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Synthesis, Characterization and Thermal Degradation Study of 2-Nitroso-1napthol- 4, 4' Diaminodiphenyl Ether-Formaldehyde Terpolymer Resin

M. B. Dewase[1], R. N. Singru[2], M. I. M. Siddique[3]
Department of Chemistry
[1]*Sarvodaya Mahavidyalaya Sindewahi, Chandrapur, Maharashtra, India,*
[2]*Tai Golwalkar Mahavidyalay, Ramtek, Nagpur, Maharashtra, India,*
[3]*Institute of Science Nagpur, Maharashtra, India,*

Abstract: ***The Terpolymer resin (2N, 1N-4, 4'DADPEF-1) was synthesized by polymerization of monomers 2-Nitroso-1Napthol and 4, 4'Diaminodiphenyl Ether with formaldehyde in 1:1:2 molar proportion. The terpolymer resin was characterized by elemental analysis, spectral studies i.e. UV-Visible, FTIR and NMR spectroscopy. The surface characteristics were examined through scanning electron microscopy (SEM) at different magnifications. The tentative structure of the terpolymer was confirmed on the basis of spectral data. Freeman – Carroll and Sharp- Wentworth methods have been applied for the calculation of kinetic parameters. The thermogravimetric analysis (TGA) was performed to evaluate the thermal degradation characteristics and to ascertain its thermal stability. The residue left over after complete decomposition was found to be negligible (0.90% found and 1.07% calculated).***

Keywords: Terpolymer, Spectral study, Kinetic parameters, TGA analysis, **spectroscopy**

I. INTRODUCTION

Polymers are one of the most important materials which have a great impact on modern life. Polymer science and technology has been developing rapidly due to its vast applications like electronic controls, insulating materials, protective adhesives, aerospace industries, food packaging, health, housing and transportation and many more. The characterization of terpolymers on the basis of elemental analysis, SEM, spectral studies i.e. UV-Visible, FTIR and NMR spectroscopy was reported by various coworkers [1-3].TGA measurements are used primarily to determine the thermal and/or oxidative stabilities of materials as well as their compositional properties.

Thermally stable terpolymers recently become beneficial to polymer chemist due to its superior characteristics. Many researchers were tried to improve the thermal stability by changing the monomer composition in polymer synthesis. Terpolymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials. Phenolic resins are known for their wide applications in various areas because of their thermal stability, easy availability, cost effectiveness, and some of their excellent properties.

The thermal stability of terpolymers has been extensively studied by employing the method of thermogravimetric analysis (TGA) by various authors and thermodynamic parameters like entropy change, free energy change, apparent entropy and frequency factor are calculated [4-6]. The results obtained are in good agreement with that of literature. In the present investigation, it has been planned to study the Synthesis, characterization and nonisothermal thermogravimetric analysis of terpolymer derived from 2-Nitroso-1Napthol ,4,4'Diaminodiphenyl Ether with Formaldehyde which has not been reported so far in literature.

II. MATERIALS

All Chemicals, 2-Nitroso-1Napthol and 4, 4' Diaminodiphenyl Ether were of A.R. grade purity which were purchased from Merck and Loba chemicals. Formaldehyde (37%) was purchased from Merck Chemicals, India. The used solvents dimethylsulphoxide (DMSO), acetone, diethyl ether petroleum ether methanol were procured from Merck, India. Double distilled water was used for complete work.

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A. Synthesis

This new terpolymer resin 2N-1N4,4'DADPEF-1 was synthesized by condensing 2-Nitroso 1Napthol (1.73 g, 0.1 mol), 4,4'Diaminodiphenyl ether (2.00 g, 0.1 mol) and formaldehyde (7.4 ml, 0.2 mol) in the molar ratio of 1:1:2 in the presence of 2M (200 ml) HCl as a catalyst at 134ºC ± 2ºC for six hours in round bottom flask attached with water condenser and was heated in oil bath with occasional shaking to ensure thorough mixing. The temperature of oil bath was controlled by dimerstat. The resinous black product obtained was removed immediately as soon as the reaction was over and hot mixture poured into ice cold water. The product was filtered and washed with hot water. Then with 10 % methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove copolymer which might be present along with 2N-1N4, 4'DADPEF-1 terpolymer. The product so obtained was further purified by reprecipitation technique. The reaction is shown as follows in Fig.1and Table 1 [7-9].

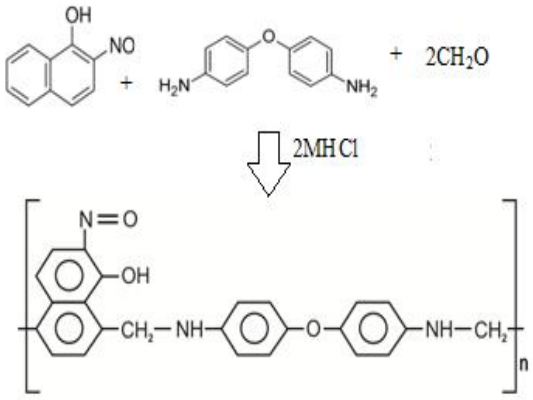


Fig.1: Synthesis of terpolymer resin 2N-1N4,4'DADPEF-1

Table1 Synthesis and physical details of 2N-1N4,4'DADPEF-1 terpolymer

Terpolymer	Reactants					
2N-1N 44' DADPEF-I	2-nitroso 1-napthol (2N-1N) Mole	4,4' diamino Diphenyl Ether (4,4'DADPE) mole	Formal-dehyde (F) mole	Catalyst 2M HCl (ml)	Yield % & Color	Melting Point K
	0.1	0.1	0.2	200	75 & black	474

III. SPECTRAL AND THERMAL STUDIES

Newly synthesized terpolymer was subject to elemental analysis for carbon, hydrogen and nitrogen on Perkin Elmer 2400 Elemental Analyser. Infra-red spectra of newly synthesized terpolymer resins have been scanned on Perkin-Elmer spectrophotometer model RX-I having resolution in KBr pallets in the wave number region of 4000 – 250 $cm^{-1.}$ ^{1}H-NMR and ^{13}C-NMR studies were performed in dimethylsulphoxide as solvent on Bruker Advance-II 400 /100 MHz proton NMR spectrophotometer. These analytical and spectral studies were carried out at Sophisticated Analytical Instrumentation Facility (SAIF) Chandigarh, Punjab University. SEM of terpolymer samples have been scanned at 150x to 3500x magnification by JEOL JSM-6380A analytical scanning electron microscope, thermograms of terpolymer samples were recorded on Perkin Elmer Purix TGA, DTA-7 thermal analyzer at heating rate of 20K per minute and in nitrogen atmosphere up to 900ºC at School of Studies in Physics and Astrophysics, at National Institute of Technology (NIT), Raipur (M.P.).

IV. RESULTS AND DISCUSSION

A. Elemental Analysis

The results of elemental analysis for carbon, hydrogen, nitrogen and oxygen content are shown in Table 2 used to assign empirical formula and empirical weight for 2N-1N4,4'DADPEF-1 terpolymer. Composition of terpolymer was assigned on the basis of elemental analysis and was found to be in good agreement with that of calculated values.

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Table 2 Elemental analysis data of 2-N-1N 4,4' DADPEF-1 terpolymer.

Terpolymer resin	% of carbon	% of hydrogen	% of nitrogen	Empirical formula of repeated unit	Empirical formula weight
2-N-1N 4,4' DADPEF-I	72.36 (72.12)	5.03 (4.84)	10.55 (10.37)	$C_{24}H_{20}N_30_3$	398

B. Ft-Ir Spectra

The FT-IR spectrum of 2N-1N 44'DADPEF-1 terpolymer has shown in Fig.2 and frequencies in Table 3. A strong band appeared at 3615cm^{-1} which may be assigned due to free phenolic –OH. A broad and strong band appeared at 3204.8cm^{-1} which may be assigned due to the >NH stretching (sec. amine). A medium and sharp band displayed at 3064.8 cm^{-1} may be assigned due to the stretching vibration of aromatic C–H group. A weak band at 2924 cm^{-1} indicates the presence of a –C--H due to alkenes stretching group. A sharp band appearing in the region of 1385 cm^{-1} may be due to--N=O (nitroso) group. A medium band appearing at 1497 cm^{-1} indicates the presence of -C=C- (aromatic) group. A strong band appeared in the region of 1251 cm^{-1} which shows -C–O--C ester (aromatic) stretching. The presence of –C—N amine group due to medium peaks at 1175 cm^{-1}. The methylenic bridge shows broad and medium peaks for stretching vibration appearing at 2853.9cm^{-1}[13-15].

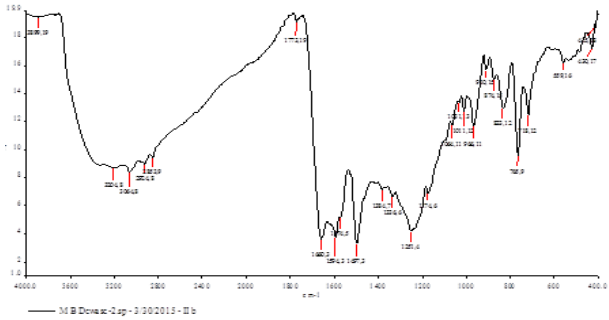


Fig. 2 : FT-IR spectra of 2N-1N 44'DADPEF-1 terpolymer resin

Table 3 FT-IR frequencies of 2N-1N 44'DADPEF-1 terpolymer resin.

Bond (group)	Expected wave number (cm^{-1})	Observed wave number (cm^{-1})
–OH (phenolic)	3600–3650	3615.0 b, st
>NH (amino.)	3100–3500	3204.8 sh, w
-C-H (aromatic)	3000–3100	3064.8 sh, m
-C-H (aliphatic)	2800-3000	2924.0
>CH_2 (methylene bridges)	2800-2950	2853.9 sh, m
-C=C-Aromatic ring	1475-1600	1497.3 sh, w
-N=O (nitroso)	1350-1550	1385.0

Sh = sharp; b = broad; st = strong; m = medium; w = weak.

C. ^{1}H-NMR Spectra

^{1}H-NMR spectrum **of** 2N-1N 44'DADPEF-1 terpolymer resin is presented in Fig 3. Spectrum reveals different patterns of peaks, since each of them possesses a set of protons having different proton environment. The significant singlet signal appearing at the region of 8.05 ppm is due to meta proton of Ar–H. A singlet observed at 7.2 ppm is due to proton of Ar–SH (thiophenol). Amino proton of –CH_2–NH–CH_2– linkage gives singlet that is observed at 6.7 ppm. Amino proton of aromatic amine gives singlet at 6.5 ppm. Methylenic proton of –NH–CH_2–CH_2– linkage gives triplet at 4.1 ppm. Singlet is observed at 2.5 ppm due to methylenic proton of Ar–CH_2–NH– linkage[16-18].

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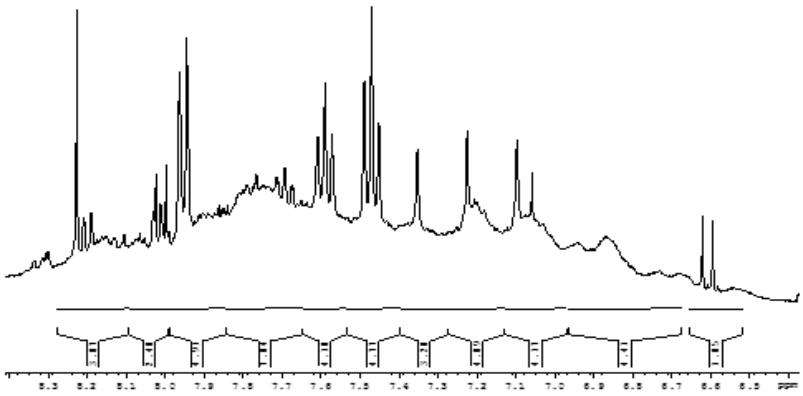


Fig 3 : ^{1}H-NMR spectrum of 2N-1N 44'DADPEF-1 terpolymer resin

D. SEM Analysis

The morphology of the reported resin sample 2N-1N 44'DADPEF-1 was investigated by SEM at different magnification Scanning electron micrographs of terpolymer resin has been recorded at 500X and 2000X magnification Fig. 4 a & b. The SEM exhibits spherulites with deep corrugation. At lower magnification the polymer shows spherulites and fridge model in which the crystals are arranged smaller in area with more closely packed structure. This indicates the crystalline nature of the polymer. The spherulites are typical crystalline formation and they grow in high viscous and concentrated solution at high magnification. The spherulites morphology of resin exhibit crystalline structure with deep corrugation which is clearly visible in SEM photographs of resin. These evidences indicate that more or less the resin shows amorphous character with less close packed surface having deep pits. The resin thus possesses amorphous and crystalline nature showing higher exchange capacity for metal ions [19-21] .

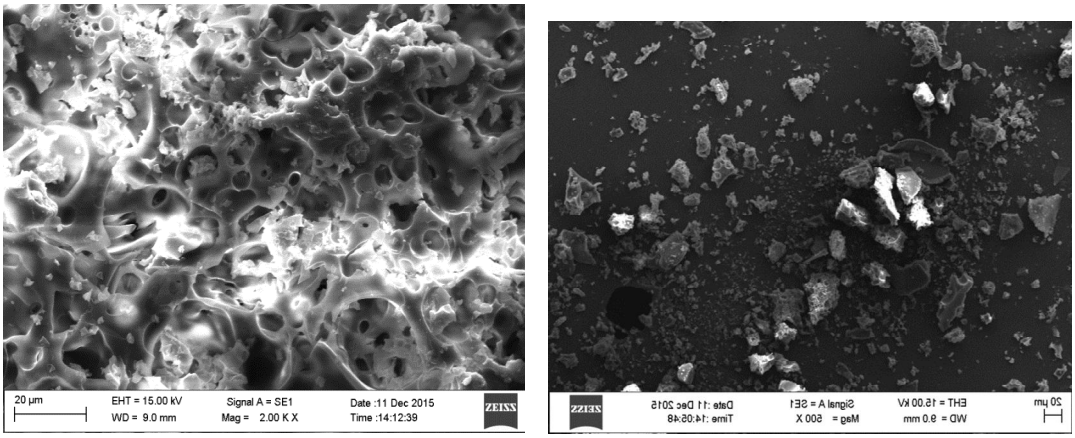


Fig. 4 a & b: SEM Micrographs of 2N-1N 44'DADPEF -1 Terpolymer Resin

E. Thermogravimetric Analysis

The modes of thermal degradation of the terpolymer 2N-1N 44'DADPEF-1 were analyzed using thermogravimetric analyzer at a heating rate of 20 °C/min in a static nitrogen atmosphere. From the results obtained by the degradation pattern as shown in Fig.5, activation energy (E_a), order of the reaction (n), entropy change (ΔS), free energy change (ΔF), apparent entropy (S^*), frequency factor (Z) were calculated by Freeman–Carroll and Sharp–Wentworth methods. The results of thermogravimetric analysis of 2N-1N 44'DADPEF-1 terpolymer are presented in Table 4. Thermogram of this terpolymer furnished three stage degradation in the temperature range 45-905^{o}C, after loss of one water molecule entrapped in the macromolecule from 45-110^{o}C,with mass loss of4.52% found and 4.40% calculated .The first stage of decomposition starts with continuous decrease in mass in the range 110-220^{o}C, corresponding to 19.85% mass loss found and19.47% calculated which represents the degradation of hydroxyl group (-OH) and nitroso group (-NO) attached to naphthalene aromatic ring. In the second stage of decomposition, cross linking sites develop a more strain in the terpolymer molecule which results a rapid mass loss of 54.77% found and 54.71% calculated in the temperature range of 220-550^{o}C, may be due to the decomposition of naphthalene ring with $-CH_2$ side chain. Third stage of decomposition

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represents the degradation of –NH side chains with diphenylether ring leads to the gradual mass loss in the temperature range 550 - 900°C.coresponding to the mass loss 99.10% found and 98.93% calculated. The residue left over after complete decomposition was found to be negligible (0.90% found and 1.07% calculated)[22-26].

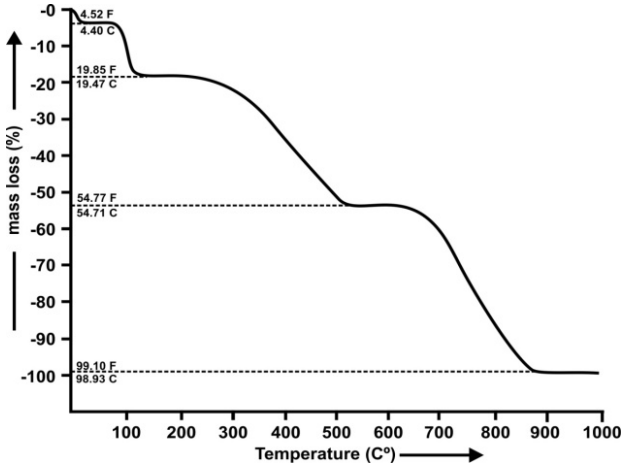


Fig. 5: Thermogram of 2N-1N 44'DADPEF -1 Terpolymer Resin

Evaluation of Kinetic Parameters by Sharp-Wentworth and Freeman-Carroll Method from TG Data:

$$\log \frac{dC/dT}{(1 - C)} = \log \alpha/\beta - \frac{Ea}{2.303RT}$$

For the calculation of activation energy Above equation gives a linear plot obtained by plotting log - log dC/dT/(1-C) as ordinate versus 1/T as on abscissa, then the slope and the intercept can be calculated.

Slope = -Ea/2.303R ∴ Ea = - 2.303 x R x Slope

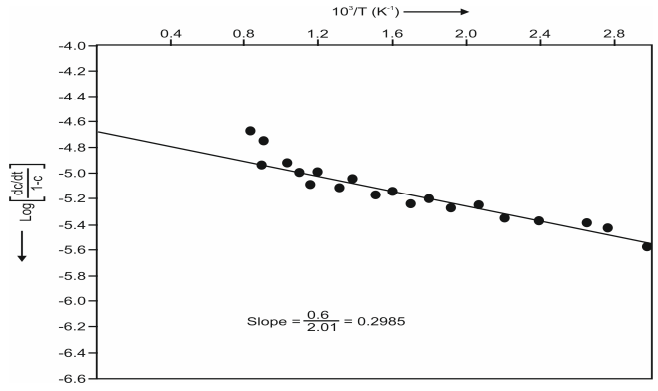


Fig.6 Sharp-Wentworth Plot of 2N-1N 44'DADPEF -1 Terpolymer Resin

Freeman-Carroll proposed an equation,

$$\frac{\Delta \log(dW/dt)}{\Delta \log Wr} = -\frac{Ea}{2.303\,R} \cdot \frac{\Delta(1/T)}{\Delta \log Wr} + n$$

A graph between $\frac{\Delta \log(dW/dt)}{\Delta \log Wr}$ versus $\frac{\Delta(1/T)}{\Delta \log Wr}$ Gives the value of E_a and n (order of reaction).

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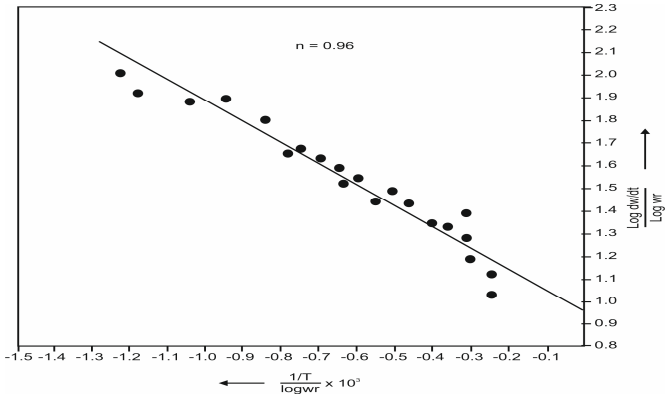


Fig.7 : Freeman-Carroll Plot of 2N-1N 44'DADPEF -1 Terpolymer Resin

By using the data obtained from above method, the different thermodynamic parameters like entropy change, free energy change, apparent entropy and frequency factor be calculated and reported in following Table 4 [27-29].

Table 4 Results of Thermogravimetric analysis of 2N-1N 44'DADPEF-1 Terpolymer Resin

Terpolymer Resin	Half decomposition temp. (K)	Energy of activation (E_a) kJ /mol. FC	SW	Entropy change (ΔS) J / mol	Free energy (ΔG) kJ /mol	Frequency factor (Z) sec.	Apparent entropy (S^*) J /mol	Order of reaction (n)
2N-1N 44'DADPEF -1	773	5.9356	5.7154	-318.51	252.15	912	-651.52	0.96

F. Discussion

The results obtained from Sharp-Wentworth and Freeman-Carroll methods were in good agreement with each other. This is expected since the decomposition of terpolymer is known not to be obeying first order kinetics perfectly as all points do not fall on the straight line in the graphs. The computed kinetic parameters are in fact only parameters of given mathematical equation which has the form of kinetic rate equation and which is used to fit the weight loss curves accompanying the thermal degradation of polymers in non-isothermal conditions. Low values of frequency factor revealed that decomposition reaction of terpolymer may be slow and no other possible reason can be given. This is further supported by the negative value of the entropy change. As a consequence these kinetic thermodynamic parameters are fictive from the point of view of chemical kinetics [30-35].

V. CONCLUSION

The proposed structure of newly synthesized terpolymer 2N-1N 44'DADPEF-1 has been confirmed which is supported by the results obtained by elemental analysis and spectral data. The values of kinetic parameter calculated from Sharp-Wentworth and Freeman-Carroll methods are also in similar order. The resin 2N-1N 44'DADPEF-1 started to degrade at 110^0C and completes at 900^0C, indicating that this terpolymer resin is thermally stable at elevated temperature therefore can be used in the polymer industry, automotive industry and other industry where need the polymer resistance to harsh environment and thermally stable polymers.

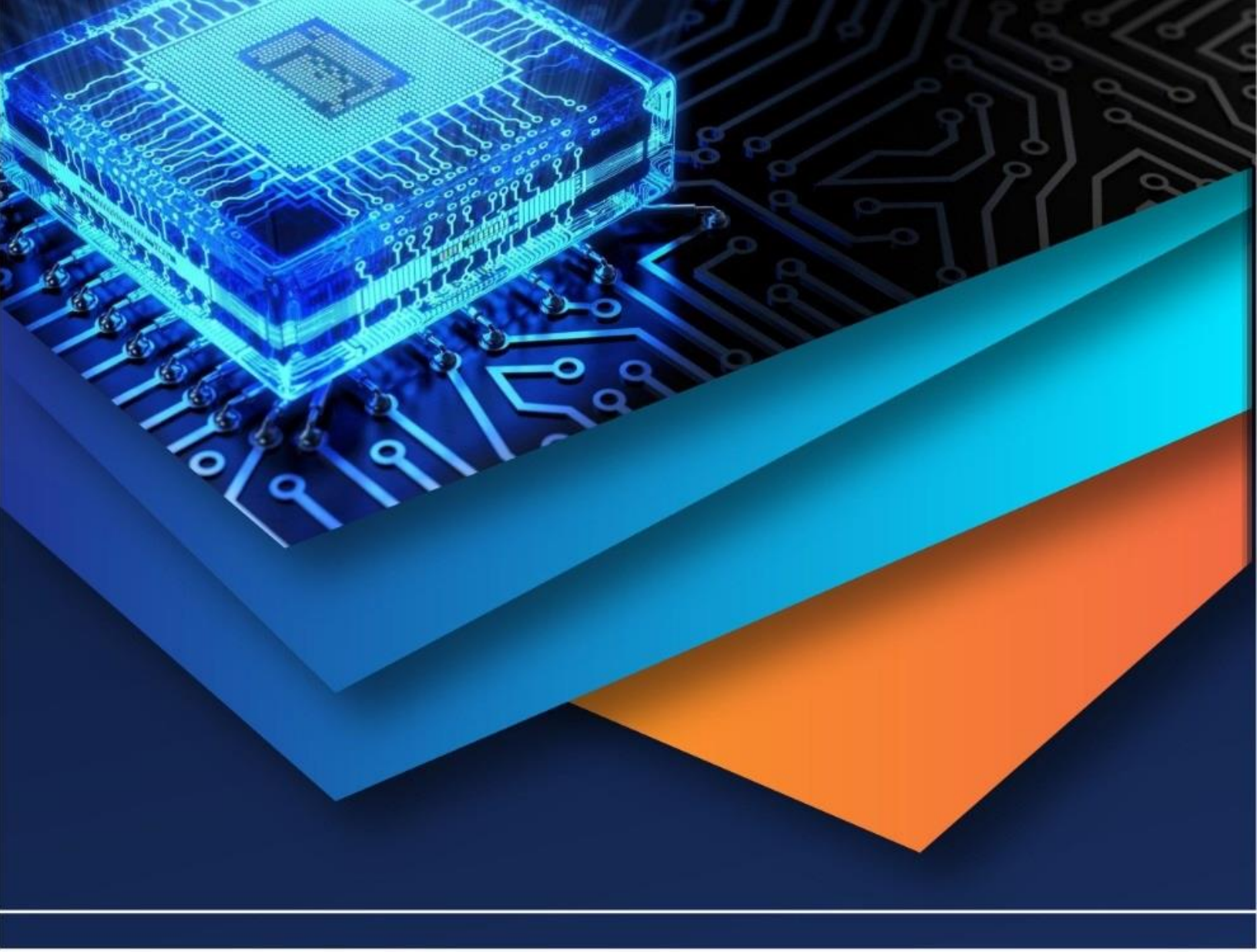
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