# POLYMER GRAFTING POTENTIAL AND REINFORCING EFFICIENCY OF NITRONE AND NITROXIDE FUNCTIONALIZED GREEN SILICA DERIVED FROM RICE HUSK ASH

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by

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Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the


**Indian Institute of Technology Delhi**

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*Dedicated to* ***Dr. Nizamuddin Sulthan Shah Qadiri Chishti****,*

*my beloved big brother, for his profound care and boundless love, which has shaped my journey with enduring lessons of willpower and patience.*

# CERTIFICATE

*This is to certify that the thesis entitled "**Polymer grafting potential and reinforcing efficiency of nitrone and nitroxide functionalized green silica derived from rice husk ash"** being submitted by **Mr. Lukkumanul Hakkim N.** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work carried out by him. Mr. Lukkumanul Hakkim N. has worked under my guidance and supervision and has fulfilled the requirements for the submission of his thesis, which, to our knowledge, has reached the requisite standard.*

*The results contained in this thesis are original and have not been submitted, in part or full, to any University or Institute for the award of any degree or diploma.*

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# ABSTRACT

In recent years, the quest for sustainable and efficient methods in material science has led to the exploration of novel approaches for synthesizing functionalized silica. This study focuses on optimizing the synthesis of functionalized green silica from sodium silicate derived from rice husk ash via co-condensation and introducing nitroxide and nitrone functionalities that can be subjected to polymer grafting as well as a reinforcing filler with elastomers.

In this study, an optimized method for synthesizing functionalized green silica from rice husk ash via co-condensation has been developed and extensively examined using conventional silanes. The method's efficiency was compared with conventional post-modification approaches on commercial precipitated silica (CPS) and commercial rice husk ash silica (CRHA) using (3-mercaptopropyl)triethoxysilane (MPTES) and (3-aminopropyl)triethoxysilane (APTES). Silane grafting density, determined through TGA analysis, revealed that the co-condensation method exhibited higher efficiency at higher loadings of silane. The synthesized green silica, derived from rice husk ash, offers a sustainable alternative to conventional silica synthesis methods. The energy-efficient functionalization method, optimized for co-condensation, was explored for its potential to enhance silica's interaction with elastomers. Comparative studies with conventional in situ silane addition were conducted using bis(triethoxysilylpropyl)tetrasulfide silane.

Furthermore, nitroxide functionalized silica was synthesized using thiol-ene reaction with 4-acryloyloxy(2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and mercaptopropyl functionalized silica. The method of functionalization, whether post-modification or co-condensation, significantly affected nitroxide loading. Nitroxide functionalized samples were subjected to polystyrene grafting, revealing that grafting density increased with conversion and initiator-to-monomer ratio. Nitrone functionalities were introduced to silica surfaces via thiol-

ene reaction, showcasing their potential in polymer grafting through enhanced spin-capturing polymerization (ESCP) and 1,3-dipolar cycloaddition. Compounding studies with styrene-butadiene rubber demonstrated the effectiveness of nitroxide and nitrone functionalities in capturing elastomer radicals during mixing, affecting curing time and mechanical properties.

This thesis highlights the usefulness of nitrone and nitroxide functionalized silica as a reinforcement in polymer matrices, offering covalent silica-polymer interactions. The compounding studies with styrene-butadiene rubber emphasize the interaction of nitrone and nitroxide functionality in silica with respect to the loading, method of functionalization, and surface area, providing insights for tuning curing time in compound preparation. Overall, this research contributes to the development of sustainable and efficient methods for functionalized silica synthesis and its application as a reinforcing agent in elastomer-based composites.

# सारांश

हाल के वर्षों में, सामग्री विज्ञान में स्थायी और कुशल विधियों की खोज ने सुनिश्चित और कुशल तरीकों की दिशा में नई कोशिशों का मार्ग दिखाया है जिससे संबद्ध सिलिका का सिंथेसिस करने के लिए। यह अध्ययन सोडियम सिलिकेट से बनाए गए चावल के छाले की राख के माध्यम से उत्पन्न संबद्ध हरित सिलिका के सिंथेसिस को अनुकूलित करने पर केंद्रित है जिसमें को-सम्मिलन और नाइट्रॉक्साइड और नाइट्रोन कार्यक्षमताओं की प्रविष्टि की गई है जो पॉलिमर ग्राफ्टिंग के लिए एक सुधारित फिलर के रूप में उपयोग किया जा सकता है।

इस अध्ययन में, एक अनुकूलित विधि का अभ्यसन किया गया है जिससे चावल के छाले की राख से हरित सिलिका का सिंथेसिस करने के लिए और सामान्य साइलेन्स का विस्तारपूर्वक परीक्षण किया गया है। इस विधि की कार्यक्षमता को व्यावासायिक प्रेसिपिटेटेड सिलिका (सीपीएस) और व्यावासायिक चावल के छाले सिलिका (सीआरएचए) पर उपयोग करके सामान्य पोस्ट-सुधारण दृष्टिकोणों के साथ तुलना की गई थी, (3-मर्कैप्टोप्रोपिल) त्रैइथॉक्सिसिलेन (एमपीटीईएस) और (3-एमिनोप्रोपिल) त्रैइथॉक्सिसिलेन (एपीटीईएस) का उपयोग करके। टीजीए विश्लेषण के माध्यम से तय हुआ सिलेन ग्राफ्टिंग घनत्व ने दिखाया कि को-सम्मिलन विधि ने सिलेन के उच्च लोडिंग पर अधिक कार्यक्षमता प्रदर्शित की। चावल के छाले से उत्पन्न हरित सिलिका ने पारंपरिक सिलिका सिंथेसिस विधियों के लिए एक स्थायी विकल्प प्रदान किया। इसे सामरिकता से अनुकूलित करने के लिए अनुकूलित उर्जा साकारक सिंथेसिस विधि का अन्वेषण किया गया था, जिसका उद्दीपन सिलिका के एलास्टोमर्स के साथ संवेग को बढ़ाने की संभावना थी। बिस (त्रैइथॉक्सिसिलाइलप्रोपिल) टेट्रासल्फाइड सिलेन का उपयोग करके परंतु सामान्य स्थानीय सिलेन जोड़न के साथ तुलनात्मक अध्ययन आयोजित किए गए।

इसके अलावा, ठायल-इन रिएक्शन के साथ 4-एक्रिलोइलोक्सी(2,2,6,6-टेट्रामेथाइलपाइपेरिडिन-1-यल)ऑक्सिल (टेम्पो) और मर्कैप्टोप्रोपिल संबद्ध सिलिका का नाइट्रॉक्साइड संबद्ध किया गया था। संबद्धीकरण की विधि, चाहे वह पोस्ट-सुधारण हो या को-सम्मिलन, नाइट्रॉक्साइड लोडिंग को प्रभावित करती थी। नाइट्रॉक्साइड संबद्ध नमूने को पॉलिस्टाइरीन ग्राफ्टिंग के लिए अवसादित किया गया, जिसने दिखाया कि अनुकूलन और प्रेरक-से-एमोनोमर अनुपात के साथ ग्राफ्टिंग घनत्व बढ़ गया। ठायल-इन रिएक्शन के माध्यम से नाइट्रोन कार्यक्षमताएं सिलिका सतहों में प्रविष्टि की गई, जो उनकी संभावना को पॉलिमर ग्राफ्टिंग के माध्यम से बढ़ाते हैं (ईएससीपी) और 1,3-डाइपोलर

साइक्लोएडिशन के माध्यम से। स्टायरीन-ब्यूटाडाइन रबर के साथ संयोजन अध्ययन ने नाइट्रॉक्साइड और नाइट्रोन कार्यक्षमताओं की प्रभावशीलता को मिश्रित करने के लिए दिखाया कि इन विशेषताओं का अच्छादनी-विज्ञान पॉलिमर मैट्रिक्स में मजबूती प्रदान करता है। स्टायरीन-ब्यूटाडाइन रबर के साथ मिश्रण अध्ययन ने दिखाया कि नाइट्रॉक्साइड और नाइट्रोन कार्यक्षमताएं मिश्रण के दौरान इलास्टोमर रेडिकल्स को पकड़ने में प्रभावी हैं, जिससे कीचिंग समय और यांत्रिक गुणधर्म प्रभावित होते हैं।

यह थीसिस नाइट्रोन और नाइट्रॉक्साइड से युक्त सिलिका की उपयोगिता को उजागर करती है जो पॉलिमर मैट्रिक्स में मजबूती के रूप में कार्य करती है, कोवेलेंट सिलिका-पॉलिमर इंटरएक्शन्स प्रदान करती है। स्टायरीन-ब्यूटाडाइन रबर के साथ सम्प्रेषण अध्ययन नाइट्रोन और नाइट्रॉक्साइड सिलिका में की जाने वाली कार्रवाई को लोडिंग, सुधारीकरण की विधि, और सतह क्षेत्र के संबंध में जोर देते हैं, जो यौगिक तैयारी में क्यूरिंग समय को ट्यून करने के लिए दृष्टिकोण प्रदान करते हैं। समग्रतः, यह अनुसंधान सिलिका संशोधन की सतत और कुशल विधियों के विकास में और इसे इलास्टोमर-आधारित कॉम्पोजिट्स में मजबूती प्रदान करने में योगदान करता है।

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# LIST OF ABBREVIATION

| | |
|---|---|
| AIBN | Azobisisobutyronitrile |
| APTES | (3-Aminopropyl)triethoxysilane |
| ATRP | Atom transfer radical polymerization |
| BET | Brunauer-Emmett-Teller surface area analysis |
| CPS | Commercial precipitated silica |
| CRHA | Commercial RHA silica |
| CRP | Controlled radical polymerization |
| Disulfide | Bis[3-(triethoxysilyl)propyl] disulfide |
| DLS | Dynamic light scattering |
| DMAP | 4-Dimethylaminopyridine |
| DMF | Dimethylformamide |
| EPR | Electron Paramagnetic Resonance |
| ESCP | Enhanced spin capturing polymerization |
| FE-SEM | Field emission - scanning electron microscopy |
| FTIR | Fourier-transform infrared |
| HTES | Hexyltriethoxysilane |
| MCPS | Mercaptopropyl functionalized commercial precipitated silica |
| MCRHA | Mercaptopropyl functionalized commercial RHA silica |
| MPTES | (3-Mercaptopropyl)triethoxysilane |

| | |
|---|---|
| NCPS | Nitrone functionalized commercial precipitated silica |
| NCRHA | Nitrone functionalized commercial RHA silica |
| NMP | Nitroxide mediated polymerization |
| NMR | Nuclear Magnetic Resonance |
| NMRC | Nitrone mediated radical coupling |
| NTPA | N-[3-(Trimethoxysilyl)propyl]aniline |
| NXCPS | Nitroxide functionalized commercial precipitated silica |
| NXCRHA | Nitroxide functionalized commercial RHA silica |
| PDI | Polydispersity index |
| PS | Polystyrene |
| RAFT | Reversible addition-fragmentation chain transfer |
| SEC | Size exclusion chromatography |
| TEMPO | 2,2,6,6-(tetramethylpiperidin-1-yl)oxyl |
| Tetrasulfide | Bis[3-(triethoxysilyl)propyl] tetrasulfide |
| Tg | Glass transition temperature |
| THF | Tetrahydrofuran |
| UV-Visible | Ultraviolet-Visible |
| XPS | X-ray photoelectron spectroscopy |