

**STUDIES ON CURING KINETICS AND THERMAL
BEHAVIOR OF PHTHALONITRILE RESIN USING
AROMATIC AMINES**

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JULY 2021

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AROMATIC AMINES**

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

JULY 2021

Dedicated to my family

CERTIFICATE

This is to certify that the thesis entitled, “**Studies on curing kinetics and thermal behavior of phthalonitrile resin using aromatic amines**” being submitted by **Mr. Devendra Kumar** to Indian Institute of Technology Delhi for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by him. Mr. Devendra Kumar has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my 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 other University or Institute for the award of any other degree or diploma.

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ACKNOWLEDGEMENTS

I wish to express my heartiest gratitude to my supervisor, Prof. (Mrs.) Veena Choudhary for her invaluable guidance and constant encouragement. Her caring attitude and co-operation have been monumental throughout my research. Through her wealth of knowledge, direction, and leadership I have been able to expand my knowledge in the area of Polymer Science and Technology. I also wish to express my profound sense of gratitude to my co-supervisor Dr. Sampa Saha for her valuable suggestions, constant encouragement and motivation throughout the research work.

I am thankful to Prof. Josemon Jacob, Prof. S.N. Maiti, Prof. A.K.Ghosh, Prof. B.K. Sathpathy, Dr. B. Tripathi and Dr. Leena Nebhani for their constant encouragement and help throughout my research work. I express my thanks to Dr. B. P. Singh of National Physical Laboratory, Delhi, India, for providing facilities to carry out experiments in their lab.

It is a pleasure for me to express my gratitude towards my entire senior that prevails in the laboratory is due to the wonderful colleagues. Their warm affection, support during tough times, nice scientific interactions, involvement and conscious as well as unconscious help have rendered my research life a bountiful time. It was really fun to work in their association. I would like to thank all my seniors Dr. Rajendra Malik, Dr. Sandeep Nath Tripathi, Dr. Pawan Verma, Dr. Sampat Singh Chouhan, Dr. V.P. Singh, Dr. Rajendra K. Singhla, Dr. Tahir Zafar, Dr. Arun Choudhary, Dr. Sanjeev Kumar, Dr. Manash, Dr. Manisha, Dr. Priyanka, Dr. Savita Meena, Dr. Rishi Sharma, Dr. Rakesh Kr. Kachhap, Dr. Meenakshi Verma, Dr. Astha Garhwal, Dr. Achla, Dr. Bindu Manchanda, Dr. Ranjana, Dr. Harjeet Singh Jaggi, Dr. Abhishek Gandhi, Dr. Shilpi, Dr. Debanga B. Konwar, Dr. Bhavna Sharma, Dr. Banpreet Kaur, Dr. Sabapathi, Dr. Swarna, Dr. Pragati, Dr. Harshita, my colleagues, Reshu, Dr. Anindya Dutta, my juniors, Smruti Mishra,

Sumbul Hafeez, Ifra, Agni Kr. Biswal, Sucharita, Prajesh, Shikha, Subhra, Shivani, Ujjwal, Srijita, Ashok Bakshi, Harshal, Vikrum Thakur, Vishwajit, Nidhi, Meenakshi, Ashwariya, Kalpana, Shaifali, Amit Kumar from IIT Delhi for their constant encouragement.

My special thanks to Mr. Surender Sharma, Mr. Shivkant, Mr. Ashok Kapoor, Mr. Islam, Mr. Gajraj, Mrs. Shalani Arora, Pramod and Sudhir Pandey for their immediate help whenever needed.

My family members deserve special attention for their support and persistent confidence in me, but I don't have words to express my gratitude for them. I am extraordinarily fortunate to have the blessings of my parents who always bless me with the shower of their love, providing inner strength, patience, emotional support and making sacrifices for my successful career. I am thankful to my younger brother Rajan Mogha to continuously appreciating me. I express my heartiest thanks to my brother Mr. Jitendra Kumar for their encouragement, constant support to complete this task and patience which enable me to pursue my career

Finally, I would like to thank everyone who helped me in the successful compilation of thesis, as well as expressing my apology that I could not mention personally one by one.

I would like to acknowledge the financial assistance received from "CSIR" which has helped me to pursue my Ph.D. without any stress.

Last but not the least I am thankful to the Almighty God in helping me to accomplish this task.

Devendra Kumar

ABSTRACT

Phthalonitrile resins are unique high-temperature, high-performance thermosetting materials with excellent properties, such as high thermal and thermo oxidative properties, flame resistance, low water absorption and high glass-transition temperature. However, the major disadvantage of phthalonitriles is high curing temperature and long curing times with a narrow processing window which restrict its use in applications where void free product is one of the requirements, particularly for durable applications such as aircrafts, adhesive and coating materials. Other requirements of phthalonitrile resins are the ease of polymerization and processability. So the perfect use of phthalonitrile resins is to understand and control the curing process and choose the correct process conditions and parameters to obtain the desired properties.

The objective of the present work was to synthesize the imide containing bisphthalonitrile monomers and investigate the curing kinetics and thermal behavior of bisphthalonitrile/aromatic amine system. Thesis comprises of six chapters. In chapter 2, synthesis and characterization of three imide containing phthalonitrile monomers prepared by reacting 4, 4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA)/ 4, 4'-oxydiphthalic anhydride (ODPA) /bisphenol-A dianhydride (BPADA) with 4-(4'-aminophenoxy) phthalonitrile is described. The monomers have been designated as FIPN, ODPA-PN and Bis-ADPN respectively. All the synthesized monomers were characterized by elemental analysis, FT-IR, ¹H-NMR and ¹³C-NMR to confirm the structure of the monomers. The thermal characterization of monomers was done using DSC and TGA to confirm the melting temperature and decomposition temperature, respectively.

In chapter 3, the curing behavior of monomers in absence or presence of diamines (4, 4'-diaminodiphenylsulfone (DDS) / 4, 4'-Oxydianiline (ODA)) was investigated using DSC at heating rate 10 °C/min. DSC scans of neat monomer showed a melting endotherm and the melting point was found to be dependent on the structure of monomer. No exotherm was observed in the DSC scans of monomers. However, in the presence of 10 weight percent of amine, endotherm (due to melting) and exotherm due to curing was observed in all the samples. The effect of different wt% (2.5, 5, 10, and 20 wt. %) of ODA on the curing behavior of FIPN monomer was studied by recording DSC traces from room temperature to 350 °C at a scanning rate of 10 °C/min. in nitrogen atmosphere. The heat of curing reaction was maximum and the curing temperature was lowest for FIPN monomer in the presence of 10 weight percent of ODA. Therefore in curing kinetics studies, concentration of diamine was kept constant at 10 weight %.

The curing kinetics of synthesized bisphthalonitrile monomers having imide linkage using 10 weight % of 4, 4'-diaminodiphenylsulfone (DDS) /4, 4'-oxydianiline (ODA) as curing agent was investigated by recording non-isothermal differential scanning calorimetric (DSC) scans at heating rates of 5 °C, 10 °C, 15 °C and 20 °C/min. Activation energy for bisphthalonitrile/ DDS and bisphthalonitrile/ODA system was calculated using Starink and Kissinger–Akahira–Sunose isoconversional method. Activation energy (E_a) was found to be dependent on the structure of monomer and curing agent. . E_a was minimum in case of Bis-ADPN/DDS or Bis-ADPN/ODA. An autocatalytic model for the phthalonitrile/diamine resin was confirmed and there was a good agreement between the calculated experimental data.

Chapter 4 discusses the effect of isothermal curing of bisphthalonitrile resins in presence of 10 weight percent of diamines on the glass transition temperature and thermal stability. The bisphthalonitrile/ amines composition was cured isothermally according to designed curing

schedule for particular samples. The structural changes during the curing were analyzed using FT-IR spectra. The glass transition temperature increased with increasing the curing temperature and time. It was also found to be dependent on structure of monomer and diamine. Thermal stability of phthalonitrile resins, cured isothermally was evaluated by recording thermo-gravimetric traces in nitrogen atmosphere. The relative thermal stability of cured phthalonitrile resin was evaluated by comparing the initial decomposition temperature (IDT), the temperature of maximum weight loss (T_{max}), the final decomposition temperature (FDT), decomposition temperature at 5,10,20 % mass loss and % char yield at 800°C. Single step decomposition was observed in all the cured samples. All the samples were stable upto 450 °C and a significant mass loss occurred beyond this temperature. The Bis-ADPN, ODPN-PN, and FIPN cured with ODA had % char in the range of 62-64%. The Bis-ADPN, ODPN-PN, and FIPN cured with DDS had % char in the range of 60-62%. The activation energy of decomposition was related to energy difference between transition and initial state in TG traces.

In chapter 5, an amino containing phthalonitrile monomer (3-APN) was synthesized and characterized (NMR, FT-IR and DSC) to prepare the carbon foam using chemical blowing agent through direct carbonization. Morphological study of foam was done using SEM. Raman spectroscopy and FT-IR monitored the structural changes during carbonization of foam. Thermal characterization of foam was done by TGA. The EMI shielding effectiveness was measured in the frequency range of 8.2-12.4 GHz (X- band frequency) and 12.4-18 GHz (Ku band frequency) to investigate their potential as effective EMI shielding materials. The EMI shielding of foam was absorption dominant and the total EMI shielding effectiveness of carbonized foam [Carbonized at 800°C] was -19 dB in the X-band and -23 dB in the Ku band. Summary, conclusions and suggestions for future work are given in chapter 6 of thesis.

सार

थैलोनायट्राइल रेजिन उत्कृष्ट गुण जैसे उच्च थर्मल और थर्मो ऑक्सीडेटिव गुण, लौ प्रतिरोध, कम जल अवशोषण और उच्च ग्लास-संक्रमण तापमान के साथ अद्वितीय उच्च तापमान, उच्च प्रदर्शन थर्मोसेटिंग सामग्री हैं, हालांकि, थैलोनायट्राइल का प्रमुख दोष उच्च क्यूरिंग तापमान और एक संकीर्ण प्रसंस्करण विंडो के साथ लंबे समय तक क्यूरिंग का समय है जो उन अनुप्रयोगों में इसके उपयोग को प्रतिबंधित करता है जहां शून्य मुक्त उत्पाद आवश्यकताओं में से एक है, विशेष रूप से टिकाऊ अनुप्रयोगों जैसे कि एयरक्राफ्ट, एडहेसिव और कोटिंग सामग्री के लिए। थैलोनायट्राइल रेजिन की अन्य आवश्यकताएं पोलीमराइजेशन और प्रोसेसिबिलिटी में आसानी हैं। इसलिए थैलोनायट्राइल रेजिन का सही उपयोग क्यूरिंग की प्रक्रिया को समझना और नियंत्रित करना और वांछित गुण प्राप्त करने के लिए सही प्रक्रिया की स्थिति और मापदंडों का चयन करना है।

वर्तमान रिसर्च कार्य का उद्देश्य इमाइड युक्त बिस्थैलोनायट्राइल मोनोमर्स को संश्लेषित करना और बिस्थैलोनायट्राइल/एरोमैटिक अमाइन सिस्टम की क्यूरिंग काइनेटिक्स और थर्मल व्यवहार की इन्वेस्टिगेशन करना था। थीसिस में छह अध्याय हैं। अध्याय दो में, ४, ४'-(हेक्साफ्लोरोइसोप्रोपाइलिडीन) डिथैलिक एनहाइड्राइड (६ एफडीए) / ४, ४'-ऑक्सीडिथैलिक एनहाइड्राइड (ओडीपीए) / बिस्फेनॉल-ए डायनहाइड्राइड (बीपीएडीए) को ४-(४'-एमिनोफेनॉक्सी) थैलोनायट्राइल के साथ प्रतिक्रिया करके तैयार किए गए तीन इमाइड युक्त थैलोनायट्राइल मोनोमर्स का संश्लेषण और लक्षण का वर्णन किया गया है। मोनोमर्स को क्रमशः एफ आइ पी एन, ओ डी पी ए-पीएन और बिस-एडीपीएन के रूप में नामित किया गया है। सभी संश्लेषित मोनोमर्स की संरचना की पुष्टि करने के लिए संरचना को एलिमेंटल अर्नॉलिसिस, एफटी-आइआर, प्रोटॉन एनएमआर और कार्बन एनएमआर के द्वारा कॅरक्टराइज़्ड किया गया। मोनोमर्स का थर्मल लक्षण वर्णन क्रमशः गलनांक और डीकंपोज़िशन टेंपरेचर की पुष्टि करने के लिए डीएससी और टीजीए का उपयोग करके किया गया।

अध्याय ३ में, डायअमाइन (४, ४'- डाइयमिनाडिफीनाइलसाउल्फोन (डीडीएस) / ४, ४'-ऑक्सिडीयेनिलीन (ओडीए)) की अनुपस्थिति या उपस्थिति में मोनोमर्स के क्यूरिंग व्यवहार की इन्वेस्टिगेशन डीएससी का उपयोग हीटिंग दर १० डिग्री सेल्सियस/मिनट की दर पर गई। नीट मोनोमर के डीएससी स्कैन में एक गलनांक एंडोथर्म दिखाया गया और गलनांक मोनोमर की संरचना पर निर्भर पाया गया। मोनोमर्स के

डीएससी स्कैन में कोई एक्जोथर्म नहीं देखा गया। हालांकि, सभी सेम्पल्स में १० वेट प्रतिशत अमाइन की उपस्थिति में, एंडोथर्म (मेल्टिंग के कारण) और क्यूरिंग के कारण एक्सोथर्म देखा गया था। एफआईपीएन मोनोमर के क्यूरिंग व्यवहार पर ओडीए के विभिन्न वेट प्रतिशत (२.५, ५, १०, और २० वेट प्रतिशत) के प्रभाव का अध्ययन १० डिग्री सेल्सियस/मिनट की स्कैनिंग दर पर रूम तापमान से ३५० डिग्री सेल्सियस तक डीएससी ट्रेसस रिकॉर्ड नाइट्रोजन अट्मॉस्फियर में करके किया गया। ओडीए के १० वेट प्रतिशत की उपस्थिति में एफआईपीएन मोनोमर की प्रतिक्रिया की गर्मी अधिकतम थी और क्यूरिंग तापमान सबसे कम था। इसलिए क्यूरिंग काइनेटिक्स अध्ययन के लिए, डाय अमाइन की सांद्रता को १० वेट प्रतिशत पर स्थिर रखा गया था। क्यूरिंग एजेंट के रूप में, ४, ४'-डाइयमिनाडिफीनाइलसाउल्फोन (डीडीएस) / ४, ४'-ऑक्सिडीयेनिलीन (ओडीए) के १० वेट प्रतिशत का उपयोग करके इमाइड लिंकेज वाले संश्लेषित बिस्थैलोनायट्राइल मोनोमर्स की क्यूरिंग काइनेटिक्स इन्वेस्टिगेशन नॉन-आइसोथर्मल डिफरेंशियल स्कैनिंग कैलोरीमेट्रिक (डीएससी) स्कैन को हीटिंग दर (५ डिग्री सेल्सियस, १० डिग्री सेल्सियस, १५ डिग्री सेल्सियस और २० डिग्री सेल्सियस/मिनट) पर रिकॉर्ड करके की गई थी। बिस्थैलोनायट्राइल/डीडीएस और बिस्थैलोनायट्राइल/ओडीए सिस्टम के लिए सक्रियण ऊर्जा स्टैरिक और किसिंजर-अकाहिरा-सुनोज आइज़ो-कॉनवेरसिओनल विधि का उपयोग कर कॅल्क्युलेटेड की गई। सक्रियण ऊर्जा को मोनोमर और क्यूरिंग एजेंट की संरचना पर निर्भर पाया गया। बीस-एडीपीएन/डीडीएस या बीस-एडीपीएन/ओडीए के केस में सक्रियण ऊर्जा न्यूनतम था। थैलोनायट्राइल /अमाइन के लिए एक ऑटोकैटलिटिक मॉडल की पुष्टि की गई और गणना और परिकलित प्रयोगात्मक डेटा के बीच एक अच्छा समझौता था।

अध्याय ४ ग्लासट्रान्ज़िशन-टेंपरेचर और थर्मल स्टेबिलिटी पर डायमाइन (१० वेट प्रतिशत) की उपस्थिति में बिस्थैलोनायट्राइल रेजिन के आइज़ोथर्मल क्यूरिंग का प्रभाव पर चर्चा करता है। बिस्थैलोनायट्राइल/अमाइन को पार्टिक्युलर सॅपल्स के लिए डिज़ाइन किए गए क्यूरिंग शेड्यूल के अनुसार आइज़ोथर्मल क्यूर्ड किया गया था। आइज़ोथर्मल क्यूरिंग के दौरान संरचनात्मक परिवर्तनों का विश्लेषण एफ टी-आइआर स्पेक्ट्रा का उपयोग करके किया गया था। क्यूरिंग तापमान और समय में वृद्धि के साथ ग्लासट्रान्ज़िशन तापमान में वृद्धि हुई। यह मोनोमर और डाइमीन की संरचना पर भी निर्भर पाया गया। नाइट्रोजन वातावरण में थर्मो-ग्रेविमेट्रिक ट्रेस रिकॉर्ड करके आइज़ोथर्मल क्यूर्ड थैलोनायट्राइल रेजिन की थर्मल स्टेबिलिटी का मूल्यांकन किया गया था।

प्रारंभिक अपघटन तापमान, अधिकतम वजन तापमान, अंतिम अपघटन तापमान, ५, १०, २० प्रतिशत वेट लॉस पर और ८०० डिग्री सेल्सियस पर प्रतिशत चार यील्ड की तुलना करके आइज़ोथर्मल क्यूर्ड थैलोनोयट्राइल रेजिन की सापेक्ष थर्मल स्टेबिलिटी का मूल्यांकन किया गया था। सभी क्यूर्ड रेजिन में एकल चरण अपघटन देखा गया। सभी सैंपल्स ४५० डिग्री सेल्सियस तक स्थिर थे और इस तापमान से परे एक सिग्निफिकेंट वेट लॉस हुआ। ओडीए से साथ क्यूर्ड हुए बिस-एडीपीएन, ओ डी पी ए-पीएन, और एफ आइ पी एन में ६२-६४ प्रतिशत की सीमा में प्रतिशत चार था। डीडीएस के साथ क्यूर्ड हुए बीएस-एडीपीएन, ओडीपीए-पीएन और एफआईपीएन में ६०-६२ प्रतिशत की सीमा में प्रतिशत चार था। अपघटन की सक्रियता ऊर्जा टीजी ट्रेस में संक्रमण और प्रारंभिक अवस्था के बीच ऊर्जा अंतर से संबंधित थी।

अध्याय ५ में, सीधे कार्बोनाइजेशन के माध्यम से रासायनिक ब्लोइंग एजेंट का उपयोग करके कार्बन फोम तैयार करने के लिए अमीनो युक्त फ़ेथलोनिट्राइल मोनोमर (३-एपीएन) को संश्लेषित और कॅरक्टराइज़्ड (एनएमआर, एफटी-आईआर और डीएससी) किया गया था। रमन स्पेक्ट्रोस्कोपी और एफटी-आईआर ने फोम के कार्बोनाइजेशन के दौरान संरचनात्मक परिवर्तनों की निरीक्षण की। फोम का थर्मल लक्षण वर्णन टीजीए द्वारा किया गया। ईएमआई परिरक्षण प्रभावशीलता को प्रभावी ईएमआई परिरक्षण सामग्री के रूप में उनकी क्षमता की जांच करने के लिए ८.२-१२.४ गीगाहर्ट्ज़ (एक्स-बैंड आवृत्ति) और १२.४-१८ गीगाहर्ट्ज़ (केयू बैंड आवृत्ति) की आवृत्ति रेंज में मापा गया था। फोम का ईएमआई परिरक्षण अवशोषण प्रभावी था और कार्बोनेटेड फोम [८०० डिग्री सेल्सियस पर कार्बनयुक्त] की कुल ईएमआई परिरक्षण प्रभावशीलता एक्स-बैंड में -१९ डीबी और केयू बैंड में -२३ डीबी थी। थीसिस के अध्याय ६ में भविष्य के कार्यों के लिए सारांश, निष्कर्ष और सुझाव दिए गए हैं।

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List of Abbreviations and Symbol

ODA	4,4'-Oxydianiline
DDS	4,4'-diaminodiphenyl sulfone
ODPA	4,4'-oxydiphthalic anhydride (ODPA)
6FDA	4,4'-(hexafluoroisopropylidene) diphthalic anhydride
BPADA	4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride)
DMF	N, N-dimethylformamide
NPN	4-nitrophthalonitrile
APPH	4-(4-aminophenoxy) phthalonitrile
FT-IR	Fourier transform infrared spectroscopy
NMR	Nuclear magnetic resonance
WAXD	Wide angle X-ray diffraction
KBr	Potassium bromide
FIPN	6FDA based imide containing bisphthalonitrile
Bis-ADPN	BPADA based imide containing bisphthalonitrile
ODPA-PN	ODPA based imide containing bisphthalonitrile
DMSO-d ₆	Deuterated dimethyl sulfoxide
TMS	Tetramethylsilane
T _m	Melting point
T _g	Glass transition temperature
DSC	Differential Scanning Calorimetry
TGA	Thermogravimetric Analysis
CDCl ₃	Deuterated chloroform
mL	Milliliter
α	Degree of conversion
T _{α}	Degree of conversion at any particular temperature
$\Delta H_{T\alpha}$	enthalpy of partially cured samples (reaction up to time T _{α})
β	Heating rate (°C/min)
ΔH_{Total}	total enthalpy of curing

E_a	activation energy
m, n	Order of reaction
T_i	Initial temperature where the first heat evolved was detected
(T_{onset})	obtained by drawing a tangent to the initial portion of exotherm
T_p	Peak exotherm temperature
(T_{end})	End temperature
ΔH	exothermic enthalpy
R^2	Correlation coefficient
A	pre-exponential factor
$CHCl_3$	Chloroform
DMAC	dimethylacetamide
DCM	Dichloromethane
T_5	Degradation-temperature at mass loss of 5%
T_{10}	Degradation-temperature at mass loss of 10%
LOI	Limiting oxygen index
DTG	Derivative thermogravimetric
IPDT	Integral procedural decomposition temperature
E	Activation energy of decomposition
FDT	Final decomposition temperature
T_{max}	Temperature at which maximum degradation occurs
A^*	area under the TG trace/area bounded by TG trace
IDT	Initial decomposition temperature
α	Fraction reacted
T_i ,	the temperature of inception of reaction
T_f ,	temperature at the point of inflection on the thermo-gram
σ	Conductivity
δ	Skin depth
R	R Resistance
ϵ'	Real dielectric permittivity
ϵ''	Imaginary dielectric permittivity
θ	Bragg diffraction angle

SEM	Scanning electron microscopy
VNA	Vector network analyzer
EMI	Electromagnetic interference
EMI SE	Electromagnetic interference shielding effectiveness
SER	Reflection loss
SEA	Absorption loss
SEM	Multiple reflections
SET	Shielding effectiveness
TEM	Transmission electron microscopy
CBA	chemical blowing agent
3-APN	3-aminophenoxy phthalonitrile
PN	Phthalonitrile