STUDIES ON NANOFIBRILLATED CELLULOSE AND CROSSLINKED POLY (VINYL ALCOHOL) BASED BIOCOMPOSITE USING SUBCRITICAL WATER/CO_2

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by

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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

Mother "Priti Lata Bhattacharjee"

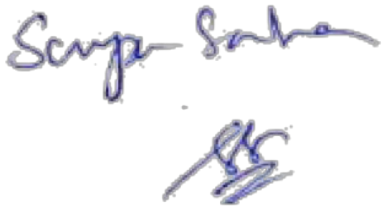
&

Father "Bijan Purkayastha"

CERTIFICATE

This is to certify that the thesis entitled, "**Studies on Nanofibrillated Cellulose and Crosslinked Poly (vinyl alcohol) based Biocomposite using Subcritical Water/CO_2**" submitted by **Ms. Srijita Purkayastha** to the **Indian Institute of Technology Delhi**, for the fulfilment of award of the degree, **Doctor of Philosophy**, is a record of bonafide research work carried out by her under our supervision and guidance. This thesis has been prepared in conformity with the rules and regulations of the **Indian Institute of Technology Delhi**, New Delhi.

The thesis, in my opinion, is worthy of consideration for award of the degree of **Doctor of Philosophy** in accordance with the regulations of the Institute. To the best of our knowledge, the results embodied in the thesis have not been submitted to any other University or Institute for the award of any other Degree or Diploma.



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ABSTRACT

In this study, novel approach of biopolymer processing by using subcritical water technology was reported. A new green extraction method of producing nanofibrillated cellulose by using subcritical water/CO_2 (SC-NFC) from softwood pulp (SWP) was developed. Subcritical water/CO_2 led to a controlled hydrolysis of SWP and the treated SWP was fibrillated by sonication to produce SC-NFC. Effect of process parameters (time, temperature and pressure) on the crystallinity and thermal properties of SC-NFC was studied to optimize the process conditions for controlled hydrolysis. The influence of the extraction process on the properties of prepared SC-NFC was studied. Nanofibrillated cellulosic materials were characterized by using morphological, chemical, thermal analysis and crystallinity studies. The SC-NFC obtained at optimum process conditions (Process pressure: 100 bar, Process temperature: 145°C and Process time: 30 minutes) showed significantly high crystallinity (66%) and high yield (75-80%) compared to that of the NFC prepared by conventional mechanical grinding method (MC-NFC). The present method of producing SC-NFC used water and pressurized CO_2 and therefore eliminated use of acids and chemicals. Plasticized poly vinyl alcohol (p-PVA) based biocomposite with SC-NFC showed significant improvement in thermal stability (36%), tensile strength (77%) with reduced water vapor transmission rate as compared to virgin p-PVA indicating their potential as nanofiller for making biocomposites. Further, a novel method of poly (vinyl alcohol) (PVA) and PVA/SC-NFC based hydrogel preparation was reported using subcritical water/CO_2 medium in presence of citric acid (CA) as crosslinker. This was a single step procedure, less time consuming and industrially viable method. In contrast, existing PVA based hydrogel preparations mainly consisted of two steps, PVA solution preparation and curing of the same. PVA powder loaded into aqueous solution of CA was taken into subcritical state by using CO_2. Water acted as plasticizer and reduced melting

temperature of PVA. Further, subcritical water acts as catalyst and reduces the crosslinkingreaction time. Additionally, CO_2 gas at 100 bar pressure, produced carbonic acid in subcritical water which also acted as mild acid catalyst for crosslinking reaction. In subcritical medium, PVA powder got melted, fused and cross-linked in a single step process to develop hydrogel. Effect of process time, process temperature and crosslinker percentage on the properties of prepared PVA hydrogels were studied. PVA/SC-NFC based biocomposite based hydrogels were prepared and characterized in the same way to achieve high mechanical property. Prepared hydrogels were characterized by thermal, chemical, morphological analysis, gel content and swelling ratio measurement, rheology and dye absorption study. Successful dye adsorption, high swelling property and high storage modulus established the potential application of prepared hydrogels in several areas such as biomedical, textile affluent filtration, water purification etc. Further, SC-NFC based foam was prepared by Pickering emulsion by using octylamine. Freeze dried wet foam showed maximum density of 0.035g/cc and corresponding compression strength was 0.24 MPa. Dye adsorption increased compared to SWP establishing potential application of prepared cellular foam as industrial affluent filtration. In this thesis, a new innovative green extraction method of nanofibrillated cellulose by using subcritical water/CO_2 medium is established and its applications are studied. Further, a new crosslinking method of poly (vinyl alcohol) and its nanofibrillated cellulose based biocomposites in subcritical water/CO_2 medium is established which can help in achieving reduced production time.

सार

इस अध्ययन में, सबक्रिटिकल जल प्रौद्योगिकी का उपयोग करके बायोपॉलिमर प्रसंस्करण के नए दृष्टिकोण की सूचना दी गई थी। सॉफ्टवुड पल्प (SWP) से सबक्रिटिकल वाटर/CO2 (SC-NFC) का उपयोग करके नैनोफाइब्रिलेटेड सेल्युलोज के उत्पादन की एक नई हरी निष्कर्षण विधि विकसित की गई थी। सबक्रिटिकल वाटर/सीओ2 ने एसडब्ल्यूपी के नियंत्रित हाइड्रोलिसिस का नेतृत्व किया और उपचारित एसडब्ल्यूपी को एससी-एनएफसी का उत्पादन करने के लिए सोनिकेशन द्वारा फ़िब्रिलेटेड किया गया। नियंत्रित हाइड्रोलिसिस के लिए प्रक्रिया की स्थिति को अनुकूलित करने के लिए एससी-एनएफसी के क्रिस्टलीयता और थर्मल गुणों पर प्रक्रिया मापदंडों (समय, तापमान और दबाव) के प्रभाव का अध्ययन किया गया था। तैयार एससी-एनएफसी के गुणों पर निष्कर्षण प्रक्रिया के प्रभाव का अध्ययन किया गया। नैनोफिब्रिलेटेड सेल्यूलोसिक सामग्री को रूपात्मक, रासायनिक, थर्मल विश्लेषण और क्रिस्टलीयता अध्ययनों का उपयोग करके चित्रित किया गया था। इष्टतम प्रक्रिया स्थितियों (प्रक्रिया दबाव: 100 बार, प्रक्रिया तापमान: 145□C और प्रक्रिया समय: 30 मिनट) पर प्राप्त एससी-एनएफसी ने उच्च क्रिस्टलीयता (66%) और उच्च उपज (75-80%) की तुलना में काफी अधिक दिखाया। पारंपरिक यांत्रिक पीसने की विधि (एमसी-एनएफसी) द्वारा तैयार एनएफसी। एससी-एनएफसी के उत्पादन की वर्तमान विधि में पानी का इस्तेमाल किया गया और सीओ 2 पर दबाव डाला गया और इसलिए एसिड और रसायनों के उपयोग को समाप्त कर दिया गया। एससी-एनएफसी के साथ प्लास्टिसाइज्ड पॉली विनाइल अल्कोहल (पी-पीवीए) आधारित बायोकंपोजिट ने थर्मल स्थिरता (36%), तन्य शक्ति (77%) में महत्वपूर्ण सुधार दिखाया है, जिसमें कुंवारी पी-पीवीए की तुलना में कम जल वाष्प संचरण दर नैनोफिलर के रूप में उनकी क्षमता का संकेत है। बायोकंपोजिट बनाने के लिए। इसके अलावा, पॉली (विनाइल अल्कोहल) (PVA) और PVA/SC-NFC आधारित हाइड्रोजेल तैयार करने की एक नई विधि को क्रॉसलिंकर के रूप में साइट्रिक एसिड

(CA) की उपस्थिति में सबक्रिटिकल वाटर/CO2 माध्यम का उपयोग करके सूचित किया गया था। यह एक एकल चरण प्रक्रिया थी, कम समय लेने वाली और औद्योगिक रूप से व्यवहार्य विधि। इसके विपरीत, मौजूदा पीवीए आधारित हाइड्रोजेल तैयारियों में मुख्य रूप से दो चरण शामिल थे, पीवीए समाधान तैयार करना और उसका इलाज करना। PVA पाउडर को CA के जलीय घोल में लोड करके CO2 का उपयोग करके सबक्रिटिकल अवस्था में ले जाया गया। पानी ने प्लास्टिसाइज़र के रूप में काम किया और पीवीए के पिघलने के तापमान को कम कर दिया। इसके अलावा, सबक्रिटिकल पानी उत्प्रेरक के रूप में कार्य करता है और क्रॉसलिंकिंग प्रतिक्रिया समय को कम करता है। इसके अतिरिक्त, 100 बार के दबाव पर CO2 गैस, सबक्रिटिकल पानी में कार्बोनिक एसिड का उत्पादन करती है जो क्रॉसलिंकिंग प्रतिक्रिया के लिए हल्के एसिड उत्प्रेरक के रूप में भी काम करती है। सबक्रिटिकल माध्यम में, पीवीए पाउडर हाइड्रोजेल विकसित करने के लिए एकल चरण प्रक्रिया में पिघल गया, फ्यूज हो गया और क्रॉस-लिंक हो गया। तैयार पीवीए हाइड्रोजेल के गुणों पर प्रक्रिया समय, प्रक्रिया तापमान और क्रॉसलिंकर प्रतिशत के प्रभाव का अध्ययन किया गया। पीवीए/एससी-एनएफसी आधारित बायोकंपोजिट आधारित हाइड्रोजेल उच्च यांत्रिक गुण प्राप्त करने के लिए उसी तरह तैयार किए गए थे और उनकी विशेषता थी। तैयार हाइड्रोजेल को थर्मल, रासायनिक, रूपात्मक विश्लेषण, जेल सामग्री और सूजन अनुपात माप, रियोलॉजी और डाई अवशोषण अध्ययन की विशेषता थी। सफल डाई सोखना, उच्च सूजन संपत्ति और उच्च भंडारण मापांक ने बायोमेडिकल, कपड़ा समृद्ध निस्पंदन, जल शोधन आदि जैसे कई क्षेत्रों में तैयार हाइड्रोजेल के संभावित अनुप्रयोग की स्थापना की। इसके अलावा, एससी-एनएफसी आधारित फोम को ऑक्टिलामाइन का उपयोग करके पिकरिंग इमल्शन द्वारा तैयार किया गया था। फ्रीज ड्राय वेट फोम ने अधिकतम घनत्व 0.035g/cc दिखाया और इसी संपीड़न शक्ति 0.24 MPa थी। औद्योगिक समृद्ध निस्पंदन के रूप में तैयार सेलुलर फोम के संभावित अनुप्रयोग को स्थापित करने वाले एसडब्ल्यूपी की तुलना में डाई सोखना में वृद्धि हुई

है। इस थीसिस में, सबक्रिटिकल वाटर/सीओ2 माध्यम का उपयोग करके नैनोफिब्रिलेटेड सेलूलोज़ की एक नई अभिनव हरी निष्कर्षण विधि स्थापित की गई है और इसके अनुप्रयोगों का अध्ययन किया जाता है। इसके अलावा, सबक्रिटिकल वाटर/सीओ2 माध्यम में पॉली (विनाइल अल्कोहल) और इसके नैनोफिब्रिलेटेड सेलूलोज़ आधारित बायोकंपोजिट्स की एक नई क्रॉसलिंकिंग विधि स्थापित की गई है जो कम उत्पादन समय प्राप्त करने में मदद कर सकती है।

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FORMAT OF THE THESIS

The thesis comprises of the following chapters

Chapter 1: Introduction and Literature Survey

Chapter 2: Materials and Experimental Methods

Chapter 3: Preparation of Nano Fibrillated Cellulose by using Subcritical water/CO_2

Chapter 4A: Preparation and Characterization of Crosslinked Poly (vinyl alcohol) in Presence of Subcritical water/CO_2 Medium

Chapter 4B: Preparation and Characterization of Crosslinked Poly (vinyl alcohol)/Nanofibrillated Cellulose based Biocomposite in Presence of Subcritical water/CO_2 Medium

Chapter 5: Preparation and Properties of Modified Nanofibrillated Cellulose based Foam

Chapter 6: Summary and Conclusions