Studies on characteristic structural colour and wettability properties of certain natural systems

Abstract

Over the years, the concept of structural colour has gained enormous attention among the researchers because of its close connection with the field of soft matter and photonics. Basically, there are two types of colour: pigmentary and structural colour. Pigmentary colour is a consequence of intense light absorption by the inorganic/organic species present in the material system. In contrast, structural colour, as the name suggests, results due to the interaction of light with microstructural geometry and is chiefly of physical origin, unlike pigmentary ones. The structural colouration, to a great extent, depends on surface microstructure, where the incident light gets reflected, scattered and deflected prohibiting certain wavelengths of light. The physical mechanisms responsible for the structural colouration are: (i) thin-film interference (ii) multilayer interference (iii) diffraction grating (iv) surface and sub-surface volume scattering, and (v) photonic crystals. Iridescence is another important phenomenon, which is responsible for structural colouration. The variation of colour with varying incident/viewing angles is known as iridescence. Nature provides innumerable examples which portray structural colouration, which includes butterflies, plants, bird feathers, insect covers and also aquatic species. The best known example of blue iridescence structural colouration is *Morpho* butterflies, which have been widely studied by several research groups. Butterfly wings constitute a complex architecture with longitudinal ridges (LR), cross ribs (CR), trabeculae, flutes, scutes which play an important role in apparent colouration. In plant kingdom, the structural colour is mainly associated with flowers, fruits and leaves. Light to bright structural colour in flowers act as cue to attract bees and bumble bees. The origin of structural colour, in fact, varies from flowers to fruits and from fruits to leaves across families and order. As an important component of biophotonics structural colour comes with a great deal of diversity in these naturally rewarding systems, which offer as valuable assets/test-beds in experimental research. The

structural colours found in natural systems are beneficial in mimicking as well as in translating certain ideas in advanced technical applications. Understanding these structures has paved the way for the fabrication of artificial designs, in which one could expect structure driven precise optical phenomena. Apart from fundamental interest, some of the frontier applications that can be taken into account are: camouflage for security purposes, sensors, displays, light emitting sources etc.

Surface wettability is another important feature that has attracted the attention of researchers due to its several potential implications in daily life as well as for industrial reasons [13]. The dewetting nature of hydrophobic/superhydrophobic surfaces has been studied for over a century. When it comes to natural system, this explicitly interesting characteristic has been noteworthy as it allows mimicking while fabricating surfaces with water-repelling properties. In order to reveal surface-wettability, one considers hydrophobic (CA>90°) and superhydrophobic (CA>150°) surfaces. For a surface to exhibit water repelling properties, surface morphology and chemical composition play dominant roles, and consequently microstructure/nanostructure makeups have an influence at large. Two basic models to explain wettability are: Wenzel and Cassie-Baxter. Wenzel model describes about representation of filling/penetration of the grooves/roughness of the surface by the water droplet. In this case, the water contact angle is expressed as $\cos\theta_w = r_\varphi \cos\theta_y$ where, θ_y and θ_w are the CA for a smooth surface and the observed CA for the rough surface under study. Here, r_φ is the roughness factor. Cassie-Baxter model is the modified version of the Wenzel model, where the water droplet stands on the surface, with air entrapped within the grooves, thus increasing the CA. The Cassie-Baxter model can be expressed as $\cos\theta_{CB} = \varphi(\cos\theta_y + 1)-1$, where, θ_{CB} is the observed contact angle and φ is the water-solid fraction. Apart from these two models, there is another one, where a liquid droplet lies in an intermediate state, known as Cassie-impregnating regime.

In nature, there are examples ranging from plants and animals to avian systems as well as insects, flies. Amongst these, plants are well known and also the best examples of self-cleaning, superhydrophobic surfaces. Moreover, there exist pseudo-superhydrophobic organisms. Ever since, Barthlott and Neinhuis have explored the lotus effect, it has stimulated interdisciplinary research, which infact, interrelates soft matter, chemical, biological perspectives. To understand the wettability properties, it is important to have knowledge on contact angle hysteresis (CAH). When a liquid droplet makes contact with the solid surface, instead of a single equilibrium position, it will have several equilibrium positions referred to as maximum and minimum positions, also known as advancing (θ_{adv}) and receding angle (θ_{rec}). The difference between advancing and receding angle is referred as CAH. In plants, the superhydrophobicity is attributed to the presence of hierarchical roughness, which has been observed in lotus leaves, rose petals, etc. The petal effect has been studied which has been represented by high CA and high adhesion to water. The existence of the micro and nanoroughnesses play an important role in determining hydrophobicity of the natural systems. Superhydrophobic surfaces with high adhesion find application in the precise transport of liquid droplets, e.g., in microfluidics over a surface without rolling and also to minimise falling of condensed droplets in jets and aircrafts.

The thesis is an attempt to reveal bifunctional properties, namely structural colour and wettability on naturally occurring specimens. To be specific, it highlights studies on a few important specimens belonging to insect, butterfly and plants. In this regard, we have chosen dragonfly (*Gynacantha Dravida*) and blue riverdamselfly (*Pseudagrion Microcephalum*) belonging to the *Coenagrionidae* family and *Odanata* order. The butterflies, viz. white admiral butterfly (*Limenitis Camilla*) of the *Nymphalidae* family with wings offering alternate white and brown patches, large-white butterfly (*Pieris Brassicae*) of the *Pieridae* family bearing complete white wings and finally, belonging to *Papilionidae* family malabar raven butterfly (*Papilio Dravidarum*) offers wings which come with unevenly distributed white-spots in the black background. Among flower bearing plants, we considered two distinctly different flower-types: *Indian rose* (*Rosacea*) and *Chinese rose* (*Hibiscus* *sinensis*). For instance, we have chosen three varieties of Indian *Rosaceae* cultivars with off-to-dark pink appearances. We also focussed on three varieties of Hibiscus flowers belonging to *Malvaceae* family. The importance of these flowers in the Indian culture is being realised since ancient times. Rose and hibiscus find special place in social events, floral decoration as well as in worships and rituals. It has been reported that both these flowers have several medicinal properties. Rose water has been in eye drops as an eye-cleaning agent, also in several mouth freshening products. Hibiscus acts as an anti-solar agent, with the ability to block ultraviolet rays, which is needed for cosmetic products.

Chapter I is the introductory chapter, where the fundamental aspects of vision, colour, structural colouration and wettability properties are discussed. The importance, occurrence and different mechanisms responsible for respective properties are highlighted. To a large extent, colour is perceived through stimulation of cone cells in the human eye by electromagnetic radiation. However, the colour of an object is achieved by the reflection/absorption of certain wavelength of light. Furthermore, reflection of light is solely dependent on the physical construction of the object, namely, the surface microstructure as well as the chemical composition. On the other hand, wetting-dewetting phenomenon, to a great extent is governed by the surface roughness and inhomogeneity available in the specimen. Thus, bifunctional features could be exploited simultaneously through careful analysis of surface morphology/microstructure. This chapter essentially deals with the background, scope and relevance of the study.

In *Chapter II*, we discuss different characterisation tools/techniques involved in the study of natural specimens. The UV-Vis-NIR reflectance data have been acquired by using a UV–VIS-NIR spectrophotometer (2450 Shimadzu Co. and PerkinElmer UV/Vis Lambda 365). Angle dependent reflectance characteristics have been acquired for specific cases in the wavelength range 400-1100 nm by employing PerkinElmer variable angle reflectance (VAR) accessory, which is capable of varying angle incidence (ϕ) in the range of 15-75°. Furthermore, in certain cases, reflectance data have been obtained by employing *s* and *p*-polaroids

(Holmarc optics) sensitive in the wavelength range of 400-700 nm. The microstructural features of the specimens were investigated through scanning electron microscopy (SEM, JEOL, JSM 6390 LV). Prior to loading for SEM imaging, the surface of the specimens was subjected to a few nm layers of Pt coating to avoid charging effect during imaging. The images are captured at different magnifications to reveal microstructural details of the samples. On the other hand, the water contact angles (CA) were measured by using a contact angle meter setup (Kyowa Interface Science Co. Ltd. DMs-401). For contact angle hysteresis study, the base of the sample was subjected to an intermittent tilt mode and the tilt was varied in the range of 0°-90°. Advancing (maximum) and receding (minimum) angles were measured with a repetition of 10 times for every degree of tilting. The data acquisition was made on a PC equipped with the standard FAMAS software®. Using the reflectance data of the samples, appropriate CIE chromaticity diagrams were plotted using CIE 1931 colour space [25].

Chapter III deals with the wetting-dewetting phenomenon as well as reflectance response in dragonfly and damselfly wings. We have chosen three parts of the dragonfly and damselfly wings, *viz*. basal, central and distal. Also, the edge part of the wings has been given importance with regards to the reflectance response. The hydrophobic response of the distal parts of the dragonfly and damselfly wings were found to be maximum, for which respective contact angles are 133° and 130° respectively. The better hydrophobic response of the distal part is attributed to the polygonal microstructural units. Using Wenzel equation, the roughness factor (r_φ) of the dragonfly and damselfly wing parts could be determined. Qualitatively, the surface roughness factor (r_φ) gives an idea about the overall roughness available at the specimen surface. On the other hand, the water-solid fraction (φ) of the three regions has been calculated using Cassie-Baxter model. The CAH of the three regions was determined and consequently, the distal part showed a higher CAH of 60°. We have predicted the limiting value of incremental CA by using C-B and Wenzel equations independently and assuming $\theta = 105^\circ$ for a smooth surface proposed by Holdgate. With theoretical treatments, we have derived an equation which connects roughness factor (r_{φ}) and water-solid fraction (φ): $r_{\varphi} = -0.47\varphi + 1.47$, provided that $\Delta\theta \ll \theta$, where $\Delta\theta$ is the increment in CA. The equation has validity upto a maximum change in CA ($\Delta\theta$) of 10.1°. Experimentally, the CA values determined for three parts have exhibited $\Delta\theta$ values as high as ~31°. And the empirical relations for the dragonfly and damselfly wings are found to be: $r_{\varphi}^{dg} = -2.91\varphi + 3.88$ and $r_{\varphi}^{dm} = -2.81\varphi + 3.83$ respectively. Moreover, the reflectance response of the basal, distal and edge parts of the dragonfly hindwings are studied. The reflectance data sets of the edge parts were subjected to appropriate curve fitting over a broad wavelength range while ensuring a minimal chi-square value. The overall spectral response is close to the associated exponential curve fitting trend of the form given by: $R=R_0\,[1-\exp(-\lambda^2/r^2_{\mu v})-\exp(-\lambda^4/r^4_{\mu s})]$. Here, $r_{\mu s}$ and $r_{\mu v}$ characterize average surface roughness contributions associated with the surface reflectance and the sub-surface volume scattering; respectively. The respective roughness parameters for the dragonfly edge specimen are estimated to be $r_{\mu s} \sim 368.5$ nm and $r_{\mu v} \sim 241$ nm. The respective parameters for the damselfly wing are estimated after proper fitting. The submicron roughness, $r_{\mu s}$ is comparable to ~ 370 nm peak maxima which is attributed to the overall surface make up of chitinous nanooblate assemblies undergoing specular reflection. In contrast, $r_{\mu v}$ is the outcome of diffusive scattering, which arises via curved surfaces and interfaces between the chitin oblates. The analysis of reflectance spectra of the edge specimens provided a clue to interrelate sub-micron surface roughness with the roughness factor, and consequently with the hydrophobic response in this specific case.

Chapter IV reports on the evaluation of structural coloration in the whole white and spotted white regions of butterfly wings on a comparative basis. In this regard, white admiral (WA, *Limentis Camilla*), large white (LW, *Pieris Brassicae*) and dark blue tiger (DBT, *Tirumala Septentrionis*) butterflies belonging to *Lepidoptera* order have been chosen. In the WA wing part, even if the white area is seen to be structurally disordered owing to presence of irregular scales and micro-beads, but reflectance response is much stronger than its brown counterpart. While sharing a common optical trend, both the white and brown parts displayed a much improved reflectance feature after ethanol uptake. The rough surface of the wing is believed to be optically smooth after insertion of ethanol into the tiny air gaps of the scale microstructure. However, LW and DBT wings offered a reverse trend with ethanol adsorption. The reflectance features of the WA and DBT, to a great extent, alter with varying angle of incidence, ϕ=15 to 75^{o}. While both the wing-types validate thin film interference mechanism for the white-appearing color, the degree of polarization vary profoundly between them (p_z =0.35 (WA), 0.06 (DBT)). However, the reflectance response exhibited by the LW wing-type was found to offer the least viewing angle dependency, but possessing varied polarization sensitivity over a broad wavelength range. The significance of structural coloration in natural systems is expected to deliberate insights and scope for generating and mimicking artificial designs which have immense potential in the field of nano-photonics and bio-photonics.

Apart from the optical features, wetting-dewetting phenomena in these specimens have also been studied. We have studied the static CA and Contact angle hysteresis (CAH) using tilting base plate methodology in each of these and have observed that due to dual roughness feature of the scales, butterfly wings show high hydrophobicity. Among the three, DBT wings show high CA of 123° and a roll-off angle at 50°, after which the droplet falls off the wing. Whereas, WA and LW shows static CA of 120 and 100 respectively, without any rolling angle.

In *Chapter V*, we have reported the microstructure-based wettability and reflectance responses of three varieties of Indian *Rosacea* (*Rosa*) cultivars, viz. white rose (*Rosa chinensis var spontanea*), (*Rosa chinensis var minima*) and dark pink rose (*Rosa chinensis var minima*). The static water contact angles (CA) and contact angle hysteresis (CAH) have been determined for the three matured specimens. The static CA for the white, light pink and dark pink rose petals were observed to be 122.5°, 111.2° and 133.3°; respectively. The roughness factor (r_φ) of the three specimens was calculated to be 2.74, 2.27 and 2.94, in case of W, LP and DP petals, respectively. The contact angle hysteresis (CAH) values are found as, 51°, 27° and 59°. Interestingly, the dark pink rose exhibited a higher CA as well as CAH value. Our results predict a comparatively higher hydrophobic response exhibited by DP specimen w.r.t. other cultivars under study. Moreover, the rose petals were dipped in four media with different Refractive Indices (*RI*), viz. ethanol (1.36), propanol (1.39) and glycerine (1.47) for about 24h. The main purpose behind liquid treatment was to introduce transient variation in the microstructural arrangement, which is likely to modify the reflectance characteristics at large. The biophotonic structural colouration including discolouration effect, as well as wetting-dewetting transition aspects are detailed in this chapter.

In *Chapter VI*, we have discussed the reflectance response for fresh, dried and solvent treated three varieties, viz. red, pink and yellow appearing Hibiscus flowers (Chinese rose), belonging to *Malvaceae* family. The angle dependent and polarisation dependent study of the petal specimens have been considered for the study. Along with the spectral response, the dewetting characteristics have been exploited. Here, the red and pink petals exhibited folded micro-papillae, whereas the yellow ones preserved flat type of cellular architecture. Upon drying, the reflectance features were found to be suppressed as a result of loss of water from the microvoids which is apparent from the scanning electron micrographs (SEM). The red hibiscus petal showed a higher static CA and low CAH value of 110.7° and 25.13° respectively. To gain physiological insights and reveal viewing angle dependency, spectral features were acquired for both fresh and dried specimens along with consideration of variable incident angles.

Chapter VII describes the main conclusions drawn from the present study, future scope and challenges in various applications, along with future prospects. It is followed by appendices, list of publications and addenda.