

**PENTAERYTHRITOL-DERIVED POLYHYDROXY
DENDRIMERS AND FLAME RETARDANT ADDITIVES**

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PENTAERYTHRITOL-DERIVED POLYHYDROXY DENDRIMERS AND FLAME RETARDANT ADDITIVES

by

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Submitted

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Dedicated to My Parents and Manish

CERTIFICATE

This is to certify that the thesis entitled “**Pentaerythritol Derived Polyhydroxy Dendrimers and Flame Retardant Additives**” being submitted by **Ms. Shikha** to the Indian Institute of Technology Delhi for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her. Ms. Shikha has worked under my guidance and supervision and has fulfilled the requirements for the submission of her 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

Pentaerythritol, an interesting and commonly available cheap raw material with four hydroxyl groups that has attracted a lot of attention. Pentaerythritol has been used to synthesize dendrimers, star polymers, block copolymers, hydrogels, and flame retardant additives. Dendrimers and flame retardant additives have been synthesized using a variety of starting compounds (ethylenediamine, pentaerythritol, dipentaerythritol, succinic anhydride, 1,1,1-tris(hydroxymethyl)propane, and phosphazene) and their derivatives. However, the ability of pentaerythritol to selectively protect and functionalize its hydroxyl groups makes it ideal for the synthesis of dendrimers and flame retardant compounds.

In the first section, starting with pentaerythritol, three new dendrimers, D1, D2, and D3 were synthesized, bearing 9, 12, and 18 peripheral hydroxyl groups, respectively, using an alkyne-azide Huisgen 1,3-dipolar cycloaddition reaction. The structural integrity and purity of the dendrimers were confirmed by ^1H and ^{13}C NMR spectroscopy, and FE-SEM studies established their near-spherical morphology. Using D2 as a macroinitiator, hyperbranched 12-arm star polymers were synthesized *via* ring-opening polymerization of L-lactide. The molar masses of the star polymers P1-P4 were controlled by changing the feed ratio of the monomer to initiator, and the star polymers exhibit narrow dispersity as determined by SEC. FESEM studies established their globular nature, and DLS measurements revealed that micelle size increases with PLA content. The amphiphilic nature of the star polymers makes them attractive materials for the removal of water-soluble dyes by phase transfer. It is found that the star polymer acts as a unimolecular micelle with an encapsulation ability for dyes such as congo red (CR), bromophenol blue (BB), and methyl orange (MO).

In the next section, a series of pentaerythritol derived phosphorous based flame retardants (FRs labeled FR1, FR2, FR3, and FR4) were synthesized, and their suitability for TPU thin films (< 100 micron) was explored. Then blends were prepared by choosing the phosphorous content in the FRTPU at 0.5-2.0 wt %. Despite their structural similarities, they exhibit drastically different flame retardancy in TPU. It is found that the addition of these additives to TPU results in a significant improvement in fire retardant efficiency. The higher char residue, compact char, and vertical flame test of FR1TPU and FR2TPU suggest that FR1 and FR2 work in the condensed phase, and they exhibit better flame-retardant efficiency compared to FR3 and pure TPU. At 2% phosphorous content, FR2 completely stopped the dripping of TPU film. The FR3TPU and FR4TPU at 2% phosphorous content showed excessive non-flamed melt drips, which suggests that these FRs catalyze the depolymerization of TPU and sharply reduce the melt viscosity, thereby increasing the dripping. The dripping removes the material from the flame zone and helps in extinguishing the flame. The low char values and open-cell foam morphology achieved for these FRTPUs suggest that they are working in the gas phase.

Another section a series of additives containing phosphate moiety (FRs labeled FR5, FR6, FR7, and FR8) were synthesized. These FRs were melt blended with TPU, and blends (FRTPUs) were prepared by choosing a phosphorous content of 0.5-2.0 wt %. After that, the strips were analyzed by the UL-94 vertical burning and LOI tests. The results of the UL-94 test showed that in FR5TPU₂, the dripping phenomena was observed however, in FR6TPU₂, FR7TPU₂, and FR8TPU₂, the dripping was completely stopped. For the neat TPU sample, the fire develops instantly after ignition with heavy flammable dripping. The surface morphology of the char residue was studied by SEM, and it was found that FR5TPU, FR6TPU, and FR7TPU form closed-cell foamy morphologies, which implies that they are acting in the condensed phase. However, FR8TPU forms an open-cell foamy morphology, which suggests the gas phase, and the presence of phosphorous by the EDX analysis supports the condensed phase

activity of this molecule in the TPU matrix.

In the final section, a new synergistic flame retardant based on phosphate functionalized silica (PhosFS) was synthesized by utilizing alkyne-azide click chemistry between 2,6,7-trioxa-1-phospha-bicyclo[2.2.2]octane, 4-(azidomethyl)-1-oxide, and propargyl functionalized silica (PFS). The presence of phosphate on the functionalized silica was confirmed by various techniques such as solid-state ^{31}P NMR, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and inductively coupled plasma-mass spectrometry (ICP-MS). The flame-retardant TPU composites exhibited excellent flame retardancy, which was demonstrated by the UL-94 and LOI results. The SEM results revealed that upon incorporation of PhosFS, the char residue of the TPU/PhosFS samples is more compact compared to the pure TPU sample. EDX and FTIR suggest that the incorporation of phosphate functionalized silica induces a synergistic effect by forming a physical barrier to restrict the combustion of the inner TPU matrix due to the production of a uniform and dense char during combustion.

सार

पेंटाएरिथ्रिटोल, चार हाइड्रॉक्सिल समूहों के साथ एक दिलचस्प और आमतौर पर उपलब्ध सस्ता कच्चा माल, जिसने बहुत ध्यान आकर्षित किया है। पेंटाएरिथ्रिटोल का उपयोग डेंड्रिमर, स्टार पॉलिमर, ब्लॉक कॉपोलिमर, हाइड्रोजेल और लौ रिटार्डेट एडिटिव्स को संश्लेषित करने के लिए किया गया है। डेंड्रिमर्स और फ्लेम रिटार्डेट एडिटिव्स को विभिन्न प्रकार के शुरुआती यौगिकों (एथिलीनडायमाइन, पेंटाएरिथ्रिटोल, डिपेंटेएरिथ्रिटोल, स्यूसिनिक एनहाइड्राइड, 1,1,1-ट्रिस (हाइड्रॉक्सीमेथाइल) प्रोपेन, और फॉस्फाज़ीन) और उनके व्युत्पन्न का उपयोग करके संश्लेषित किया गया है। हालांकि, अपने हाइड्रॉक्सिल समूहों को चुनिंदा रूप से संरक्षित और कार्यात्मक बनाने के लिए पेंटाइरीथ्रिटोल की क्षमता इसे डेंड्रिमर्स और ज्वाला मंदक यौगिकों के संश्लेषण के लिए आदर्श बनाती है।

पहले खंड में, पेंटाएरिथ्रिटोल से शुरू होकर, तीन नए डेंड्रिमर, डी1, डी2 और डी3 को संश्लेषित किया गया था, जिसमें क्रमशः 9, 12, और 18 परिधीय हाइड्रॉक्सिल समूह होते हैं, जो एक एल्काइन-एज़ाइड हुसिजेन 1,3-द्विध्रुवीय साइक्लोडिशन प्रतिक्रिया का उपयोग करते हैं। डेंड्रिमर्स की संरचनात्मक अखंडता और शुद्धता की पुष्टि ^1H और ^{13}C NMR स्पेक्ट्रोस्कोपी द्वारा की गई, और FE-SEM अध्ययनों ने उनके निकट-गोलाकार आकारिकी की स्थापना की। मैक्रोइनिटिएटर के रूप में डी2 का उपयोग करते हुए, हाइपरब्रांच्ड 12-आर्म स्टार पॉलिमर को एल-लैक्टाइड के रिंग-ओपनिंग पोलीमराइजेशन के माध्यम से संश्लेषित किया गया था। स्टार पॉलिमर P1-P4 के दाढ़ द्रव्यमान को मोनोमर के फ्रीड अनुपात को आरंभकर्ता में बदलकर नियंत्रित किया गया था, और स्टार पॉलिमर एसईसी द्वारा निर्धारित संकीर्ण फैलाव प्रदर्शित करते हैं। FESEM अध्ययनों ने उनकी गोलाकार प्रकृति की स्थापना की, और DLS मापों से पता चला कि PLA सामग्री के साथ मिसेल का आकार बढ़ता है। स्टार पॉलिमर की एम्फीफिलिक प्रकृति उन्हें चरण हस्तांतरण द्वारा पानी में घुलनशील रंगों को हटाने के लिए आकर्षक सामग्री बनाती है। यह पाया गया है कि स्टार पॉलीमर कांगो रेड (सीआर), ब्रोमोफेनॉल ब्लू (बीबी), और मिथाइल ऑरेंज (एमओ) जैसे रंगों के लिए एक एनकैप्सुलेशन क्षमता के साथ एक गैर-आणविक मिसेल

के रूप में कार्य करता है।

अगले खंड में, पेंटाइरीथ्रिटोल व्युत्पन्न फॉस्फोरस आधारित लौ रिटार्डेंट्स (FR1, FR2, FR3, और FR4 लेबल वाले FRs) की एक श्रृंखला को संश्लेषित किया गया था, और TPU पतली फिल्मों (<100 माइक्रोन) के लिए उनकी उपयुक्तता का पता लगाया गया था। फिर FRTPU में फॉस्फोरस सामग्री को 0.5-2.0 wt % पर चुनकर मिश्रण तैयार किए गए। अपनी संरचनात्मक समानताओं के बावजूद, वे टीपीयू में अत्यधिक भिन्न ज्वाला मंदता प्रदर्शित करते हैं। यह पाया गया है कि टीपीयू में इन एडिटिक्स को जोड़ने से अग्निरोधी दक्षता में उल्लेखनीय सुधार होता है। FR1TPU और FR2TPU के उच्च चार अवशेष, कॉम्पैक्ट चार और ऊर्ध्वाधर लौ परीक्षण से पता चलता है कि FR1 और FR2 संघनित चरण में काम करते हैं, और वे FR3 और शुद्ध TPU की तुलना में बेहतर लौ-प्रतिरोधी दक्षता प्रदर्शित करते हैं। 2% फॉस्फोरस सामग्री पर, FR2 ने टीपीयू फिल्म के टपकने को पूरी तरह से रोक दिया। 2% फॉस्फोरस सामग्री पर FR3TPU और FR4TPU ने अत्यधिक नॉन-फ्लेम मेल्ट ड्रिप्स को दिखाया, जो बताता है कि ये FRs TPU के डीपोलीमराइजेशन को उत्प्रेरित करते हैं और तेजी से पिघले हुए चिपचिपाहट को कम करते हैं, जिससे टपकता बढ़ जाता है। टपकाव सामग्री को लौ क्षेत्र से हटा देता है और लौ को बुझाने में मदद करता है। इन FRTPU के लिए प्राप्त निम्न चार मान और ओपन-सेल फोम आकारिकी से पता चलता है कि वे गैस चरण में काम कर रहे हैं।

एक अन्य खंड में फॉस्फेट की मात्रा (FR5, FR6, FR7, और FR8 लेबल वाले FRs) युक्त एडिटिक्स की एक श्रृंखला को संश्लेषित किया गया था। इन FRs को TPU के साथ मिश्रित किया गया था, और मिश्रणों (FRTPUs) को 0.5-2.0 wt % की फॉस्फोरस सामग्री का चयन करके तैयार किया गया था। उसके बाद, स्ट्रिप्स का विश्लेषण UL-94 वर्टिकल बर्निंग और एलओआई टेस्ट द्वारा किया गया। UL-94 परीक्षण के परिणामों से पता चला है कि FR5TPU2 में, टपकने की घटना देखी गई थी, हालांकि FR6TPU2, FR7TPU2, और FR8TPU2 में, टपकना पूरी तरह से बंद हो गया था। टीपीयू के साफ नमूने के लिए, ज्वलनशील टपकाव के साथ आग लगने के तुरंत बाद आग लग जाती है। चार अवशेषों की सतह

आकारिकी का अध्ययन SEM द्वारा किया गया था, और यह पाया गया कि FR5TPU, FR6TPU, और FR7TPU बंद-कोशिका झागदार आकारिकी बनाते हैं, जिसका अर्थ है कि वे संघनित चरण में कार्य कर रहे हैं। हालांकि, FR8TPU एक ओपन-सेल झागदार आकारिकी बनाता है, जो गैस चरण का सुझाव देता है, और EDX विश्लेषण द्वारा फॉस्फोरस की उपस्थिति TPU मैट्रिक्स में इस अणु की संघनित चरण गतिविधि का समर्थन करती है।

अंतिम खंड में, 2,6,7-ट्राईऑक्सा-1-फॉस्फैबिसाइक्लो [2.2.2] ओकटाइन, 4- (एज़िडोमिथाइल) के बीच एल्काइन-एज़ाइड क्लिक रसायन का उपयोग करके फॉस्फेट फंक्शनल सिलिका (PhosFS) पर आधारित एक नया सहक्रियात्मक लौ रिटार्डेंट संश्लेषित किया गया था।)-1-ऑक्साइड, और प्रोपरगिल फंक्शनल सिलिका (PFS)। क्रियाशील सिलिका पर फॉस्फेट की उपस्थिति की पुष्टि विभिन्न तकनीकों जैसे सॉलिड-स्टेट ^{31}P NMR, फूरियर ट्रांसफॉर्म इंफ्रारेड स्पेक्ट्रोस्कोपी (FTIR), थर्मोग्रैविमेट्रिक एनालिसिस (TGA), और इंडक्टिवली कपल्ड प्लाज्मा-मास स्पेक्ट्रोमेट्री (ICP-MS) द्वारा की गई थी। फ्लेम-रिटार्डेंट टीपीयू कंपोजिट ने उत्कृष्ट फ्लेम रिटार्डेंसी का प्रदर्शन किया, जिसे यूएल-94 और एलओआई परिणामों द्वारा प्रदर्शित किया गया था। SEM परिणामों से पता चला कि PhosFS को शामिल करने पर, TPU/PhosFS नमूनों के चार अवशेष शुद्ध TPU नमूने की तुलना में अधिक कॉम्पैक्ट होते हैं। ईडीएक्स और एफटीआईआर का सुझाव है कि फॉस्फेट कार्यात्मक सिलिका का समावेश दहन के दौरान एक समान और घने चार के उत्पादन के कारण आंतरिक टीपीयू मैट्रिक्स के दहन को प्रतिबंधित करने के लिए एक भौतिक अवरोध बनाकर एक सहक्रियात्मक प्रभाव उत्पन्न करता है।

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LIST OF ABBREVIATIONS AND SYMBOLS

%	Percent
δ	Chemical shift
s	Singlet
d	Doublet
br	Broad signal
vs	Versus
cm	Centimeter
mm	millimeter
g	Gram
mg	Milligram
mol	Mole
mmol	Millimole
M	Molar
mL	Millilitre
ppm	Part per million
$^{\circ}\text{C}$	Degree centigrade
h	Hours
Min	Minutes
ν	Frequency
MHz	Megahertz
λ_{max}	Absorption maximum
T_5	Decomposition temperature at 5% weight loss

T_d	Decomposition temperature
e.g.	For example
i.e.	That is
D	Dispersity
M_w	Weight average molecular weight
M_n	Number average molecular weight
A_{eff}	Adsorption efficiency
N_2	Nitrogen
Ar	Argon
APTS	3-Aminopropyltriethoxysilane
AFS	Amine functionalized silica
DCM	Dichloromethane
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
FT-IR	Fourier transform infrared spectroscopy
PFS	Propargyl functionalized silica
PhosFS	Phosphate functionalized silica
GPC	Gel permeation chromatography
HRMS	High resolution mass spectra
ICPMS	Inductively coupled plasma mass spectrometry
LOI	Limiting oxygen index
NMR	Nuclear magnetic resonance

POCl ₃	Phosphorous oxychloride
SEM	Scanning electron microscope
SEM-EDX	Scanning electron microscopy-energy dispersive X-ray spectroscopy
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TMS	Tetramethylsilane
TEOS	Tetraethoxysilane
TPU	Thermoplastic polyurethane
TLC	Thin layer chromatography
UV-Vis	Ultraviolet-visible
UL-94	Underwriter laboratory-94
CH ₃ COOH	Acetic acid
(CH ₃ CO) ₂ O	Acetic anhydride
CCl ₄	Carbon tetrachloride
CHCl ₃	Chloroform
(CH ₃) ₂ O	Diethyl ether
CH ₂ Cl ₂	Dichloro methane
CH ₃ OH	Methanol
EtOH	Ethanol
HCl	Hydrochloric acid
HBr	Hydrobromic acid
H ₂ SO ₄	Sulphuric acid
H ₂ O	Water
NaH	Sodium hydride

NaOH	Sodium Hydroxide
Na ₂ CO ₃	Sodium Carbonate
Na ₂ SO ₄	Sodium Sulphate
KOH	Potassium Hydroxide