POLYMER CRYSTALLIZATION UNDER CONFINEMENT IN ELECTROSPUN NANOFIBERS

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by

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DEDICATED WITH EXTREME AFFECTION AND GRATITUDE TO

my parents Mr. Brajabasai Samanta and Ms. Chandana Samanta

my research supervisor Prof. Bhanu Nandan

my wife Ms. Archana Samanta

CERTIFICATE

This is to certify that the thesis titled **"Polymer Crystallization Under Confinement in Electrospun Nanofibers"** being submitted by **Mr. Pratick Samanta** 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.

(Prof. Bhanu Nandan)
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ABSTRACT

The crystallization behaviour of polymers has been one of the most fascinating research area in polymer science for last several decades. With the advent of nanotechnology and focus shifting to understanding the properties of materials in nano-dimensions, a lot of focus is on understanding crystallization behavior of polymers when present in nanoshaped materials. 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 nanofibers composed of an immiscible blend of an amorphous and a crystalline polymer, with the latter forming the dispersed phase in the nanofibers, offers an interesting system for studying the effect of confinement on the crystallization behaviour. In this case, the limited radial dimension of the nanofibers may restrict the length scale of phase separation between the immiscible constituents, so as to generate the domains in nanodimensions. The confinement induced crystallization behaviour observed in such systems is expected to provide information under non-equilibrium processing conditions. Hence, in this research, the crystallization behavior of polymers has been investigated in the electrospun nanofibers in order to gain vital fundamental understanding of confined crystallization in polymeric materials.

The present study mostly focussed on understanding the confined crystallization behaviour of poly(ethylene oxide) (PEO) in nanofibers electrospunned from polystyrene (PS)/PEO blends. The results obtained was further compared with their corresponding as-casted samples. The PEO weight fraction was varied from 0.1 to 0.4. It was found that an abrupt shift in the nucleation mechanism from heterogeneous to homogeneous occurs when the PEO weight fraction was decreased from 0.3 to 0.2 in the nanofibers. The change of nucleation mechanism implied a drastic reduction of the spatial continuity of PEO domains in the nanofibers, which was not encountered in the cast film. The melting temperature and crystallinity of the PEO crystallites developed in the nanofibers were also significantly lower than those in the corresponding cast films. The phenomena observed were reconciled by the morphological observation, which revealed that the phase separation under the radial constraint of the nanofibers led to the formation of small-sized fibrillar PEO domains with limited spatial connectivity. The thermal treatment of the PS/PEO blend nanofibers above

the glass transition temperature of PS induced an even stronger confinement effect on PEO crystallization. It was also observed that the overall crystallization behaviour further depended on the PEO molecular weight. Furthermore, within the confined domains, PEO of two different molecular weights were found to cocrystallize which otherwise exhibited phase segregated crystallization behaviour. This was attributed to the restricted mobility of the PEO chains within the confined domains. However, such geometrical confinement could not restrict the phase separated crystallization behaviour of mixtures of two polymers with different chemical structure in the electrospun nanofibers fabricated from the ternary blends of PS, PEO, and poly(ε-caprolactone) (PCL). Furthermore, the homogenous nucleation of both PEO and PCL was suppressed whereas the heterogeneous nucleation was enhanced in the ternary blend nanofibers even at very low weight fraction of PEO or PCL. It will be shown that the promotion of heterogeneous nucleation was due to the coupling between the crystallization and the concentration fluctuations of liquid-liquid phase separation of PEO/PCL mixture dispersed in the PS matrix in the ternary blend nanofibers. The present study provides new insights into the effect of confinement on the crystallization behavior in crystalline/crystalline blend in the absence of junction point constraint. The dispersed phase stability was further improved using polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) block copolymer as a compatibilizer in the PS/PEO blend nanofibers. The compatibilizer was found to locate at the interfacial region reducing the interfacial tension which led to the formation of finer and uniformly sized PEO droplets in PS/PEO blends. Such reduction of PEO domains in glassy PS matrix imposed further strong geometrical restriction on PEO crystallization. As a result, additional reduction in crystallization temperature and percentage crystallinity was observed for the PEO in the PS/PEO nanofibers. The present study has demonstrated that the confinement driven crystallization behavior in electrospun nanofibers could be very interesting and also complex.

सारांश

बहुलको का क्रिस्टलीकरण व्यवहार पिछले कई दशकों से बहुलक विज्ञान के सबसे आकर्षक अनुसंधान क्षेत्रों में से एक रहा है। नैनो प्रौद्योगिकी अनुसंधान के विकास और नैनो-आयामी पदार्थो के गुणों को समझने के साथ बहुत से बहुलको के व्यवहार, जब वे नैनो-आयामो मे उपस्थित हों, पर भी केंद्रित किया गया है। यह इस तथ्य से प्रेरित होता है कि बहुलक के नैनो-आयामी परिरोध में क्रिस्टलीकरण व्यवहार के किसी भी तरह की बाधा से पदार्थो के गुणों में काफी बदलाव आ सकता है। इसलिए, नैनो-आयामी परिरोध के तहत बहुलक क्रिस्टलीकरण की समझ बहुलक के गुणों के संशोधन लिए आवश्यक है जब यह नैनो संबंधित अनुप्रयोगों में इस्तेमाल किया जाता है। इलेक्ट्रोस्पन नैनोतंतु जो कि एक अनियतरूपी और एक क्रिस्टलीय बहुलक के अमिश्रणीय मिश्रण से बना है, जिसमे क्रिस्टलीय बहुलक नैनोतंतु में फैले हुए चरण का निर्माण करता है, क्रिस्टलीकरण व्यवहार पर नैनो-परिरोध के प्रभाव का अध्ययन करने के लिए एक रोचक विषय प्रदान करता है। इस मामले में, नैनोतंतुओ के सीमित व्यासीय आयाम, असंतुलनशील घटक के बीच चरण पृथक्करण के लम्बाई के पैमाने को सीमित कर सकते हैं, ताकि नैनो-आयामी क्षेत्र उत्पन्न हो सकें। ऐसी व्यवस्था में बनाये गये नैनो-परिरोध से प्रेरित क्रिस्टलीकरण व्यवहार असंतुलन प्रसंस्करण स्थितियों के तहत महत्वपूर्ण जानकारी प्रदान कर सकता है। इसलिए, इस शोध में, बहुलक के सीमित क्रिस्टलीकरण की महत्वपूर्ण मौलिक जानकारी समझने के लिए बहुलक के क्रिस्टलीकरण व्यवहार की जांच इलेक्ट्रोस्पन नैनोतंतु में की गई है।

वर्तमान अध्ययन में ज्यादातर पॉलीस्टाइरिन (पीएस) / पाली (एथिलीन ऑक्साइड) (पीईओ) मिश्रणों से विद्यमान इलेक्ट्रोस्पन नैनोतंतुओ में पीईओ के नैनो-परिरोध क्रिस्टलीकरण व्यवहार को समझने पर केंद्रित है। प्राप्त परिणामों को उनके संबंधित निक्षेपित प्रतिरूप के साथ तुलना की गई । पीईओ वजन अंश 0.1 से 0.4 के बीच परिवर्तित किया गया ।

यह पाया गया कि केंद्रक तंत्र में विषमरूपी से समरूपी में एक अचानक बदलाव तब होता है जब पीईओ वजन-अंश नैनोतंतु में 0.3 से 0.2 तक घट जाता है। केंद्रक तंत्र में बदलाव नैनोतंतु में पीईओ क्षेत्र की स्थानिक निरंतरता की भारी कमी को निरूपित करता है, जो निक्षेपित सतह में नहीं था। नैनोतंतुओ में विकसित पीईओ क्रिस्टलाइट का पिघलने का तापमान और क्रिस्टलिनिटी भी संबंधित निक्षेपित सतहो की तुलना में काफी कम थे। रूपात्मक अवलोकन से देखने पता चला कि नैनोतंतुओ के व्यासीय बाधा के तहत चरण अलग होने के कारण सीमित स्थानिक संयोजकता के साथ छोटे आकार के पीईओ तंतुओ गठित हो गये थे । पीएस के कांच संक्रमण तापमान (Tg) के ऊपर पीएस / पीईओ मिश्रण नैनोतंतु के उष्ण उपचार ने पीईओ क्रिस्टलीकरण पर एक भी मजबूत परिरोध प्रभाव को प्रेरित किया। आगे यह भी देखा गया कि संपूर्ण क्रिस्टलीकरण व्यवहार पीईओ परमाणु भार पर भी निर्भर करता है। इसके अलावा, सीमित क्षेत्रों के भीतर, दो अलग-अलग परमाणु भार के पीईओ को क्रिस्टलाइज़ कर पाए जो अन्यथा अलग-अलग क्रिस्टलीकरण व्यवहार दर्शाते थे । इसके लिए प्रतिबंधित क्षेत्र के भीतर पीईओ श्रंखला की प्रतिबंधित गतिशीलता को जिम्मेदार ठहराया गया। हालांकि, इस तरह के ज्यामितीय परिरोध, पीएस, पीईओ और पॉली (ε-कैपोलैक्टोन) (पीसीएल) के त्रि-मिश्रण से निर्मित इलेक्ट्रोस्पन नैनोतंतुओ में विभिन्न रासायनिक संरचना के साथ दो बहुलको के मिश्रण के चरण से अलग क्रिस्टलीकरण व्यवहार को प्रतिबंधित नहीं कर सके। इसके अलावा, पीईओ और पीसीएल दोनों के समरूप केंद्र क्रिस्टलीकरण को अवरोधित किया, जबकि पीईओ या पीसीएल के बहुत कम वजन अंश पर त्रि-मिश्रण नैनोतंतुओ में विषमरूप केंद्र क्रिस्टलीकरण को बढ़ाया गया था। यह दिखाया गया कि विषमरूप केंद्र क्रिस्टलीकरण का प्रचार क्रिस्टलीकरण और पीईओ / पीसीएल द्रव - द्रव चरण मिश्रण में एकाग्रता के उतार-चढ़ाव के बीच युग्मन के कारण था जो त्रि- मिश्रण नैनोतंतुओ में पीएस आव्यूह में छितरा हुआ था। वर्तमान अध्ययन में संगम बिन्दु बाधा की अनुपस्थिति में क्रिस्टलीय / क्रिस्टलीय बहुलक मिश्रण में क्रिस्टलीकरण व्यवहार पर परिरोध के प्रभाव में नई अंतर्दृष्टि प्रदान करता है। पीएस / पीईओ मिश्रण नैनोतंतुओ में अनुरूपक के रूप में पॉलीस्टाइरिन ब्लॉक-पॉली (एथिलीन ऑक्साइड) (PS-b-PEO) खंड सह-बहुलक का इस्तेमाल करके फैलने वाले चरण की स्थिरता में और अधिक सुधार किया

गया। अनुरूपक उक्त तलों के बीच स्थापित किया गया जिससे उक्त तलों के बीच का क्षेत्रीय तनाव कम हो गया और पीएस / पीईओ मिश्रणों में बेहतर और समान रूप से आकार वाले पीईओ बूंदों का निर्माण हुआ। पारदर्शक पीएस आव्यूह में पीईओ क्षेत्र की इस तरह की कमी ने पीईओ क्रिस्टलीकरण पर और अधिक मजबूत ज्यामितीय प्रतिबंध लगाया। फलस्वरूप, पीएस / पीईओ नैनोतंतुओ में पीईओ के लिए क्रिस्टलीकरण तापमान और प्रतिशत क्रिस्टलिनिटी में अतिरिक्त कमी देखी गई थी। वर्तमान अध्ययन में यह दर्शाया गया है कि इलेक्ट्रोस्पन नैनोतंतुओ में नैनो-आयामी बाधित क्रिस्टलीकरण व्यवहार बहुत रोचक और जटिल भी हो सकता है।

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LIST OF SYMBOLS AND ABBREVIATIONS

T_g	*Glass transition temperature*
AAO	*Anodic aluminum oxide*
PVDF	*Poly(vinylidine floride)*
PSF	*Polysulfone*
PAN	*Poly(acrylonitrile)*
PEO	*Poly(ethylene oxide)*
PS	*Polystyrene*
PS-b-PEO	*Polystyrene-block-Poly(ethylene oxide)*
PCL	*Poly(ε-caprolactone)*
SEM	*Scanning electron microscopy*
DSC	*Differential scanning calorimetry*
SAXS	*Small and wide angle X-ray scattering*
WXRD	*Wide angle X-ray diffraction*
WAXS	*Wide angle X-ray scattering*
G_c	*Gibb's free energy in the crystalline state*
G_a	*Gibb's free energy in the amorphous state*
Tm	*Melting temperature*
T_m^0	*Equilibrium melting temperature*
G_c^0	*Bulk crystal free energy for equilibrium crystals*
G_s	*Surface free energy*
G_d	*Free energy due to chain defects*
a	*Length*
b	*Width*
l	*Thickness*
σ_e	*Fold free surface energy*
Δh_f^0	*Heat of fusion of crystal composed of fully extended chains*
γ	*Ratio of crystal thickness to thickness of the crystalline nucleus*
l_g^*	*Critical thickness of the crystalline nucleus*
T_c	*Crystallization temperature*
σ	*Surface energy*

$-\Delta g_f^0$	*Change of free energy during crystallization from melt*
$X(t)$	*Fractional crystallinity at time 't'*
t	*Time*
k	*Crystallization rate constant*
n	*Avrami exponent*
ΔH_{melt}	*Change of enthalpy per unit volume in melt*
ΔS_{melt}	*Change of entropy per unit volume in melt*
ΔG^*_{nuclei}	*Critical dimension of nuclei*
I	*Nucleation rate*
G	*Growth rate*
K_1	*Constant related to the surface energy*
K_2	*Constant related to the surface energy*
n_1	*Constant*
n_2	*Constant*
H–L theory	*Hoffman– Lauritzen theory*
ΔE	*Actual energy barrier*
χ	*Temperature-dependent Flory-Huggins parameter*
N	*Degree of polymerization*
f	*Volume fraction*
BCC	*Body centred cubic*
C-A	*Crystalline-amorphous*
T_g^A	*Glass transition temperature of the A block*
T_{ODT}	*Order-disorder transition temperature*
PCL-b-P4VP	*Poly(4-vinylpyridine)-block-Poly(ε-caprolactone)*
P4VP	*Poly(4-vinylpyridine)*
PEO-b-PB	*Poly(ethylene oxide)-block-Poly(butadiene)*
PS-b-PLLA	*Poly(styrene)-block-Poly(L-lactide)*
TEM	*Transmission electron microscope*
PE-b-PEP	*Poly(ethylene)-block-Poly(ethylene-propylene)*
PE-b-PEE	*Poly(ethylene)-block-Poly(ethylethylene)*
C-C	*Crystalline-b-Crystalline*
T_{c1}	*Crystallization temperature of one block*
T_{c2}	*Crystallization temperature of second block*

PCL-b-PE	*Poly(ε-caprolactone)-block-Polyethylene*
PLLA-b-PEO	*Poly (L-lactide)-block-Poly(ethylene oxide)*
PLLA-b-PCL	*Poly (L-lactide)-block-Poly(ε-caprolactone)*
PEO-b-PCL	*Poly(ethylene oxide)-block-Poly (ε-caprolactone)*
PS-b-PEO	*Polystyrene-block-Poly(ethylene oxide)*
PS-b-PEO-b-PCL	*Polystyrene-block-Poly(ethylene oxide)-block-Poly(ε-caprolactone)*
2-D	*Two dimensional*
M_e	*Entanglement molecular weight*
v_d	*Volume of polymer in one AAO nanochannel*
n_n	*Related to crystal nucleation machanism*
n_{gd}	*Related to crystal growth dimension*
P(VDF-TrFE)	*Poly(vinylidene fluoride trifluoroethylene)*
D_{AAO}	*AAO domain size*
θ	*Angle*
EAA	*Poly(ethylene-co-acrylic acid)*
β	*Crystal form of PDVF*
α	*Crystal form of PDVF*
γ'	*Crystal form of PDVF*
PA6	*Polyamide 6*
PBS	*Poly(butylene succinate)*
PAN	*poly(acrylonitrile)*
BSE	*Back-scattered electron*
DMF	*Dimethylformamide*
DCM	*Dichloromethane*
M_n	*Number average molecular weight*
M_w	*Weight average molecular weight*
iPP	*Isotactic polypropylene*
M_v	*Viscosity average molecular weight*
T_g^{PS}	*Glass transition temperature of polystyrene*
T_a	*Annealing temperature*
w_{PEO}	*Weight fraction of PEO*
w_{PCL}	*Weight fraction of PCL*
δ	*Solubility parameter*

LLPS	*Liquid-liquid phase separation*
UCST	*Upper critical solution temperature*
N_A	*Avogadros number*
D_{vs}	*Volume-to-surface average diameter of the domains*
ρ	*Density*
ϕ_b	*Block copolymer volume fraction*
n_i	*Number of domains*
Σ_o	*Maximum block copolymer coverage*
Σ	*Block copolymer coverage*
$\Lambda/2$	*Half of the lamellar spacing in the ordered block copolymer*
PS-b-PMMA	*Polyethylene-block- Poly(methyl methacrylate)*