

STUDY OF MINIATURIZATION OF SURFACE PATTERNS AND SELF- ORGANIZATION OF CARBONACEOUS NANOPARTICLES ON SOFT THIN FILMS AND THEIR APPLICATIONS

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by
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to



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I would like to dedicate this thesis to my loving husband and daughter

Certificate

This is to certify that the thesis titled “**Study of Miniaturization of surface patterns and self-organization of carbonaceous nanoparticles on soft thin films and their applications**” being submitted by **Ms. Surita Basu** in the Department of Chemical Engineering, Indian Institute of Technology Delhi for the award of the degree of Doctor of Philosophy, in Chemical Engineering is a record of original, bonafide research work carried by her under my guidance and supervision. In my opinion, the thesis has reached the standards fulfilling the requirements of the regulations relating to the degree. The results contained in this thesis have not been submitted for award of any other degree, associateship or similar title of any university or institute.

Jayati Sarkar 27/9/21
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Surita Basu

Abstract

Thin films are of paramount interest in daily customary life. Patterns formed in thin films are of more advanced importance. These micro and nano patterns on solid and liquid film is not only used in microelectronics but has emerged as a winner in other recent developments such as in fabrication of lab-on-chip devices for biomedical purposes, coating and adhesives as functional and self-cleaning material, various scaffolds for tissue engineering, and many more. The budding application of these patterns in thin film have led to the replacement of hard, exuberant and costly forms of lithography techniques giving way to low cost “self-organization” and “self-assembly” technique. Self-organization requires external energy source and therefore is dissipative and non-equilibrium but self-assembly is a spontaneous equilibrium process. A thin film in a confined region due to competition between intermolecular forces and surface tension becomes unstable and patterns arise on the surface of thin liquid films due to the competitive nature between the excess intermolecular interactions and interfacial tension. Another kind of pattern formation is observed at the surface of a soft elastic film when the film is brought in close proximity of a contactor. The interaction forces between the film and the contactor destabilizes the film surface, while the stored elastic energy tries to restore the film to original configuration. These antagonistic forces give rise to instabilities in the surface and thus results in meso/nano scaled morphological surface feature. Miniaturization of patterns is a new addition to this flock of studies. The process of making miniaturization of these patterns formed due to self-assembly is of much interest due to its ability to create small size and portability, low sample size, volume and cost reduction. The formation of miniaturized surface morphologies over a soft thin elastic film of micron range thickness (h), when cast on various patterned substrates created from: naturally available intrinsically rough water lily leaves, commercially available sinusoidally patterned compact disks and cubic boxes created by electron beam lithography were investigated experimentally. The evolving surface patterns formed had varying structures of columns to labyrinth to cavities during the adhesion and debonding cycle, irrespective of which the engendered dominant wavelength (λ) remained at a miniscule length scale and is depended solely on its RMS roughness. It was observed experimentally that the length scales of the patterns formed decreased linearly with increase in substrate amplitude and regardless of the substrate pattern geometry used depended solely on its RMS roughness such that $\lambda h = 2.96 - 18.2 \cdot (\text{RMS}/h)$. The study indicates the redundancy in creating very costly regular geometrical patterned substrates for miniaturization and instead advocates the use of

intrinsically rough natural surface replicas to be used as patterned substrates for cost-effective fabrication of miniaturized surface patterns at such soft interfaces. The spontaneous self-assembly of the carbon nanoparticles- graphene and carbon nanotube intensify over the self-assembled patterns formed on the thin polymeric film. The dewetting dynamics of the underlying film influences the formation of unique self-assembled graphene patterns at the interface between graphene and a thin polystyrene film by various approaches- graphene-polymer composite thin film, polymer thin film with graphene nanoparticles as a bilayer and graphene nanoparticles drop- cast over the array of dewetted holes on polymeric thin-film. When a minute amount of graphene dispersed in a solvent is added on PS and spin-coated into a thin film, the concentration gradient caused by centrifugal force leads to a Marangoni flow that in conjunction with the dewetting of the underlying PS at the edges lead to a series of very interesting, striking and self-assembled morphologies of graphene. At the particle enriched zone near the center, the graphene-particles exhibit morphologies ranging from folds, wrinkles, flakes, onion-rings to blob structures depending on the aspect ratio. The increase in graphene nanoparticle concentration and the annealing temperature in this regime leads to formation of clusters. The graphene-particles thrown to the periphery are found to march back towards the central portion leading to the unique formation of very ordered nano-scale scratches on the PS substrate. The nanoparticles that end up into the confined rims in the intermediate region get twisted into nano-ribbons and dendrimers. The increase in concentration of graphene nanoparticles and temperature leads to formation of fingering morphologies in this region. The increase in the temperature near the dewetting regime caused the polymer in presence of high concentration of graphene nanoparticles to form a floral pattern on the surface of the film. The polystyrene-graphene nanoparticles composite when spin-coated together to form a thin film over a substrate, it was observed that these nanoparticles self-assemble in a Voronoi tessellation of ribbon-like structure along with the suppression of dewetting of thin polystyrene film at this stage. The graphene nanoparticles dispersed in solvent were casted over the instability based dewetting patterns formed on the surface of the thin polystyrene film causing the graphene nanoparticles to arrange in a polygonal array of dots prompted by the dynamics and morphology of dewetting. The reversals of the dewetted patterns were observed in this process because of the solvent evaporation and Marangoni flow. Moreover, without the aid of any high-end instrumentation or process, different origami structures were formed by the presence of different forces and the underlying dewetting dynamics. The instability of a polymeric thin film, when cast either as a mobile underlying support-layer of a bilayer assembly, as a mixture, or as a template,

affects the self-assembly and arrangement of carbon nanotube (CNT) nanoparticles dispersed over/with it. The interplay of the different forces, like centrifugal, dewetting, Marangoni, electrostatic, assist the mobile nanoparticles in arranging themselves into circular ring-like structures. The congruence of the length-scales of the self-assembled circular ring and the dewetted length-scales of the thin polystyrene film reveals that the influence of dewetting dynamics is majorly responsible for the incipience of ring formations. The nanoparticles not involved in circular-ring-self-assembly formation are driven by Marangoni force (effective due to difference in surface tension values because of nanoparticle concentration difference) and engender nano-scratches over the polymeric surface. The bending of the carbon nanotubes is an energetically favoured self-organization process controlled by the shape formation energy. Finally, surface corrugations such as columns, labyrinths and cavities evolved spontaneously due to instability on the surfaces of a thin soft elastic PDMS film in adhesive contact with a contactor along with the oleophilic nature of the film help in selective adsorption of the oil from the oil-water mixture into the intervening surface spaces. The increase in RMS surface roughness brought about either by increase in adsorbent weight or by formation of a columnar structure (instead of cavities or labyrinths) was found to have a significant incremental effect on the true surface area creation by formation of increased number of oil adsorption sites: leading to higher oil penetration and thus, higher oil adsorption. For 0.3wt% of adsorbent, adsorption was found to be maximum for columnar structures at 23%, followed by cavities at 15% and minimum with labyrinth at around 12%. The ratio (d_p/d_a) of the substrate pore size dimension (d_p) to the surface oil droplet dimension (d_a) in crude oil, motor oil, diesel and petrol were found to be progressively lower and hence the maximum adsorption and penetration in the columnar patterns was recognized in case of crude oil. Additionally, the circular rings of CNTs formed throughout the PS surface, can be used to identify trace amounts of oil from an oil-water mixture by selective adsorption. This thesis contributes on creating spontaneous patterns on soft thin film embedded with/without carbonaceous nanoparticles via different approaches with enhanced surface properties.

सार

दैनिक प्रथागत जीवन में पतली फिल्में सर्वोपरि हैं। पतली फिल्मों में बनने वाले पैटर्न अधिक उन्नत महत्व के होते हैं। ठोस और तरल फिल्म पर इन सूक्ष्म और नैनो पैटर्न का उपयोग न केवल माइक्रोइलेक्ट्रॉनिक में किया जाता है, बल्कि हाल के अन्य विकासों में एक विजेता के रूप में उभरा है, जैसे बायोमेडिकल उद्देश्यों के लिए लैब-ऑन-चिप उपकरणों के निर्माण में, कार्यात्मक और स्व-सफाई सामग्री के रूप में कोटिंग और चिपकने वाले, ऊतक इंजीनियरिंग के लिए विभिन्न मंचान, और भी बहुत कुछ। पतली फिल्म में इन पैटर्नों के नवोदित अनुप्रयोग ने कम लागत वाली "स्व-संगठन" और "स्व-संयोजन" तकनीक का मार्ग प्रशस्त करते हुए लिथोग्राफी तकनीकों के कठिन, विपुल और महंगे रूपों के प्रतिस्थापन का नेतृत्व किया है। स्व-संगठन के लिए बाहरी ऊर्जा स्रोत की आवश्यकता होती है और इसलिए यह अपव्यय और गैर-संतुलन है लेकिन स्व-संयोजन एक सहज संतुलन प्रक्रिया है। एक सीमित क्षेत्र में एक पतली फिल्म इंटरमॉलिक्युलर बलों और सतह तनाव के बीच प्रतिस्पर्धा के कारण अस्थिर हो जाती है और अतिरिक्त इंटरमॉलिक्युलर इंटरैक्शन और इंटरफेशियल तनाव के बीच प्रतिस्पर्धी प्रकृति के कारण पतली तरल फिल्मों की सतह पर पैटर्न उत्पन्न होता है। एक अन्य प्रकार का पैटर्न गठन एक नरम लोचदार फिल्म की सतह पर देखा जाता है जब फिल्म को एक संपर्ककर्ता के करीब लाया जाता है। फिल्म और संपर्ककर्ता के बीच संपर्क बल फिल्म की सतह को अस्थिर कर देता है, जबकि संग्रहीत लोचदार ऊर्जा फिल्म को मूल विन्यास में बहाल करने का प्रयास करती है। ये विरोधी ताकतें सतह में अस्थिरता को जन्म देती हैं और इस प्रकार मेसो/नैनो स्केल्ड मॉर्फोलॉजिकल सरफेस फीचर में परिणत होती हैं। पैटर्न का लघुकरण अध्ययन के इस झुंड के लिए एक नया अतिरिक्त है। छोटे आकार और सुवाह्यता, कम नमूना आकार, मात्रा और लागत में कमी बनाने की क्षमता के कारण स्व-संयोजन के कारण बनने वाले इन पैटर्नों का लघुकरण करने की प्रक्रिया बहुत रुचि की है। माइक्रोन रेंज की मोटाई (एच), जब से निर्मित विभिन्न पैटर्न वाले सबस्ट्रेट पर डाली जाती है: प्राकृतिक रूप से उपलब्ध आंतरिक रूप से खुरदरे पानी के लिली के पत्ते, व्यावसायिक रूप से उपलब्ध साइनसोइडली पैटर्न वाले कॉम्पैक्ट डिस्क और इलेक्ट्रॉन बीम लिथोग्राफी द्वारा बनाए गए क्यूबिक बक्से की प्रयोगात्मक रूप से जांच की गई थी। विकसित सतह के पैटर्न में आसंजन और डिबॉन्डिंग चक्र के दौरान स्तंभों की भूलभुलैया से लेकर गुहाओं तक की अलग-अलग संरचनाएं थीं, इसके बावजूद कि उत्पन्न प्रमुख तरंग दैर्ध्य (λ) एक छोटी लंबाई के पैमाने पर बना रहा और पूरी तरह से इसके आरएमएस खुरदरापन पर निर्भर है। यह प्रयोगात्मक रूप से देखा गया था कि सबस्ट्रेट आयाम में वृद्धि के साथ गठित पैटर्न की लंबाई के पैमाने रैखिक रूप से कम हो गए और सबस्ट्रेट पैटर्न ज्यामिति की परवाह किए बिना पूरी तरह से इसके आरएमएस खुरदरापन पर निर्भर करता है जैसे कि $h = 2.96-$

18.2 * (RMS / h)। अध्ययन लघुकरण के लिए बहुत महंगा नियमित ज्यामितीय पैटर्न वाले सबस्ट्रेट्स बनाने में अनावश्यकता को इंगित करता है और इसके बजाय आंतरिक रूप से किसी न किसी प्राकृतिक सतह प्रतिकृतियों के उपयोग को ऐसे नरम इंटरफेस पर लघु सतह पैटर्न के लागत प्रभावी निर्माण के लिए पैटर्न वाले सबस्ट्रेट के रूप में उपयोग करने की वकालत करता है। कार्बन नैनो-कणों-ग्राफीन और कार्बन नैनोट्यूब की स्वतःस्फूर्त स्व-संयोजन पतली बहुलक फिल्म पर बने स्व-इकट्टे पैटर्न पर तेज हो जाती है। अंतर्निहित फिल्म की डीवेटिंग गतिकी ग्राफीन और विभिन्न दृष्टिकोणों द्वारा एक पतली पॉलीस्टायर्न फिल्म के बीच इंटरफेस में अद्वितीय स्व-इकट्टे ग्राफीन पैटर्न के गठन को प्रभावित करती है- ग्राफीन-पॉलीमर मिश्रित पतली फिल्म, बाइलर और ग्राफीन नैनोकणों के रूप में ग्राफीन नैनोकणों के साथ बहुलक पतली फिल्म पॉलीमेरिक थिन-फिल्म पर डीवेटेड होल की सरणी पर ड्रॉप-कास्ट। जब विलायक में छितरी हुई ग्रेफीन की एक मिनट की मात्रा को पीएस पर जोड़ा जाता है और एक पतली फिल्म में स्पिन-लेपित किया जाता है, तो केन्द्रापसारक बल के कारण होने वाली सांद्रता प्रवणता एक मारंगोनी प्रवाह की ओर ले जाती है जो किनारों पर अंतर्निहित पीएस के डीवेटिंग के साथ होती है। ग्राफीन के बहुत ही रोचक, हड़ताली और स्व-इकट्टे आकारिकी की एक श्रृंखला। केंद्र के पास कण समृद्ध क्षेत्र में, ग्राफीन-कण पहलू अनुपात के आधार पर सिलवटों, झुर्रियों, गुच्छे, प्याज के छल्ले से लेकर बूँद संरचनाओं तक आकारिकी प्रदर्शित करते हैं। इस शासन में ग्राफीन नैनोकणों की सांद्रता और एनीलिंग तापमान में वृद्धि से गुच्छों का निर्माण होता है। परिधि में फेंके गए ग्राफीन-कणों को मध्य भाग की ओर वापस मार्च करते हुए पाया जाता है, जिससे पीएस सबस्ट्रेट पर बहुत ही क्रमबद्ध नैनो-स्केल खरोंच का अनूठा गठन होता है। नैनो-कण जो मध्यवर्ती क्षेत्र में सीमित रिम्स में समाप्त हो जाते हैं, नैनो-रिबन और डेंड्रिमर में मुड़ जाते हैं। ग्राफीन नैनोकणों और तापमान की सांद्रता में वृद्धि से इस क्षेत्र में फिंगरिंग आकारिकी का निर्माण होता है। डीवेटिंग शासन के पास तापमान में वृद्धि ने बहुलक को ग्रेफीन नैनोकणों की उच्च सांद्रता की उपस्थिति में फिल्म की सतह पर एक पुष्प पैटर्न बनाने के लिए प्रेरित किया। पॉलीस्टाइरीन-ग्राफीन नैनोपार्टिकल्स मिश्रित जब एक सबस्ट्रेट पर एक पतली फिल्म बनाने के लिए एक साथ स्पिन-लेपित होता है, तो यह देखा गया कि ये नैनोपार्टिकल्स रिबन जैसी संरचना के वीरोनोई टेसेलेशन में स्वयं-इकट्टे होते हैं और साथ ही पतली पॉलीस्टायरीन फिल्म के डीवेटिंग के दमन के साथ मंच। सॉल्वेंट में बिखरे हुए ग्राफीन नैनोकणों को पतली पॉलीस्टायर्न फिल्म की सतह पर बने अस्थिरता आधारित डीवेटिंग पैटर्न पर डाला गया था, जिससे ग्राफीन नैनोकणों को डीवेटिंग की गतिशीलता और आकारिकी द्वारा प्रेरित डॉट्स के बहुभुज सरणी में व्यवस्थित करने का कारण बनता है। इस प्रक्रिया में विलायक के वाष्पीकरण और मारंगोनी प्रवाह के कारण ओसित पैटर्न का उलट देखा गया। इसके अलावा, किसी भी उच्च अंत इंट्रूमेंटेशन या प्रक्रिया की सहायता के बिना,

विभिन्न ओरिगेमी संरचनाओं का गठन विभिन्न बलों की उपस्थिति और अंतर्निहित डीवेटिंग गतिकी द्वारा किया गया था। एक बहुलक पतली फिल्म की अस्थिरता, जब एक मिश्रण के रूप में, या एक टेम्पलेट के रूप में, एक बाइलेयर असेंबली की मोबाइल अंतर्निहित समर्थन-परत के रूप में डाली जाती है, तो कार्बन नैनोट्यूब (सीएनटी) नैनोकणों के स्वयं-संयोजन और व्यवस्था को प्रभावित करती है। यह। विभिन्न बलों की परस्पर क्रिया, जैसे केन्द्रापसारक, डीवेटिंग, मारंगोनी, इलेक्ट्रोस्टैटिक, मोबाइल नैनोकणों को खुद को गोलाकार रिंग जैसी संरचनाओं में व्यवस्थित करने में सहायता करते हैं। स्व-इकट्टे वृत्ताकार वलय की लंबाई-तराजू की अनुरूपता और पतली पॉलीस्टाइनिन फिल्म के डीवेट लंबाई-तराजू से पता चलता है कि रिंग संरचनाओं की शुरुआत के लिए डीवेटिंग डायनामिक्स का प्रभाव प्रमुख रूप से जिम्मेदार है। सर्कुलर-रिंग-सेल्फ-असेंबली गठन में शामिल नहीं नैनोकणों को मारंगोनी बल (नैनोपार्टिकल एकाग्रता अंतर के कारण सतह तनाव मूल्यों में अंतर के कारण प्रभावी) द्वारा संचालित किया जाता है और बहुलक सतह पर नैनो-खरोंच पैदा करता है। कार्बन नैनोट्यूब का झुकना एक ऊर्जावान रूप से पसंदीदा स्व-संगठन प्रक्रिया है जिसे आकार निर्माण ऊर्जा द्वारा नियंत्रित किया जाता है। अंत में, कॉलम, लेबिरिथ और कैविटी जैसे सतह के गलियारों का विकास एक पतली नरम लोचदार PDMS फिल्म की सतहों पर अस्थिरता के कारण एक संपर्ककर्ता के साथ चिपकने वाले संपर्क में और फिल्म की ओलेओफिलिक प्रकृति के साथ तेल से तेल के चयनात्मक सोखने में मदद करता है। - बीच की सतह के स्थानों में पानी का मिश्रण। आरएमएस सतह खुरदरापन में वृद्धि या तो सोखने वाले वजन में वृद्धि या स्तंभ संरचना के गठन (गुहाओं या लेबिरिथ के बजाय) के कारण हुई, तेल सोखना की बढ़ी हुई संख्या के गठन से वास्तविक सतह क्षेत्र निर्माण पर एक महत्वपूर्ण वृद्धिशील प्रभाव पाया गया। साइटों: उच्च तेल प्रवेश और इस प्रकार, उच्च तेल सोखना के लिए अग्रणी। सोखना के 0.3wt% के लिए, 23% पर स्तंभ संरचनाओं के लिए सोखना अधिकतम पाया गया, इसके बाद गुहाओं में 15% और न्यूनतम भूलभुलैया के साथ लगभग 12% पाया गया। कच्चे तेल, मोटर तेल, डीजल और पेट्रोल में सतह के तेल की छोटी बूंद आयाम (डीडी) के लिए सबस्ट्रेट छिद्र आकार आयाम (डीपी) का अनुपात (डीपी / डीडी) उत्तरोत्तर कम पाया गया और इसलिए अधिकतम सोखना और प्रवेश में कच्चे तेल के मामले में स्तंभ पैटर्न को मान्यता दी गई थी। इसके अतिरिक्त, पीएस सतह पर गठित सीएनटी के गोलाकार छल्ले का उपयोग चयनात्मक सोखना द्वारा तेल-पानी के मिश्रण से तेल की ट्रेस मात्रा की पहचान करने के लिए किया जा सकता है। यह थीसिस उन्नत सतह गुणों के साथ विभिन्न दृष्टिकोणों के माध्यम से कार्बनयुक्त नैनोकणों के साथ/बिना एम्बेडेड नरम पतली-फिल्म पर सहज पैटर्न बनाने में योगदान देता है।

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LIST OF ABBREVIATION

PDMS: Polydimethyl siloxane

EBL: Electron Beam Lithography

RMS: Root mean square

h: Thickness of thin film

UVO: ultra violet ozone radiation

UVC: ultra violet C radiation

PS: Polystyrene

GP: Graphene nanoparticles

MWCNT: Multiwall carbon nanotubes

CNT: Carbon nanotubes

LIST OF SYMBOLS

β_p : patterned substrate amplitudes

$\beta=\beta_p/h$: substrate amplitude to film thickness ratios

RMS': RMS/h