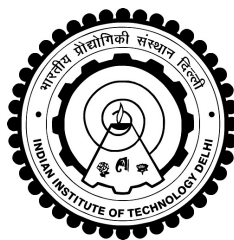


HYDRODYNAMIC STABILITY OF POLYMER FIBRE SPINNING

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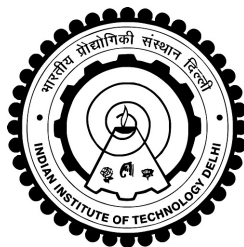
by

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Submitted

*in fulfilment of the requirements of the degree of Doctor of Philosophy
to the*



Indian Institute of Technology Delhi

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Dedicated to my family ...

“My brain is only a receiver, in the Universe there is a core from which we obtain knowledge, strength and inspiration. I have not penetrated into the secrets of this core, but I know that it exists.”

- Nikola Tesla

Certificate

This is to certify that the thesis titled “**Hydrodynamic Stability of Polymer Fibre Spinning**” being submitted by **Mr. Karan Gupta** in the Department of Chemical Engineering, Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy**, is a record of bona-fide research work carried out by him 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 the award of any other degree, associateship or similar title of any university or institution.

Dr. Paresh Chokshi

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For your individual roles in making me what I am, and what I have achieved today - I dedicate this thesis to my family.

The greatest gratitude to an unknown and scientifically unverifiable existence that favourably conspires to reward me, often unjustifiably. Some people call it God.

New Delhi

Karan Gupta

Abstract

The polymer fibres are usually produced by the spinning technique in which elongational stress is applied to polymer solution or melt. The high extensional viscosity of the fluid renders it spin-able under mechanical drawing resulting in micron-sized smooth filaments with very high mechanical strength. Fibres so produced offer high strength to weight ratio making them suitable for various technological applications. The polymer fibre spinning process suffers from a type of hydrodynamic instability which manifests in the form of travelling wave oscillations along the fibre length. As a result, the diameter of the final product fibre lacks uniformity and admits fluctuations in cross-section area. If understood properly, this instability can be either delayed or suppressed completely to generate smooth fibres without thick-thin variations in diameter while achieving maximum possible production rate. To achieve this goal, the quantitative knowledge of the critical parameters influencing the onset of instability and the nature of bifurcation in the region of transition point is essential. With this objective, the thesis examines the stability behaviour of the spinning process of an entangled polymer, to gain comprehensive understanding towards operating guidelines for stable spinning.

The travelling wave instability that renders fluctuations in the fibre cross-section area is known as the *draw resonance*, and it occurs when the draw ratio DR (ratio of drawing to extrusion speed) is above a certain critical value DR_c . The onset of the instability is strongly influenced by the rheology of the polymeric fluid. The extensional flow of a polymeric fluid during fibre spinning process is studied using both linear and weakly nonlinear stability analyses. The nonlinear extensional rheology of the entangled polymer is described with the help of eXtended Pom-Pom (XPP) model which exhibits strain hardening effect, an essential property for the fibre spinning. The linear stability analysis constructs the stability diagram indicating stable and unstable regimes on the $DR_c - De$ plane. Here, De is the Deborah number defined as the ratio of polymer relaxation time to the flow time scale, and it quantifies the elasticity of the extensional flow. The weakly nonlinear analysis reveals the nature of bifurcation at

the critical point (DR_c) and constructs a finite amplitude manifold providing insight into the severity of draw resonance phenomena. The effect of fluid elasticity on the nature of bifurcation and the finite amplitude branch is examined, and the findings are correlated to the extensional rheological behaviour of the polymer fluid. For flows at small De (Newtonian fluid-like flow), the spinning flow exhibits supercritical Hopf bifurcation at the critical point. In the linearly unstable region, the equilibrium amplitude of the disturbance shows a limit cycle behaviour. As the fluid elasticity (De) is increased (polymer-like flow), initially, the equilibrium amplitude decreases below its Newtonian value reaching the lowest value for De when the strain hardening effect is maximum. Upon further increase in elasticity, the material undergoes strain softening behaviour leading to severe draw resonance. Interestingly, at certain high De , the bifurcation crosses over from supercritical to subcritical nature.

Further, the analysis is extended to account for the non-isothermal conditions during spinning flow in which the spin-line loses heat by convection to the surrounding air as well as by solvent evaporation. The non-isothermal effects influence the rheology of the fluid through viscosity, which is taken to be dependent on temperature as well as the concentration. The enhancement in viscosity driven by spin-line cooling leads to delay in the onset of draw resonance, indicating the stabilising role of non-isothermal effects. For spinning of an exemplary polyethylene-decalin polymer, it is shown that solvent evaporation is a stronger stabilisation mechanism than heat convection. Weakly nonlinear stability analysis reveals the role of nonlinearities in the finite amplitude manifold in the vicinity of the flow transition point. For low to moderate Deborah numbers, the bifurcation is supercritical, and the equilibrium amplitude of the resonating state is smaller for the non-isothermal spinning in comparison to the isothermal case. For very fast flows in the regime of high Deborah numbers, the finite amplitude manifold crosses over to a subcritical state. In this limit, the nonlinearities due to non-isothermal conditions render the flow more prone to destabilisation even in the linearly stable regime of $DR < DR_c$, by reducing the minimum threshold amplitude.

We also examine the role of extrudate-swell in the stability of the fibre spinning flow. The flexibility in the fibre profile at the upstream end of the flow, a feature absent in the previous analyses ignoring extrudate-swell, plays a stabilising role. However, for a given flow, extrudate-swell implies stronger effective extension than indicated by the apparent draw ratio, defined based on capillary area. This higher effective extension tends to decrease the critical draw ratio for the onset of draw resonance, suggesting a destabilising role of extrudate-swell. The destabilising role dominates the overall

stability behaviour. The sensitivity of the stability behaviour to a change in rheological parameters and the die geometry is studied. The finite amplitude disturbances are also considered using the weakly nonlinear stability analysis to understand the nature of flow in the proximity of the transition point. The flow exhibits supercritical Hopf bifurcation for low to moderate Deborah numbers that cross over to the subcritical manifold as Deborah number is increased beyond a certain crossover value. The extrudate-swell effect tends to lower the Deborah number for the crossover to the subcritically unstable state. The results obtained emphasise the importance of a proper consideration of the extrudate-swell phenomenon in the analysis of spin-line stability.

As a way to stabilise the process in the high- De range of interest to produce high-strength fibres, the spinning of bilayered fibres is also investigated. The arrangement of unentangled/entangled polymer in a concentric sheath/core setup is assumed, where the rheological descriptions of unentangled/entangled fluids are modelled by the UCM/XPP models respectively. Stability of such a setup is dominated by the dynamics of entangled fluid till moderate De range, post which a significant improvement in stability is realised when dynamics of unentangled fluid begins to dominate. Apart from the increase in the stable operating region, the maximum achievable De for stable spinning (of UCM phase) is also improved. Finally, the effect of dispersity in polymer molecular weight on the stability of fibre spinning process is investigated. The polydispersity strongly influences the rheology and hence the overall stability, which is investigated by considering 1, 2, 3 and 4 mode relaxation spectra of XPP molecules. The analysis reveals a neutral stability behaviour that is a combined effect of slow and fast relaxing modes.

Overall, the stability of spinning flow of a highly entangled polymeric fluid is analysed using both the linear as well as weakly nonlinear stability analyses. The stability behaviour is strongly correlated to the nonlinear rheology of the fluid. Hence, any parameter affecting the rheology, for example, temperature, concentration or polydispersity, directly influences the stability diagram. Comprehensive knowledge of the stability behaviour enables one to modify either the material properties or the processing conditions such that the draw resonance is suppressed.

सारांश

बहुलक रेशों का उत्पादन आमतौर पर कताई तकनीक द्वारा होता है, जिसमें पिघले या घुले हुए बहुलक पर दीर्घी प्रतिबल लगाया जाता है। तरल की अधिक दीर्घी श्यानता उसे कताई योग्य बनाती है, जिसके परिणामस्वरूप माइक्रोन पैमाने के उच्च खिंचाव शक्ति वाले रेशें बनते हैं। इस तरह उत्पादित उच्च शक्ति से वजन के अनुपात वाले रेशें कई तकनीकी अनुप्रयोगों के लिए उपयुक्त होते हैं। बहुलक रेशा कताई प्रक्रिया एक प्रकार की तरलगत्यात्मक अस्थिरता से पीड़ित हो जाती है, जो रेशे की लम्बाई के साथ यात्रा करती प्रदोलित तरंगों के रूप में प्रकट होती है। इसके नतीजतन रेशों के व्यास में समानता की कमी आती है, जिससे अनुप्रस्थ काट क्षेत्र में विविधता उत्पन्न हो जाती है। यदि सही ढंग से समझा जाए तो ये अस्थिरता टाली या पूर्णतया दबाई जा सकती है, ताकि एकसमान रेशों का उत्पादन अधिकतम वेग से हो सके। इस लक्ष्य को प्राप्त करने के लिए इस अस्थिरता की शुरुआत को प्रभावित करने वाले महत्वपूर्ण प्राचलों का मात्रात्मक ज्ञान और संक्रमण बिंदु के क्षेत्र में हौप्फ़ विभाजन का व्यवहार जानना आवश्यक है। इस उद्देश्य के साथ यह वाद उलझे हुए बहुलक की कताई प्रक्रिया के स्थिरता व्यवहार का परीक्षण करती है, ताकि स्थिर कताई के संचालन दिशानिर्देशों में व्यापक समझ हासिल हो।

यात्रा करती अस्थिर तरंग जो रेशे के काट क्षेत्र में विविधता उत्पन्न करती है उसे *ड्रॉ अनुनाद* के रूप में जाना जाता है, और ऐसा तब होता है जब *ड्रॉ* अनुपात DR (*ड्रॉइंग* गती से बहिर्वेधन गती का अनुपात) एक निश्चित निर्णायक मूल्य DR_c से अधिक होता है। अस्थिरता की शुरुआत बहुलक तरल के प्रवाह विशिष्टता से काफ़ी प्रभावित होती है। कताई प्रक्रिया के दौरान बहुलक तरल के दीर्घी प्रवाह का अध्ययन रेखीय एवं प्रायः अरेखीय स्थिरता विश्लेषण, दोनों से किया गया है। उलझे हुए बहुलक की अरेखीय दीर्घी प्रवाह विशिष्टता का वर्णन एक्सटेंडेड पौम-पौम (XPP) प्रतिमान की मदद से किया गया है। यह प्रतिमान तनाव से सख्ती का प्रभाव प्रदर्शित करता है, जो कि रेशा कताई के लिए एक आवश्यक स्वभाव है। रेखिक स्थिरता विश्लेषण एक आरेख बनाता है जो स्थिर और अस्थिर क्षेत्र $DR_c - De$ सह पर दर्शाता है। यहां, डेबोराह संख्या De की परिभाषा बहुलक के शिथिलकरण समय से प्रवाह कालक्रम का अनुपात है, और ये दीर्घी प्रवाह के प्रत्यास्थता का मूल्यांकन करता है। प्रायः अरेखीय स्थिरता विश्लेषण निर्णायक मूल्य (DR_c) पर हौप्फ़ विभाजन की प्रकृति के उजागर करता है और एक सीमित आयाम उपखंड बनाता है जो कि *ड्रॉ अनुनाद* की गहनता में अंतरदृष्टि प्रदान करता है। तरल

प्रत्यास्थता के विभाजन की प्रकृति एवं सीमित आयाम उपखंड पर असर परखा गया है, और परिणामों को दीर्घी प्रवाह विशिष्टता के साथ सहसंबद्धित किया गया है। कम De (न्यूटोनियन तरल जैसे) प्रवाह के लिए, कताई प्रवाह निर्णायक बिंदु पर सुपरक्रिटिकल हौफ़ विभाजन प्रदर्शित करता है। रेखिक अस्थिर क्षेत्र में, प्रदोलित तरंगों का संतुलित आयाम एक सीमा चक्र व्यवहार दिखाता है। जैसे ही तरल प्रत्यास्थता को बढ़ाया जाता है (बहुलक जैसा प्रवाह), शुरुआत में, प्रदोलित तरंगों का संतुलित आयाम अपने न्यूटोनियन मूल्य से घट जाता है, और अपने सबसे कम मूल्य पर पहुंचता है जब तनाव से सख्ती का प्रभाव अधिकतम होता है। प्रत्यास्थता में और वृद्धि के बाद, पदार्थ तनाव से नमी का प्रभाव दिखाता है जो कि ड्रॉ अनुनाद की गहनता को बढ़ाता है। दिलचस्प बात यह है कि, किसी ऊँचे De पर हौफ़ विभाजन की प्रकृति सुपरक्रिटिकल से सबक्रिटिकल में परिवर्तित हो जाती है।

इसके अलावा, यह विश्लेषण कताई प्रवाह के दौरान असमतापीय परिस्थितियों को शामिल करता है जिस से कताई-धारा संवहन और वाष्पन के द्वारा वातावरण को गर्मी खो देता है। असमतापीय प्रभाव तरल की श्यानता के माध्यम से प्रवाह विशिष्टता पर असर दिखाता है। इस श्यानता की निर्भरता तापमान और एकाग्रता पर ली गई है। कताई-धारा शीतलन के द्वारा श्यानता में वृद्धि ड्रॉ अनुनाद को विलंबित करती है, जिस से असमतापीय परिस्थितियों का स्थिर करने वाला व्यवहार इंगित होता है। एक उदाहरणी पॉलिइथायलीन-डिकैलिन बहुलक कताई के लिए यह दिखाया गया है कि विलायक वाष्पीकरण गर्मी संवहन की तुलना में प्रमुख स्थिरकरण क्रियाविधि है। प्रायः अरेखीय स्थिरता विश्लेषण अरेखिक समीकरणों की भूमिका उजागर करता है जो कि प्रवाह संक्रमण बिंदु के निकट सीमित आयाम उपखंड पर प्रभाव डालता है। कम से मध्यम डेबोराह संख्याओं के लिए विभाजन सुपरक्रिटिकल होता है, और प्रदोलित तरंगों का संतुलित आयाम असमतापीय परिस्थितियों के लिए समतापीय परिस्थितियों की तुलना में छोटा होता है। ऊँचे डेबोराह संख्याओं में अत्यंत तीव्र प्रवाह के लिए सीमित आयाम उपखंड सबक्रिटिकल अवस्था में परिवर्तित हो जाता है। इन मूल्यों के लिए, प्रवाह के रेखीय स्थिर क्षेत्र $DR < DR_c$ में होते हुए भी, असमतापीय परिस्थितियों से संबंधित अरेखिक समीकरण न्यूनतम अवसीमा आयाम को घटा कर अस्थिर होने की प्रवृत्ति बढ़ाता है।

इस वाद में कताई प्रवाह की स्थिरता में बर्हिवेध-सृजन की भूमिका की भी जंच की गई है। कताई प्रवाह के पूर्व ऊपरी छोर पर धारा की रुपरेखा में नम्यता, एक ऐसी विशेषता जो कि बर्हिवेध-सृजन को अनदेखा करने वाले पिछले विश्लेषणों में अनुपस्थित है, एक स्थिर भूमिका निभाती है। हालांकि, किसी भी दिये गये प्रवाह के लिए प्रत्यक्ष केशिका क्षेत्र से परिभाषित ड्रॉ अनुपात से संबद्धित खिंचाव की तुलना में, बर्हिवेध-सृजन से परिभाषित ड्रॉ अनुपात अधिक खिंचाव का संकेत करता है। यह उच्च प्रभावी खिंचाव ड्रॉ अनुनाद की शुरुआत करने वाले निर्णायक ड्रॉ अनुपात में कमी लाता है, जो कि बर्हिवेध-सृजन की अस्थिर भूमिका सुझाता है। अस्थिर भूमिका संपूर्ण स्थिरता व्यवहार में हावी होती

है। प्रवाह विशिष्ट प्राचलों और केशिका ज्यामिति में बदलाव का स्थिरता व्यवहार की संवेदनशीलता पर अध्ययन किया गया है। सीमित आयाम अस्थायित्वों को प्रायः अरेखीय स्थिरता विश्लेषण के द्वारा जाँचा गया है, ताकि संक्रमण बिंदु के निकट प्रवाह की प्रकृति को समझा जाए। कम से मध्यम डेबोराह संख्याओं के लिए प्रवाह सुपरक्रिटिकल हौप्फ़ विभाजन प्रदर्शित करता है, और जैसे ही डेबोराह संख्या एक उत्तीर्णावी मूल्य से परे बढ़ता है, वह सबक्रिटिकल उपखंड में परिवर्तित हो जाता है। बर्हिवेध-सूजन प्रभाव डेबोराह संख्या के उस उत्तीर्णावी मूल्य को कम कर देता है जो प्रवाह को सबक्रिटिकल अस्थिर अवस्था में लाता है। प्राप्त परिणाम बर्हिवेध-सूजन का कताई-धारा के स्थिरता विश्लेषण में उचित मनन के महत्व पर जोर देता है।

उच्च शक्ति वाले रेशों के उत्पादन के हित में ऊँचे De पैमाने पर अधिक स्थिरता लाने के लिए, द्विस्तरित रेशा कताई की जाँच की गई है। यह व्यवस्था अनउलझे/उलझे बहुलकों को संकेंद्रित आवरण/आन्तरक मान कर उनके प्रवाह विशिष्टताओं का वर्णन XPP/UCM प्रतिमानों से करती है। ऐसी व्यवस्था की स्थिरता मध्यम De पैमाने तक उलझे हुए तरल के गतिकी से प्रभुत्वित होता है, जिसके पश्चात स्थिरता में काफ़ी सुधार होने लगता है जब अनउलझे हुए तरल के गतिकी का प्रभुत्व शुरू होता है। स्थिर संचालन क्षेत्र में बढ़ोत्तरी के अलावा, स्थिर कताई के लिए UCM तरल की अधिकतम साध्य De भी सुधरती है। अंत में, रेशा कताई प्रक्रिया में बहुलक आणविक वजन की प्रकीर्णन का प्रभाव जाँचा गया है। प्रकीर्णन प्रवाह विशिष्टता और अतः संपूर्ण स्थिरता पर अतयंत प्रभावशाली होता है, जो कि XPP आणविकों वाले १, २, ३, एवं ४ अवयवों के शिथिलिकरण वर्णक्रमों का विचार करके जाँचा गया है। विश्लेषण से यह पता चलता है कि तटस्थ स्थिरता व्यवहार धीमे और तेज शिथिलिकरण अवयवों का एक संयुक्त असर है।

अंततः, उलझे हुए बहुलक तरल की कताई प्रवाह के स्थिरता का विश्लेषण किया गया है, जिसके लिए रेखिक और प्रायः अरेखिक स्थिरता विश्लेषण दोनों का उपयोग किया गया है। स्थिरता व्यवहार तरल की अरेखिक प्रवाह विशिष्टता से सुदृढ़ता से सहसंबद्धित होता है। इसलिये, प्रवाह विशिष्टता को प्रभावित करने वाला कोई भी प्राचल, जैसे कि तापमान, एकाग्रता, या फिर प्रकीर्णन, सीधे स्थिरता आरेख पर असर डालता है। स्थिरता व्यवहार का व्यापक ज्ञान किसी को सक्षम बनाता है पदार्थ की विशेषताओं या फिर प्रसंसकरण परिस्थितियों को बदलने के लिये, ताकि ड्रॉ अनुनाद को दबाया जा सके।

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List of symbols

Symbol	Definition
a	Dimensionless spin-line area
h	Material heat transfer coefficient
k	Harmonic index of the fundamental wave
k_a	Air thermal conductivity
k_d	Parameter in equilibrium extrudate-swell estimation law
k_l	Harmonic index of inhomogeneities for problem set (k, n)
l	Landau constant, the nonlinear growth rate, $= l_r + i l_i$
m_d	Parameter in equilibrium extrudate-swell estimation law
n	Amplitude order
n_p	Power law exponent
p	Index of the Deborah number against axial stress for shear flow
q	Number of branches at backbone ends (XPP parameter)
r	XPP molecule relaxation time ratio (backbone orientation/stretch)
s	Complex-valued linear growth rate, $= s_r + i s_i$
t	Time co-ordinate (fast time scale)
v	Dimensionless spin-line velocity
v_a	Dimensionless cross-current cooling air velocity
x	Solvent mass fraction in polymer solution
z	Dimensionless axial co-ordinate
A	Variation of amplitude with slow time scale
A_e	Equilibrium amplitude of draw resonance cycles
A_{th}	Threshold amplitude of spin-line perturbation tolerance
B	Swell ratio (ratio of maximum to die-exit diameter)
B_0	Maximum swell ratio (equilibrium extrudate-swell when $F_s = 0$)
C_p	Specific heat capacity of polymer solution
C_{pa}	Specific heat capacity of cooling air

D_d	Diameter of the extruder capillary (die)
D_{sa}	Solvent diffusivity in cooling air
De	Deborah number
DR	Draw ratio (ratio of take-up to extrusion speed)
E	Dimensionless activation energy
F	Effect of chain stretch on viscoelastic behaviour of an XPP polymer
$\mathcal{F}$	Spinning force
G	Elastic (plateau) modulus of polymer
I	Identity matrix
Ja	Jakob number
L	Dimensional length of the spin-line
L_d	Length of the extruder capillary (die)
L_h	Latent heat of vaporisation of solvent
M_w	Weight average molecular weight
M_s	Solvent molar mass
R_0	Dimensional spin-line radius at die-exit
R_g	Universal gas constant
St_m	Mass Stanton number
St_t	Thermal Stanton number
T	Dimensionless spin-line temperature
T_a	Dimensionless temperature of cooling air
T_g	Glass transition temperature
Tr	Trouton's ratio of extensional to zero shear viscosity
$\mathcal{T}$	Time co-ordinate (slow time scale)
Y	General control variable for a process
Y_c	Critical value of control variable for a process
α	Nahme-Griffith/ thermal Peclet number
$\dot{\gamma}$	Averaged shear rate within extruder capillary (die)
$\dot{\gamma}_w$	Wall shear rate within extruder capillary (die)
ϵ	Small number in order-of-magnitude analysis
$\dot{\epsilon}$	Extension rate
η	Extensional viscosity of spin-line
λ	Longest relaxation time of the polymer
ν_a	Air kinematic viscosity
ρ	Density of polymer solution

ρ_a	Density of cooling air
$\boldsymbol{\tau}$	Stress tensor
ϕ	General spin-line variable
$\bar{\phi}$	Steady-state profile of the general spin-line variable
$\hat{\phi}$	Amplitude of imposed perturbation
ϕ'	Perturbed component of the general spin-line variable
$\tilde{\phi}$	Eigenfunction of the general spin-line variable
ψ	Cooling air velocity influence on spin-line
ξ	Changing viscosity and temperature influence on spin-line
ω	Frequency of perturbations
Λ	XPP molecule chain stretch ratio (extended/equilibrium length)
Σ_{zz}	Total normal stress in axial direction