the morphology of the latex sphere

The results of the particle size analysis and refractive index measurements along with the resultant color are shown in the following Table 2.

Table 2: Particle Size and Refractive Index measurements

Emulsion	Concentration St/MMA/AA/HEMA (g)	Particle Diameter (nm)	d ₅₀ (nm)	Refractive Index	Color
1	38/0/0/0	232-399	294	1.3634	GREEN
7	38/2/0/2	245-339	275	1.3655	VIOLET
8	38/2/0/4	161-835	425	1.3508	GREEN
9	38/2/1/1	268-440	332	1.3629	WHITE

Increase in particle size was observed with increase in concentration of HEMA which is due to the high viscosity of HEMA. Due to the limited methods available to measure the refractive index of solids, the refractive index of polymeric nanoparticles in powder form couldn't be measured. The effect of concentration of styrene, MMA, AA, HEMA could be clearly seen in the values of refractive index tabulated in Table 2.

The emulsions were checked for the presence of free monomer using FT-IR Spectroscopy. The results of the FT-IR spectra of the emulsions are shown below in Figure 18.

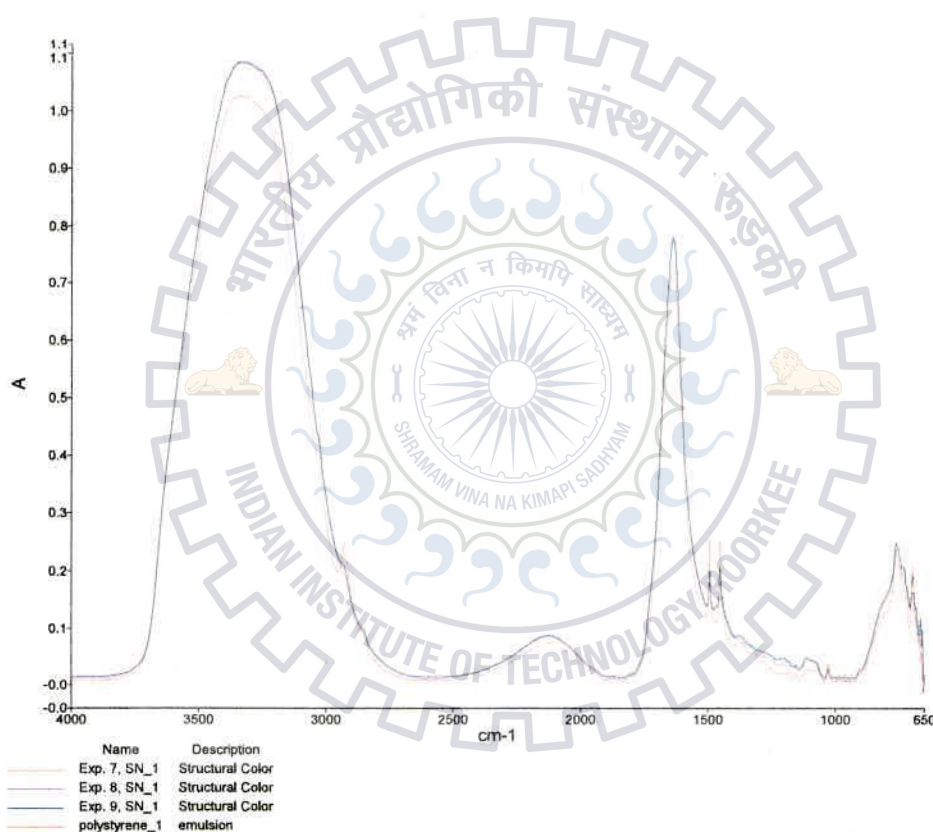


Figure 18: FT-IR absorbance spectra of emulsion from Emulsion 1, 7-9

It can be analysed from the FT-IR spectra that the presence of peaks at 1452 cm^{-1} (aromatic alkene) and 2927 cm^{-1} (C-H stretch) confirms the presence of polystyrene. The presence of peaks at 3340 cm^{-1} (O-H group) and 1638 cm^{-1} (ester carbonyl) confirms the presence of MMA and HEMA. The absence of peak corresponding to $>\text{C}=\text{C}<$ indicates the absence of free monomer. The notation of Exp. 7, 8, 9 in Figure 12 correspond to Emulsion 7, 8, 9 respectively whereas polystyrene correspond to Emulsion 1.

The emulsions were sprayed onto the metal panels to check for color. Emulsions 7 and 8 gave corresponding colors on spraying. The colors observed depended on the particle size distribution and refractive index of the emulsions. With increase in particle size, color shifted from violet to green. The photographic images of the emulsions that were sprayed onto the panels were shown below in Figure 19.

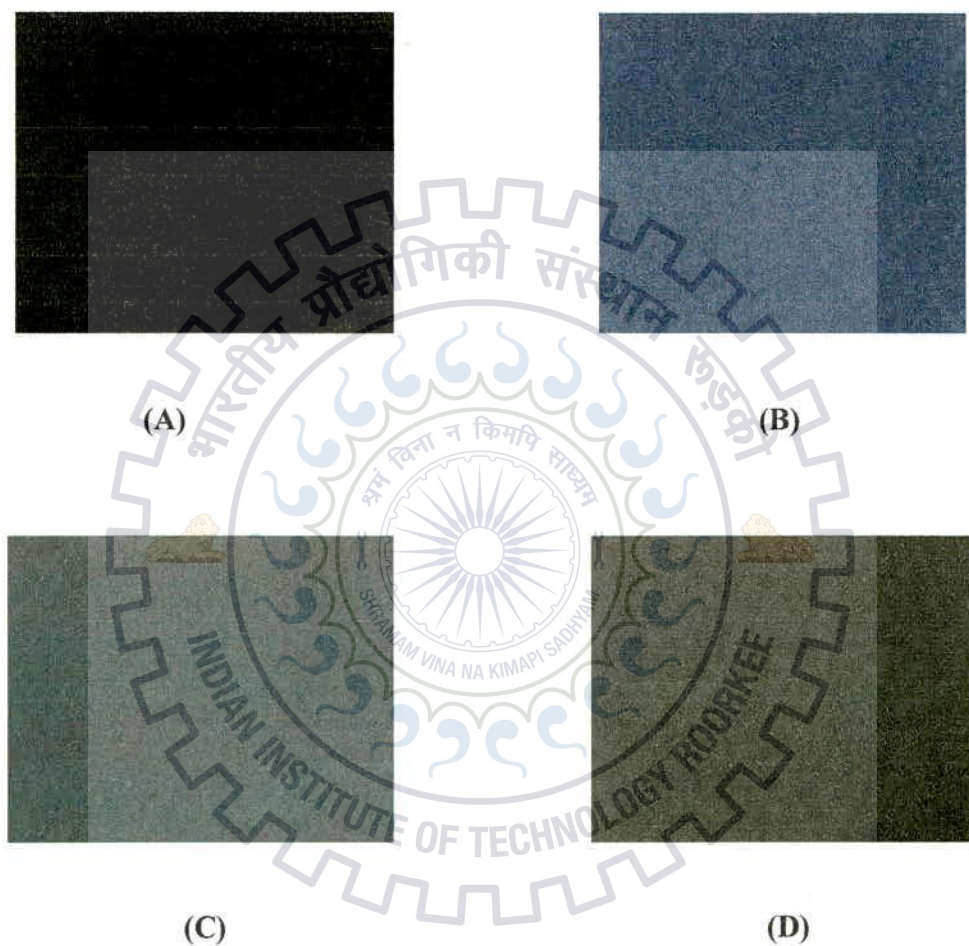


Figure 19: Photographic images of the panels sprayed with emulsions (A) Reference – Metal panel (B) Emulsion 7 (C) Emulsion 8 (D) Emulsion 9

The color obtained on the panels was identified with the help of UV-Vis-NIR spectroscopy. The results of the UV-Vis-NIR Spectroscopy are shown below in Figure 20.

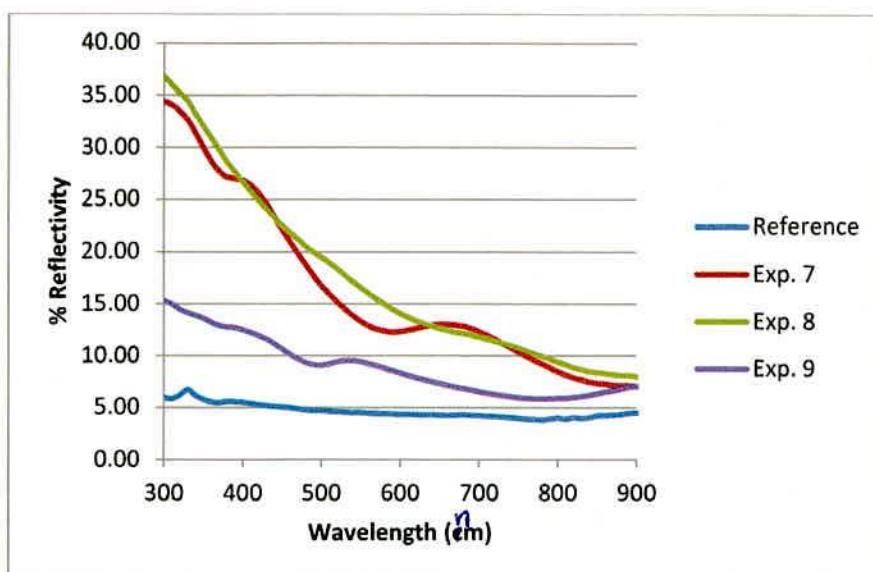


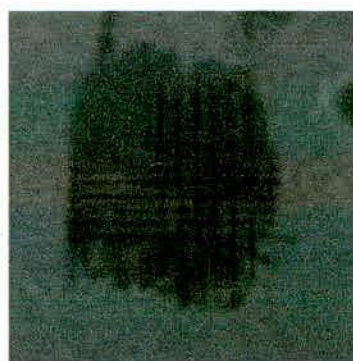
Figure 20: UV-Vis-NIR Spectroscopy images of films of Emulsion 7, 8, 9 sprayed onto black panel

It can be observed from Figure 20 that the wavelength corresponding to the peak was 400 nm and 640 nm which mean that the panels which were sprayed with Emulsion 7 reflected majority of violet color and a minority of red color. For data pertaining to Emulsion 8, no peaks were observed which might be due to the diffraction from particles of various sizes as particle size distribution was wide which can be seen form Table 2. Similarly, the UV-Vis spectra of the Emulsion 9 showed that the reflectance was maximum for peaks corresponding to 400 nm and 520 nm. However, the corresponding reflectance value was very low which means that the observed color doesn't correspond to particular color in the visible spectrum. The data obtained in UV-Vis-NIR spectroscopy is in good agreement with the colors obtained upon spraying the emulsions onto the substrate which can be seen in Figure 19.

The results of the adhesion test performed on the panels after day 1 of spraying are shown below in Figure 21:



(A)



(B)

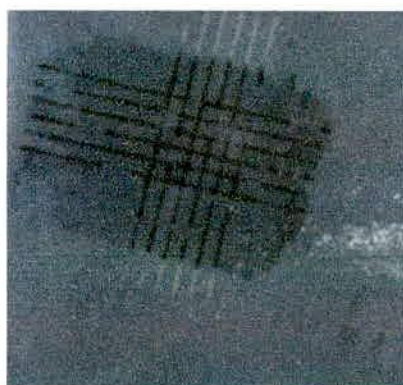


(C)

Figure 21: Results of the adhesion test performed on Day 1 (A) Emulsion 7 (B) Emulsion 8 (C) Emulsion 9

It can be seen from Figure 21 that fraction of the nanoparticles were removed from the surface (which got adhered to the tape) while fraction of them were still anchored to the metal panel. The anchoring of the nanoparticles to the substrate indicates that the respective particles have adherence to the substrate. Care should be taken to improve the curing time in order to get better results in adhesion test.

Alternatively, we made an attempt to increase the adhesion *via* increasing the curing time of emulsions after application on a substrate as showed below in Figure 22. It can be observed from Figure 22 that the adherence of the nanoparticles to the substrate improved on heating which is reflected in the adhesion test as most of the nanoparticles got adhered to the substrate during the test. The color of the panels retained upon heating. However, if heated for more than 7 minutes, the color on the panels was lost. It indicated that temperature and time of heating should be optimised for the nanoparticles to get hardened against the substrate without losing the color.



(A)



(B)

Figure 22: Results of the adhesion test performed on Day 1 for Emulsion 7 (A) Before heating (B) After heating

The adhesion characteristics in nanoparticles with core-shell morphology were attributed to the presence of hydroxyl groups in HEMA. It has been found from literature that some of the sulphate groups get anchored to the surface of the nanoparticles and contribute to the negative charge of the respective nanoparticles. No reason has been found yet for the migration of sulphate radicals onto nanoparticles. More concrete conclusions can be drawn once zeta potential measurements are available. The adhesion of the nanoparticles onto the substrate improved on long standing which can be attributed to the hardening of the nanoparticles against the substrate due to loss of water molecules.

3.4 Conclusion

Poly(styrene-co-MMA-co-HEMA) nanoparticles produced structural color. The adhesion characteristics of nanoparticles which had HEMA didn't differ much when compared to acrylic acid based nanoparticles. Methods to improve adhesion involved heating the emulsion coated panels at high temperatures for a short time or else curing the panels by placing them at room temperatures for 1-2 weeks. At this point we are even unsure if the surfactant had shielded the anionic carboxylic groups from exhibiting the adhesion characteristics. As the anionic latexes had adhesion issues with post coated panels, electronic deficient latexes were synthesised to check if it helps in adhesion promotion, will be discussed in the following chapter.

Chapter 4: Synthesis of poly(styrene-co-MMA-co-EDM) nanoparticles

4.1 Introduction

Anionic emulsions (containing acrylic acid in Chapter 2) have been most widely used to produce structural color. However, as anionic latexes didn't produce satisfactory results, we shifted our focus to synthesize latexes containing electron deficient monomer using surfactant free emulsion polymerization for structural color applications.

Surfactant free emulsion polymerization stands out among other techniques because the particles prepared have lower size distribution and easy to purify the nanoparticles compared to other methods. Mainly three kinds of mechanisms, i.e. homogeneous nucleation, oligomer micellization and a coagulation mechanism, have been proposed to explain the formation of stable polymer particles without emulsifier. Normally one of the following reactant components is used in a reaction for the system to obtain colloidal stability.

- a. Ionizable initiators such 2, 2'-azobis (2-amidinopropane) dihydrochloride
- b. Hydrophilic co-monomer
- c. Electron deficient co-monomer

In practice, particle size can be easily controlled by the concentration of the initiator, ionic strength and the concentration of the ionizable co-monomer. Synthesis of surfactant free emulsion co-polymerisation of styrene with electron deficient monomer in the presence of ethanol as a co-solvent was reported by Liu et al.¹⁹ Preparation of electron deficient functional polymer latexes and measurement of non-volatile monomer conversion was studied by Yang et al.²⁰

Materials having electron deficient substances are well known to have good adhesion on substrates. However, the proposed EDM cannot be polymerized using anionic surfactants. Synthesis of such latexes has been well established in the literature. However, no published articles were found from literature on structural color using electron deficient emulsions. We have started synthesizing styrene-EDM latexes as per the literature²¹ and then modified it further by adding MMA as another co-monomer. Herein, we have showed a feasible method to produce structural color using latexes containing electron deficient materials. Adhesion of electron deficient groups towards the substrate has been tested. The electron deficient group acts as an adhesion promoter here.

As per the literature, it was presumed that the nanoparticles will have core-shell morphology²¹. The polymeric nanoparticles were successfully synthesized and have been characterized further. The emulsion polymerisation adopted the same mechanism as shown in the following Figure 23. The polymerisation takes place in three stages. In stage (A), the reaction vessel contains uniform solution of EDM and water. The monomer styrene added to the reaction vessel in stage (A) in a drop wise manner forms monomer droplets in stage (B) and EDM will slowly migrate towards styrene. As the initiator was added to the vessel, polymerisation of styrene and EDM will take place to form the core-shell nanoparticles.

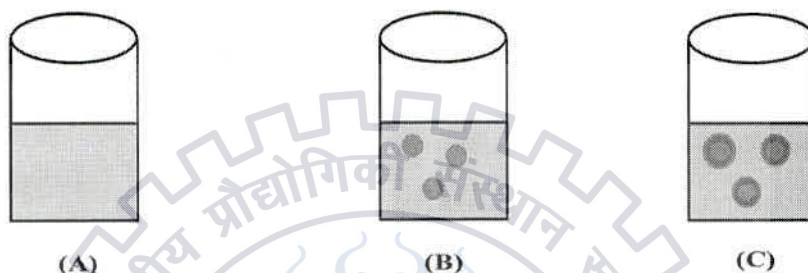


Figure 23: Mechanism of surfactant free emulsion polymerisation

4.2 Synthesis of nanoparticles

4.2.1 Materials

Styrene and EDM have been used for synthesis of nanoparticles. EDM has been used as it results in adhesion. Styrene forms the core and provides the strength to the particle. EDM was procured from Sigma Aldrich and used as received. Water soluble initiator was received from Aldrich and used as received.

4.2.2 Synthesis procedure

The typical polymerisation procedure used for synthesis of Emulsion 10 has been discussed here. The three necked 500 mL round bottomed glass vessel was charged with 200ml of deionised water containing 4 g of EDM. A nitrogen blanket and a stirring rate of 350 rpm of the propeller were maintained throughout the reaction. The water solution was deoxygenated by bubbling with nitrogen for 40 min. After de-oxygenation, the temperature was increased to 50°C. Previously de-inhibited and de-oxygenated styrene was added to the reaction vessel in a drop wise manner. The reaction mixture was kept at 70°C for 0.5 h followed by the addition of an aqueous solution of 0.96 g of ABMP. The polymerization was then carried out at 80°C for 5-6 h with continuous stirring. The emulsions were collected after the polymerisation and stored for 24 h to observe any settling of particles. However, no settling of particles was

observed. The emulsions were used for further color applications. Similar protocol has been used for Emulsions 11, 12 and the detailed ingredients are tabulated in Table 3.

4.2.3 Characterization

The procedure for particle size analysis, refractive index measurements, FT-IR, color testing, adhesion test, UV-Vis-NIR spectroscopy were followed as per the protocol mentioned in Section 2.2 of Chapter 2.

4.3 Results and discussion

The polymeric nanoparticles synthesized were presumed to have core-shell morphology as shown in Figure 24 based on the prior art as observed in the literature²¹. As the dispersing medium is hydrophilic, the hydrophobic styrene was expected to form the core and covalently attached by poly(methyl methacrylate-co-EDM) to form the shell.

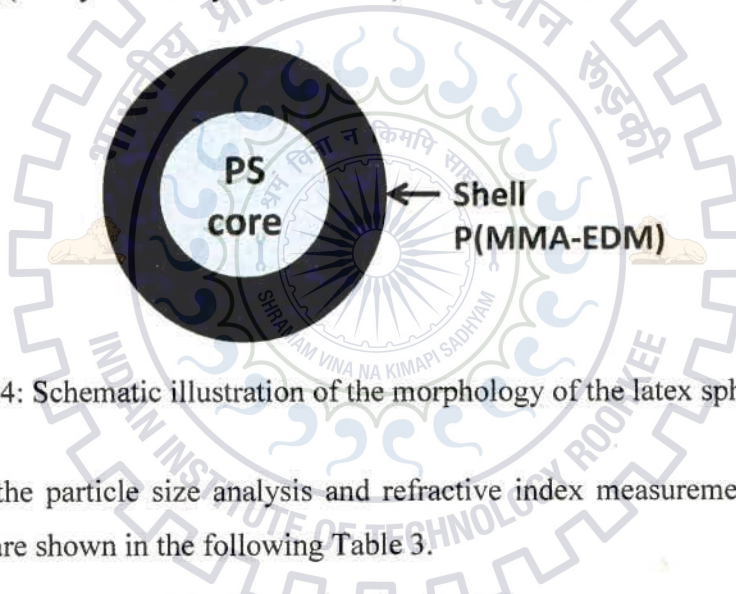


Figure 24: Schematic illustration of the morphology of the latex sphere

The results of the particle size analysis and refractive index measurements along with the resultant color are shown in the following Table 3.

Table 3: Particle Size and Refractive Index measurements

Emulsion	Concentration St/MMA/EDM (g)	Particle Diameter (nm)	d_{50} (nm)	Refractive Index	Color
10	38/0/4	57-192	89	1.3759	BLUE
11	38/2/2	23-117	39	1.3659	BLUE
12	38/2/4	78-391	101	1.3671	BLUE

The particle size of the nanoparticles synthesised was around 50-120 nm.

Due to the limited methods available to measure the refractive index of solids, the refractive index of polymeric nanoparticles in powder form couldn't be measured. The effect of

concentration of styrene, MMA and EDM could be clearly seen in the values of refractive index as depicted in Table 3. As the concentration of EDM was increased, refractive index of the emulsions also increased.

The emulsions were checked for the presence of free monomer using FT-IR Spectroscopy. The results of the FT-IR spectra of the emulsions are shown below in Figure 25.



Figure 25: FT-IR absorbance spectra of Emulsions 10, 11, 12

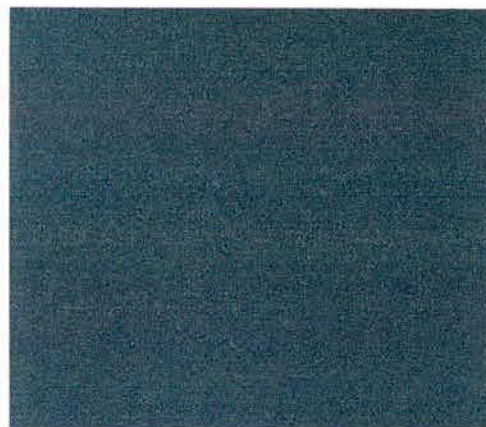
It can be analysed from the FT-IR spectra that the presence of peaks at 1452 cm^{-1} (aromatic alkene) and 2927 cm^{-1} (C-H stretch) confirms the presence of polystyrene. The presence of peaks at 1492 cm^{-1} (C-N stretch) and 1638 cm^{-1} (ester carbonyl) confirms the presence of EDM. The absence of peak corresponding to $>\text{C}=\text{C}<$ indicates the absence of free monomer. The notation of Exp. 10, 11, 12 in Figure 12 correspond to Emulsion 10, 11, 12 respectively.

Emulsions 10 and 11 gave color upon spraying on aluminium panel. The color observed depended on the particle size distribution and refractive index of the emulsions. Although the size of the particles was small, blue color was observed which perhaps might be due to the higher refractive index of the nanoparticles.

The photographic images of the emulsions that were sprayed onto the panels were shown below in Figure 26.



(A)



(B)



(C)



(D)

Figure 26: Photographic images of the panels sprayed with emulsions (A) Reference – Metal panel (B) Emulsion 10 (C) Emulsion 11 (D) Emulsion 12

The color obtained on the panels was identified with the help of UV-Vis-NIR spectroscopy. The results of the UV-Vis-NIR Spectroscopy are shown below in Figure 27.

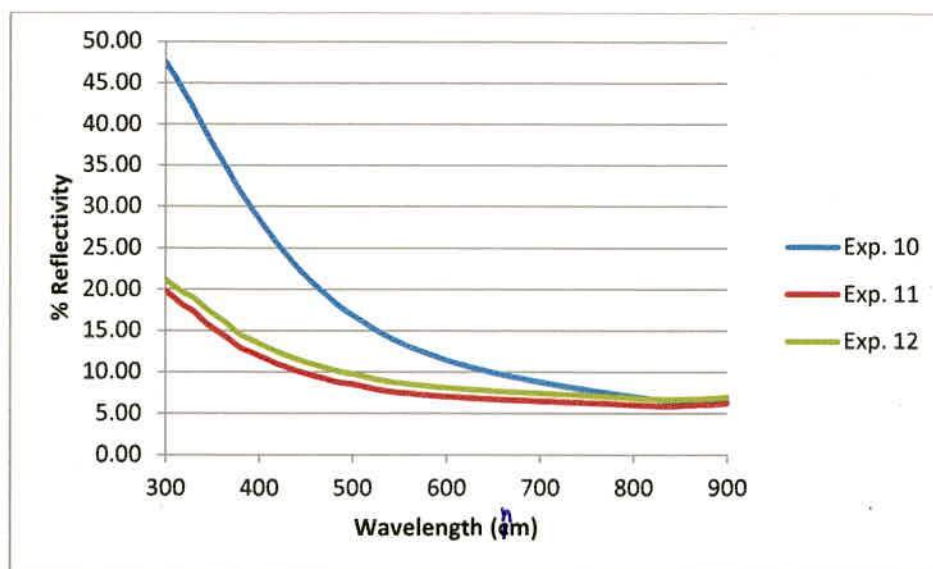


Figure 27: UV-Vis-NIR spectra of films obtained from Emulsions 10, 11, 12

From Figure 27, it can be seen that reflectivity of the films decreased with increase in the wavelength of the incident light. However, there was not much concordance between the colors observed in Figure 26 and the corresponding UV-Vis-NIR spectra. Optimisation of the film thickness for UV-Vis-NIR spectra should be done in order to obtain better results.

The results of the adhesion test performed on the panels after day 1 of spraying are shown below in Figure 28.

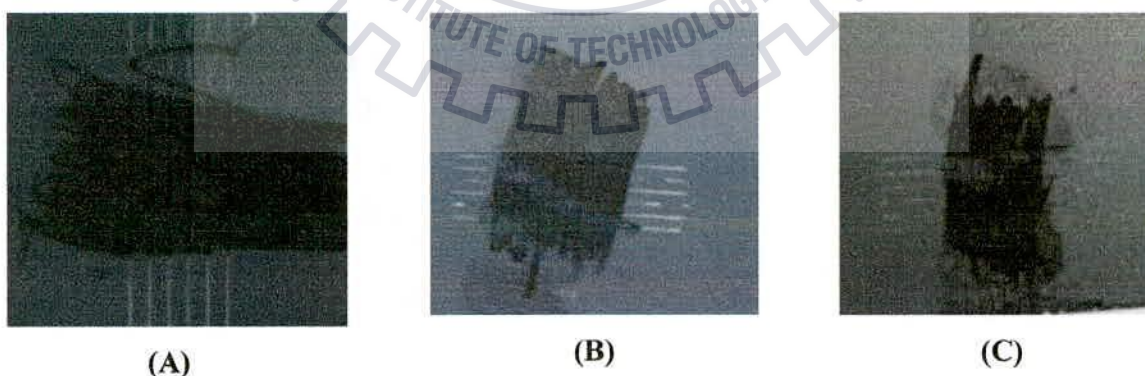


Figure 28: Results of the adhesion test performed on Day 1 for (A) Emulsion 10 (B) Emulsion 11 (C) Emulsion 12

It can be seen from Figure 28 that fraction of the nanoparticles were removed from the surface (which got adhered to the tape) while fraction of them were still anchored to the metal

panel. The anchoring of the nanoparticles to the substrate indicates that the respective particles have adherence to the substrate. Care should be taken to improve the curing time in order to get better results in adhesion test. However, concrete results couldn't be drawn based on the results of the adhesion test involving AA, HEMA and EDM.

Alternatively, we made an attempt to increase the adhesion *via* increasing the curing time of emulsions after application on a substrate as showed below in Figure 29.



Figure 29: Results of the adhesion test performed on Day 1 for Emulsion 10 (A) Before heating (B) After heating

The adhesion characteristics in nanoparticles with core-shell morphology were attributed to the presence of electron deficient groups in EDM. More concrete conclusions can be drawn once zeta potential measurements are available. The adhesion of the nanoparticles onto the substrate improved on long standing which can be attributed to the hardening of the nanoparticles against the substrate due to loss of water molecules. From Figure 29, it can be observed that the adherence of the nanoparticles to the substrate improved on heating which is reflected in the adhesion test as most of the nanoparticles got adhered to the substrate during the test. The color of the panels retained upon heating. However, if heated for more than 7 minutes, the color on the panels was lost. It indicated that sufficient time should be provided for the nanoparticles to get hardened against the substrate.

4.4 Conclusion

Synthetic electron deficient nanoparticles exhibited structural color. Electron deficient nanoparticles imparted good adhesion towards the substrate compared to acrylic acid and HEMA based nanoparticles. The adhesion even improved upon heating the substrate.

Chapter 5: Summary and future work

We have successfully mimicked and standardised the concept of structural color by synthetic 3D photonic nanoparticles. Various colors in the visible region were obtained which depended on the particle size, refractive index of the nanoparticles. So far, anionic and electron deficient nanoparticles have been synthesized in order to show the idea of structural color. The emulsions and the corresponding films have been successfully characterized using particle Size Analyzer, FT-IR, Automatic Cross Hatch Cutter, UV-Vis-NIR spectroscopy.

Various methods were tried in order to enhance the adhesion of nanoparticles towards the substrate. Some of the methods adopted and the results are listed below:

- Emulsions 1 and 3 were sprayed onto the substrate and left undisturbed at room temperature for 2 weeks. This resulted in improvement on adhesion of nanoparticles against the substrate.
- Emulsions were sprayed onto metal substrate which is heated to 80°C and then again kept at 80°C in oven for one day – The nanoparticles got slowly hardened against the substrate with time without losing the color.
- Emulsion 3 was mixed with binder and then sprayed – the integrity of the particles was lost and no color was observed upon spraying.
- Emulsion 3 was sprayed onto the substrate after the application of binder – the prior application of binder to the substrate before spraying the emulsions didn't have much immediate effect on adhesion.
- Emulsion 3 was sprayed onto the substrate after the application of Silane A-187 adhesive – wettability of the substrate wasn't good by emulsion.
- Emulsion 3 was sprayed onto the substrate after the application of Silane A-187 adhesive and wetting additive BY-306 – color was observed upon application of high pressure and reduction of distance between spray gun and substrate.
- Emulsions were sprayed onto metal substrate and then again kept at 100°C oven – the color was lost if the panel was kept in the oven for 10 min.
- Emulsions were sprayed onto aluminium substrate and then again kept at 100°C oven – the nanoparticles got hardened against the substrate if the panel was kept in the oven

for 3-4 min.

The results of the adhesion test have already been discussed earlier in chapter 2, 3 and 4. Apart from them, the panels which were sprayed with emulsions have been tested for rub resistance and the results are shown below.

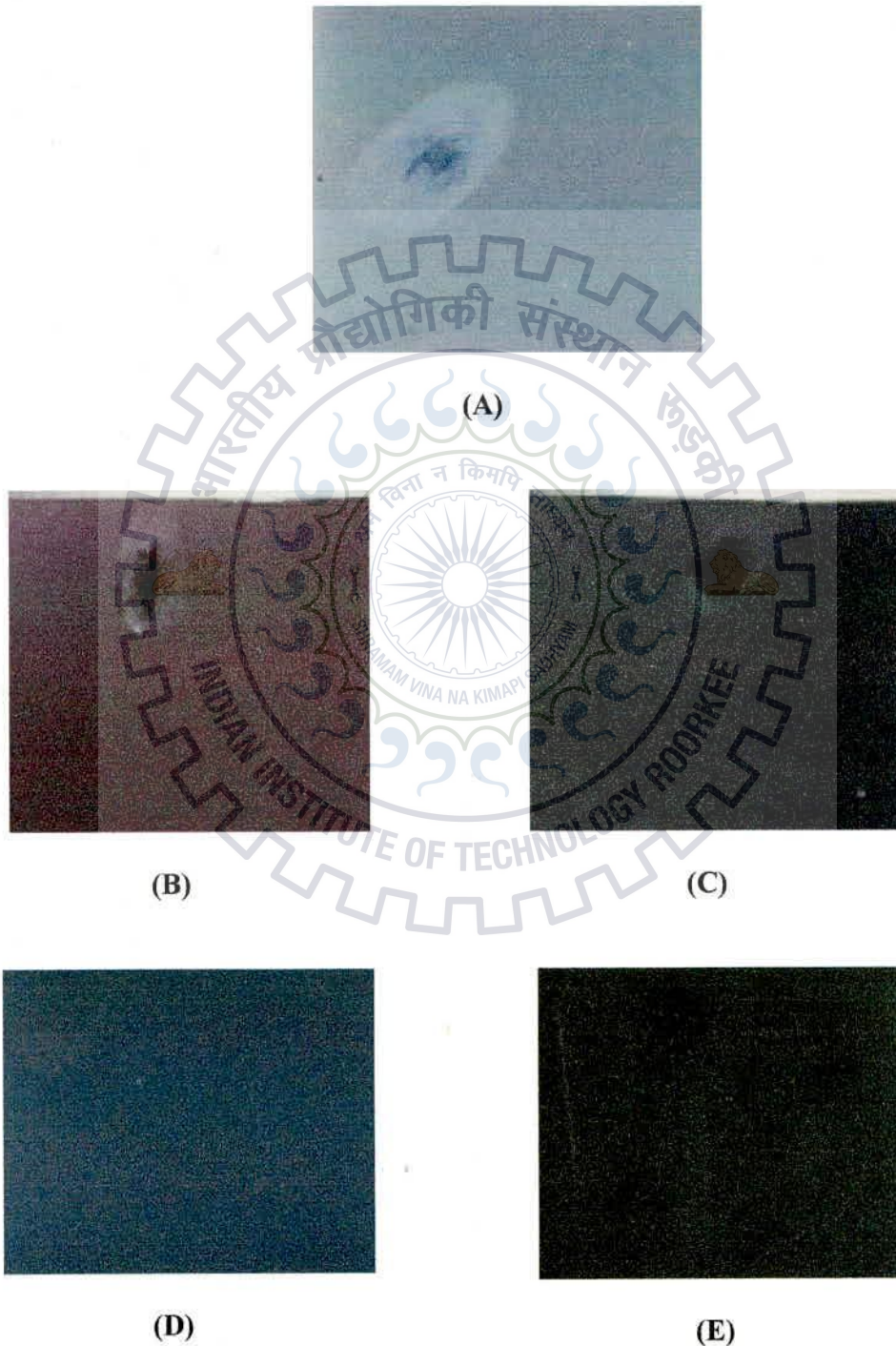
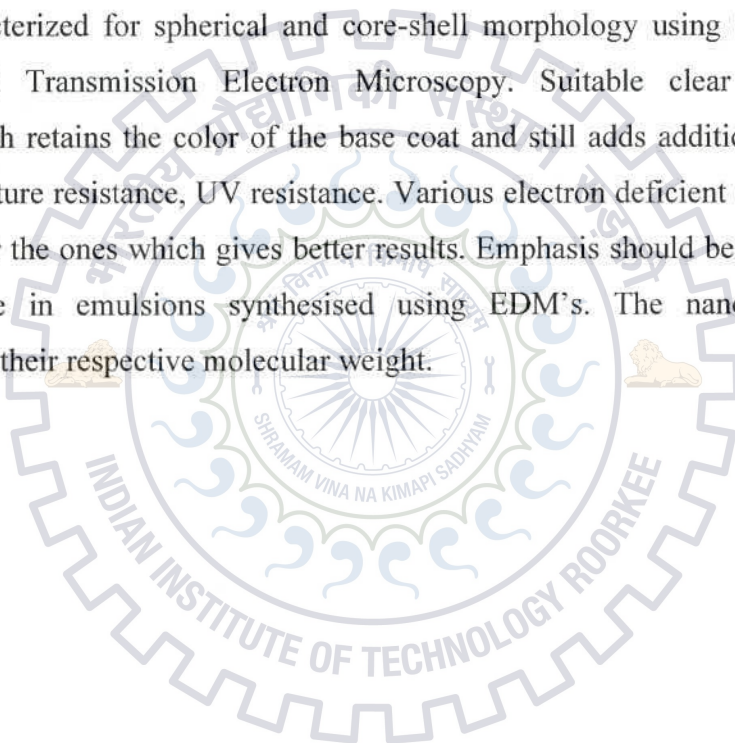


Figure 30: Photographic images of the panels that were rubbed gently with hand (A) Emulsion 1 (B) Emulsion 3 (C) Emulsion 7 (D) Emulsion 10 (E) Emulsion 11

It can be noticed from the above Figure 30 that the nanoparticles of Emulsion 10 exhibited good adhesion towards the substrate when compared to others as the nanoparticles, when removed from the substrate under mild pressure as well as rubbing. Above all, it should be kept in mind that sufficient hardening time should be provided so that moisture will be lost and particles get hardened against the substrate which helps in adhesion.

The above mentioned preliminary Emulsions in Chapter 5 showed that there is a need to optimise temperature and time of heating keeping the degradation temperature and glass transition temperature of nanoparticles in mind so that the nanoparticles get hardened against the substrate. Unimodal narrow size distribution nanoparticles helps in obtaining color of particular wavelength. Focus should be laid in obtaining such particles. The nanoparticles should be characterized for spherical and core-shell morphology using Scanning Electron Microscopy and Transmission Electron Microscopy. Suitable clear coat should be synthesized which retains the color of the base coat and still adds additional value such as good gloss, moisture resistance, UV resistance. Various electron deficient compounds can be tried to check for the ones which gives better results. Emphasis should be laid on increasing the particle size in emulsions synthesised using EDM's. The nanoparticles can be characterized for their respective molecular weight.



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