POLYMER CRYSTALLIZATION UNDER HIERARCHICAL CONFINEMENT IN ELECTROSPUNFIBRES

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by

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DEPARTMENT OF TEXTILE AND FIBRE ENGINEERING

Submitted
in fulfilment of the requirements of the degree of Doctor of Philosophy
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This Thesis is dedicated with extreme gratitude to…

My research supervisor Prof. Bhanu Nandan

All the teachers who nourished me throughout my academic journey.

My Family

CERTIFICATE

This is to certify that the thesis titled **“Polymer Crystallization Under Hierarchical Confinement in Electrospun fibres”** being submitted by **Mr. Sanchayan Pal**to Indian Institute of Technology Delhi, for the award of ***Doctor of Philosophy*** degree, is a record of bonafide research work carried out by him. He has worked under my guidance and supervision and fulfilled the requirements for the submission of thesis which has attained the standard required for a Ph.D. degree of this institute. The work carried out to complete the thesis has not been submitted for degree or diploma in any institute in part or full.

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असतोमासद्गमय।तमसोमाज्योतिर्गमय।

Sanchayan

ABSTRACT

From the beginning, to tune the physical properties of polymer, blending of two or more polymers have been a common practice. It is well-known that the crystallization behaviour of a polymer blend is much more complex as compared with the constituting homopolymers due to influence of different factors like interaction in between the blend components, physical properties and crystallization kinetics of individual blend components etc. The complexity in the crystallization behavior reaches to a much higher level in case both the constituting polymers of the blends are miscible and crystallizable. In this case, the interplay between the crystallization of two components makes the analysis as well as understanding of the morphology and crystallization of the binary blend system very difficult. Here, the difference in the melting temperatures of the two crystallizable polymers plays a significant role in governing the final crystalline morphology of the blend system.

Moreover, recently, with the advent of nanotechnology, the importance of crystallization behavior in nanosized domains, formed in practical systems, have gained more attention. This is driven by the fact that any perturbation of crystallization behaviour in confinement may significantly alter the properties of the materials. Hence, an understanding of the polymer crystallization under nano-confinement is necessary for tailoring of the polymer properties when used in nanotechnology related applications. The electrospun fibres processed from polymer blends, where a crystalline polymer is present as a dispersed phase, depicts a nice example of such non-equilibrium systems where the radial dimensions of the fibres restrict the size of the dispersed phase domains. The confined crystallization behavior of polymers in electrospun nanofiber, hence, has received lot of interest in last few years. In the present study, the crystallization and morphological behavior of different crystalline/crystalline melt miscible polymer blends have been investigated in bulk state as well as under confinement in the electrospun fibres in order to gain vital fundamental understanding of crystallization in crystalline/crystalline (C/C) polymer mixtures.

For a more comprehensive understanding of the crystallization behaviour of C/C polymer blends under confinement, the present research focussed on investigating two classically different C/C blends in bulk as well as in confined state. The first blend system was composed of poly(ethylene oxide) (PEO) and poly(1,4-butylene adipate) (PBA) where the constituent polymers had almost similar melting temperatures. The crystallization behaviour as well as blend morphology of PBA/PEO blend was thoroughly studied. The crystalline structure and morphology of the PEO/PBA blends were found to be governed by a strong competition between the faster crystallization kinetics of PEO and relatively much higher nucleation density of PBA. Furthermore, the crystallization behaviour of PBA/PEO blend confined by surrounded PS matrix, in electrospun fibres of polystyrene (PS)/PBA/PEO ternary blends, was investigated systematically. The results obtained in electrospun fibre system has been compared with their corresponding as-casted film as well as homopolymers under similar confined environment. A promotion of the heterogenous nucleation of both PEO and PBA was observe in the ternary blend fibres. Also, the chain orientation memory favoured the formation of α-crystals of PBA in the PEO/PBA as well as PS/PEO/PBA blend fibres. The second C/C blend system studied consisted of PEO and poly (L-lactide) (PLLA) where the constituting polymers had a wide difference in their melting temperatures. Due to broad difference in melting temperature, on cooling from melt state, the PLLA/PEO blends underwent sequential crystallization. Hence, PLLA crystallized first and subsequently PEO crystallized within the existing template formed by PLLA crystals. Furthermore, under confinement, in electrospun fibres from the ternary blend of PS/PLLA/PEO, the geometrical confinement restricted the phase separation of PLLA and PEO during crystallization due to which, during crystallization of PLLA, a large fraction of PEO were trapped into the interlamellar region of PLLA which resulted in the formation of very defective PLLA crystals. Such defective crystals were found to melt at significantly low temperatures. Moreover, during crystallization, the PEO experienced a very high degree of confinement by the pre-existing PLLA crystals and surrounding hard glassy matrix of PS. This resulted in the formation of thin and defective PEO crystal lamellae which melted at a very low temperature.

The present study also focussed on understanding the role of spinning solvent in the morphology and, hence, the confined crystallization behavior of polymer in electrospun fibres from amorphous/crystalline blend. The investigated PS/PEO blend fibres formed phase separated structure in the fibres, where the minority PEO component was present as the dispersed phase in the PS matrix. It was found that the dielectric constant and volatility of the spinning solvent may profoundly affect the morphology of the electrospun blend fibres and, hence, the crystallization behavior of the minority component. The research reported in the thesis highlights the complex crystallization behaviour of crystalline polymer mixtures under confinement especially in electrospun fibres and will catalyse further research in this direction.

शोध सार

शुरू से ही किसी बहुलक (पॉलिमर) के भौतिक गुणों को किसी भी मात्रा में बदलने के लिए दो या दो से अधिक बहुलक का सम्मिश्रण एक आम अभ्यास रहा है। यह सर्वविदित है कि विभिन्न कारक जैसे की मिश्रण घटकों के बीच पारस्परिक क्रिया, किसी विशेष मिश्रण घटक के भौतिक गुण तथा स्फटिकरण के प्रभाव के कारण एक बहुलक मिश्रण का स्फटिकरण , गठित समबहुलक की तुलना में बहुत अधिक जटिल होता है। स्फटिकरण में जटिलता तब और भी अधिक हो जाती है, जब मिश्रणों के दोनों गठन बहुलक मिश्रणीय और स्फटीय होते हैं। ऐसे में दो घटकों के स्फटिकरण के बीच परस्पर क्रिया विश्लेषण को कठिन तथा बाइनरी ब्लेंड सिस्टम के आकारिकी और स्फटिकरण की समझ को बहुत जटिल बना देती है। यहां, दो स्फटीय बहुलक गलनांक में अंतर मिश्रण प्रणाली के अंतिम स्फटिकरण आकारिकी को नियंत्रित करने में महत्वपूर्ण भूमिका निभाता है।

बीते समय में नैनो-प्रौद्योगिकी के आगमन के साथ प्रायोगिक प्रणाली में उत्पन्न हुए नैनो-कार्यक्षेत्र में स्फटिकरण के महत्व ने शोध में काफी ध्यान आकर्षित किया हैं। यह इस तथ्य से प्रेरित है कि परिरोध में स्फटिकरण व्यव्हार में ज़रा से परिवर्तन से सामग्री के गुणों में काफी बदलाव आ सकता है। इसलिए, नैनो-प्रौद्योगिकी से संबंधित अनुप्रयोगों में उपयोग किए जाने पर बहुलक गुणों को बदलने के लिए नैनो-कार्यक्षेत्र के तहत बहुलक स्फटिकरण की समझ आवश्यक है। बहुलक मिश्रणों से संसाधित एलेक्ट्रोस्पन फाइबर ,जहां एक स्फुटीय बहुलक एक परिक्षेपित प्रावस्था के रूप में मौजूद होता है, ऐसे गैर-संतुलन प्रणालियों का एक अच्छा उदाहरण दर्शाता है जहां फाइबर के त्रिज्यीय आयाम परिक्षेपित प्रावस्था के आकार को प्रतिबंधित करते हैं। इसलिए बीते कुछ वर्षों में इलेक्ट्रोस्पन नैनो-फाइबर में बहुलक के सीमित स्फटिकरण व्यवहार को शोध में बहुत रूचि प्राप्त हुई है। इस अध्ययन में, विभिन्न स्फुटीय/स्फुटीय (C/C) पिघले हुए मिश्रणीय बहुलक मिश्रणों के स्फटिकरण और रूपात्मक व्यवहार की जांच की गई है। स्फुटीय/स्फुटीय (C/C) बहुलक मिश्रणों में स्फुटीयकरण की मौलिक समझ हासिल करने के लिए जांच आयतन अवस्था में और साथ ही परिरोध में एलेक्ट्रोस्पन फाइबर के तहत की गई है।

परिरोध में (C/C) बहुलक मिश्रणों के स्फटिकरण व्यवहार की अधिक व्यापक समझ के लिए, वर्तमान शोध में दो अलग-अलग (C/C) मिश्रणों की आयतन की अवस्था और परिरोध की अवस्था में जांच पर ध्यान केंद्रित किया गया है। पहली मिश्रण प्रणाली poly(ethylene oxide) (PEO) और poly(1,4-butylene adipate) (PBA) से बनायी गयी, जहां घटक बहुलकों का गलनांक सामान था। स्फटिकरण व्यवहार के साथ-साथ PBA/PEO मिश्रण के मिश्रण आकारिकी का गहन अध्ययन किया गया। PEO/PBA मिश्रणों की स्फुटीय संरचना और आकारिकी PEO के तेज स्फटिकरण गतिकी और PBA के अपेक्षाकृत उच्च न्यूक्लिएशन घनत्व के बीच एक मजबूत प्रतिस्पर्धा द्वारा नियंत्रित होती है। इसके अलावा, पॉलीस्टाइनिन (PS/PBA/PEO) त्रिगुट मिश्रणों के एलेक्ट्रोस्पन

फाइबर में घिरे PS आव्यूह द्वारा सीमित PBA/PEO मिश्रण के स्फटिकरण व्यवहार की व्यवस्थित रूप से जांच की गयी। एलेक्ट्रोस्पन फाइबर सिस्टम में प्राप्त परिणामों की तुलना उनकी समान-कास्ट फिल्म के साथ-साथ एक समान सीमित वातावरण के तहत समबहुलक के साथ की गई है। PEO और PBA दोनों के विषम न्यूक्लियेशन की वृद्धि त्रिगुट मिश्रण फाइबर में देखि गयी थी। इसके अलावा, चेन ओरिएंटेशन मेमोरी ने PEO/PBA के साथ-साथ (PS)/PBA/PEO) मिश्रण फाइबर में PBA के α-स्फटिक के गठन का समर्थन किया। अध्ययन किए गए दूसरे C/C मिश्रण प्रणाली में PEO और poly (L-lactide) (PLLA) शामिल थे जहां गठित बहुलक के गलनांक में व्यापक अंतर था। गलनांक में व्यापक अंतर के कारण, पिघली हुई अवस्था से ठंडा होने पर, PLLA/PEO मिश्रित क्रमिक स्फटिकरण से गुजरता है। इसलिए, PLLA ने पहले स्फटिककृत किया और बाद में PEO को PLLA स्फटिक द्वारा बनाए गए मौजूदा टेम्पलेट के भीतर स्फटिककृत किया। इसके अलावा, परिरोध में PS/PLLA/PEO के त्रिगुट मिश्रण से एलेक्ट्रोस्पन फाइबर में, ज्यामितीय परिरोध ने क्रिस्टलीकरण के दौरान PLLA और PEO के चरण पृथक्करण को प्रतिबंधित कर दिया, जिसके कारण PLLA के स्फटिकरण के दौरान, PEO का एक बड़ा अंश PLLA के इंटरलामेलर क्षेत्र में फंस गया, जिसके परिणामस्वरूप बहुत ही दोषयुक्त PLLA स्फटिक बन गए। ऐसे दोषयुक्त स्फटिक काफी कम तापमान पर पिघलते पाए गए। इसके अलावा, स्फटिकरण के दौरान, PEO ने पहले से मौजूद PLA स्फटिक और PS के आसपास के कठोर आइनेदार मैट्रिक्स द्वारा बहुत उच्च स्तर की कैद का अनुभव किया। इसके परिणामस्वरूप पतले और दोषयुक्त PEO स्फटिक पटलिका का निर्माण हुआ जो बहुत कम तापमान पर पिघल गया।

वर्तमान अध्ययन ने आकृति विज्ञान में कताई विलायक की भूमिका को समझने पर भी ध्यान केंद्रित किया और इसलिए, अनाकार / स्फटिकीय मिश्रण से एलेक्ट्रोस्पन फाइबर में बहुलक के सीमित स्फटिकरण व्यवहार को समझने पर ध्यान केंद्रित किया है। जांच किए गए PS/PEO मिश्रण तंतुओं ने तंतुओं में चरण से अलग संरचना का गठन किया, जहां अल्पसंख्यक PEO घटक PS मैट्रिक्स में बिखरे हुए चरण के रूप में मौजूद थे। यह पाया गया कि कताई विलायक का परावैद्युतांक और अस्थिरता एलेक्ट्रोस्पन मिश्रण फाइबर के आकारिकी को गहराई से प्रभावित कर सकती है और इसलिए, अल्पसंख्यक घटक के स्फटिकरण व्यवहार को प्रभावित कर सकती है। शोध प्रबंध में रिपोर्ट किए गए शोध विशेष रूप से एलेक्ट्रोस्पन फाइबर में परिरोध के तहत स्फटिकीय बहुलक मिश्रणों के जटिल स्फटिकरण व्यवहार पर प्रकाश डालते हैं और इस दिशा में आगे के शोध को उत्प्रेरित करेंगे।

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LIST OF SYMBOLS AND ABBREVIATIONS

iPP	*Isotactic polypropylene*
sPP	*Syndiotactic polypropylene*
G	*Gibb's free energy*
G_c	*Gibb's free energy at crystalline state*
G_a	*Gibb's free energy at amorphous state*
PE	*Polyethylene*
Δg_f^0	*Bulk free energy of crystallization*
a, b, l	*Dimensions of a crystal*
σ_e	*The fold surface free energy*
σ	*The side surface free energy*
ΔG^*	*The activation energy*
T_m	*The melting temperature*
T_c	*The crystallization temperature*
T_g	*The Glass transition temperature*
T_{m°	*Equilibrium melting temperature*
MDs	*Microdomains*
AAO	*porous anodic aluminium oxide membrane*
PEO	*Poly (ethylene oxide)*
PLLA	*Poly (L-Lactide)*
$t_{1/2}$	*Half time of crystallization*
PEO-b-PB	*Poly (ethylene oxide)-block-Polybutylene*
PS-b-PEO	*Poly (styrene)-block- Poly (ethylene oxide)*
2D	*Two dimentional*
SAXS	*Small Angle X-ray Scattering*
PVDF	*poly(vinylidine fluoride)*
PS	*Poly(styrene)*

C/C	*crystalline/crystalline*
C/A	*crystalline/amorphous*
PC	*polycarbonate*
PBA	*poly(1,4 butylene adipate)*
AFM	*Atomic Force Microscopy*
E	*Energy*
SCs	*stereocomplex crystallites*
PDLA	*Poly(D-lactide)*
PEG	*Poly(ethylene glycol)*
PCL	*Polycaprolactone*
UCST	*Upper Critical Solution Temperature*
LCST	*Lower Critical Solution Temperature*
DSC	*Differential Scanning Calorimetry*
$\boldsymbol{\emptyset_2}$	*Volume fraction of high* T_m *component*
$\boldsymbol{k_1}$	*Rate of transport of polymer chains across the liquid-solid boundary*
$\mathbf{k_2}$	*Rate of segregation*
D	*Diffusion coefficient,*
d	*The maximum distance over which the amorphous component has to diffuse away during crystallization*
$\boldsymbol{G_m}$	*Growth rate*
$\boldsymbol{\Delta F_m^*}$	*Free energy of nucleus formation*
PBSU	*Poly(butylene succinate)*
$\boldsymbol{\alpha}$	*Polymorphic structure*
$\boldsymbol{\beta}$	*Polymorphic structure*
$\boldsymbol{\gamma}$	*Polymorphic structure*
PES	*poly(ethylene suberate)*
POM	*Polyoxymethylene*

EF	*Electrospun fibre*
CF	*Casted Film*
NMR	*Nuclear Magnetic Resonance*
nm	*Nanometer*
wt%	*Weight%*
1D	*One dimensional*
PLOM	*Polarised Optical Microscope*
SEM	*Scanning Electron Microscope*
WAXD	*Wide Angle X-Ray Diffraction*
WAXS	*Wide Angle X-Ray Scattering*
DCM	*Dichloromethane*
DMF	*N,N,-Dimethylformamide*
M_v	*Viscosity Average Molecular Weight*
M_w	*Weight Average Molecular Weight*
M_n	*Number Average Molecular Weight*
LS	*Lamellar Stacks*
B/E	*Poly(1,4 butylene adipate) /Poly (ethylene oxide) blend*
ΔT_m	*Difference in melting temperature of blend components*
S/B/E	*Poly(styrene)/Poly(1,4 butylene adipate) /Poly (ethylene oxide) blend*
S/B	*Poly(styrene)/Poly(1,4 butylene adipate) blend*
S/E	*Poly(styrene)/Poly (ethylene oxide) blend*
LLPS	*Liquid-Liquid phase separation*
L/E	*Poly(L-Lactide) / Poly(ethylene oxide)*

PS-b-LLA	*poly(styrene)-block-poly(L-lactide)*
PS-b-PEO	*poly(styrene)-block-poly(ethylene oxide)*
S/L	*Poly(styrene)/Poly(L-lactide) blend*
S/E	*Poly(styrene)/Poly(ethylene oxide) blend*
PB-b-PEO	*Poly(butadiene)-block-poly(ethylene oxide)*
S/L/E	*Poly(styrene)/Poly(L-lactide)/Poly(ethylene oxide) blend*
PSF	*Polysulfone*
δ	*Solubility Parameter*
ε	*Dielectric Constant*
C/D	*Chloroform/N,N,-Dimethylformamide mixture*
D/D	*Dichloromethane/ N,N,-Dimethylformamide mixture*
$\Delta H_{c,he}$	*Enthalpy for heterogeneous crystallization*
$\Delta H_{c,ho}$	*Enthalpy for homogeneous crystallization*