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Improvement in Polysulfone(PSf) Film Properties by Porogen Concept

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Abstract*:Polysulfone (PSf) is the most widely used polymer for preparation of ultrafiltration membranes. Its preparation need to be optimized to obtain membranes with desired qualities. PEG can be used as porogenic additive in these membranes, but the formation of membranes and PEG leaching need to be defined for better performance. The preparation and leaching analysis of polysulfone (PSf) based dense membrane with PEG as an additive was investigated. PEG with MW of 6000 was found to be optimum material with easy membrane formation. A defect free stable membrane formation was observed till 10 % PEG content (w/w) of PSf in membrane. During leaching the membranes showed better leaching characteristics without any change in volume till temperature of 30 °C. The constant volume indicated an increased porosity, which would improve the membrane transport properties.

Keywords -Polysulfone (PSf), Polyethylene-glycol (PEG), Porogen, Leaching, Morphology.

I. INTRODUCTION

Over the last decade, porous polymers have grabbed an increased attention due to their commercial importance and potential applications in industrial and research fields [1],[2],[3]. The properties of these polymers such as reactivity, functionality, surface area, pore volume, pore size, and porosity of a polymer are highly tunable [4]. Tuning of these properties is target specific; depending on the application areas of the polymers [3]. They can be attuned by varying physical or chemical parameters during synthesis. Physical parameters include stirring speed, reaction time and temperature, reactor and stirrer specifications during synthesis and molding. Whereas chemical parameters like monomer, initiator, cross-linker, cross-link density, porogen (solvating/non-solvating), and their amount are another factors attributing to polymer properties [5].

Apart from these parameters, use of porogen is another significant method to vary polymeric properties. It is one of the influencing parameter affecting porosity, surface area and morphology of the polymer [6]. Porogen is used for porosity generation. It may be of solvating or non-solvating type depending on its solubility parameter. The solvating porogen is generally preferred to generate micro/mesopores whereas bad solvent is widely used to generate meso/macropores polymer [7,8]. This porosity depends upon effect of a good or bad pore generating solvent on phase separation which influences the polymer properties [8]. Such use of porogens is one of the most significant methods used for morphology optimization during membrane preparation.

Due to their ease of use and wide range of choice additives are essential and have an important effect on the formation of membrane structure, during membrane preparation [9]. They affect membrane and transport properties by enlarging or preventing macro-void formation, enhancing pore formation, improving pore interconnectivity, and/or introducing hydrophilicity [10]. The additives can be water, inorganic salts, low molecular weight organics, surfactants, polymers, mineral fillers or their mixture [11], [12], [13], [14]. The role of additives has been reported as pore-forming agents or pore modifiers [11]. Their behavior can be explained in terms of their water-soluble character, salt effect or their effects on solvent capacity, phase inversion kinetics and thermodynamic properties [15].

Among the various polymeric membrane materials used for preparation of membrane solution polysulfone (PSf) is an attractive material due to its properties [12]. PSf based membranes are commercially available and are most-widely used [9] because of its properties, ease of formation and modification [13]. Their properties can be modifies and optimized by use of additives [16]. Among the additives, polymers especially poly(vinyl pyrrolidone) (PVP) and poly (ethylene glycol) (PEG) are considered as the best additives in PSf membrane preparation [16], [17],[18].PEG has been extensively used as additive to enhance the membrane preparation. Application of PEG for improvement in membrane selectivity as well as improvement in transport flux by pore formation due to its hydrophilic nature is reported [19]. PEG 400 was used to improve hydrophilicity of PSf based membranes [18]. An appropriate amount of PEG 400 also used to prevent the macro-void formation in PSf based membranes [20].A major effect of PEG content in the copolymers on UF membrane structure, property and performance as well as fouling tolerance is reported [21].

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The membranes prepared from PSf-g-PEG copolymers are bio-inert and can be used in bio-separations [22]. The PSf based membranes prepared with PSf-g-PEG as an additive showed the graft copolymer preferentially segregated to the membrane surface, endowing the membrane with enhanced wet ability, porosity and protein resistance [23]. PSf-g-PEG based membranes showed suppression in drug adsorption and promoted cell self-assembly [24]. The PSf-g-PEG based hollow fiber membranes possessed excellent industrial applicability owing to its desirable antifouling property for an extremely long-term operation [25].

In present paper, an attempt was made on preparation of dense membrane of PSf with PEG-6000 as an additive. Formation of membrane and leaching analysis effect of porogenic material PEG was done. Effect of leaching conditions, parameters and concentrations on properties of PSf based membranes was investigated.

II. EXPERIMENTAL

A. Materials

Polysulfone (synthesis grade) was obtained from Otto Chemei Pvt. Ltd. India. *N,N'*-Dimethylacetamide (DMAc) of synthesis grade was obtained from Loba Chemei Pvt. Ltd. India. Polyethylene Glycol(PEG) with molecular weight 6000 (PEG-6000), 9000 (PEG-9000) and 20000 (PEG-20000)were obtained from High Purity Lab. Pvt. Ltd. India, Sisco Research Lab. Pvt. Ltd. India and Alfa Aesar England, respectively.

B. Membrane casting

Dense polymeric films were used as membranes in current investigation. These membranes were prepared by solvent evaporation. A 2 % (w/v) solution of PSf was prepared in 25 ml of DMAc. Measured quantity of PEG to make the concentration of 5, 10, 15 and 20% (w/w of PSf) was added to the solution. After complete dissolution of polymer, the solution was poured in Petri plate. The Petri dish was maintained in oven at 80°C for 48 hr, under dry atmosphere on leveled surface. Formed membranes were peeled off and further dried in vacuum oven at 60°C for 48 hr, to insure complete removal of solvent. Obtained membranes were preserved in dry place, until further application.

C. Instrumental Analysis

The Fourier transform infrared (FTIR) spectra of formed PSf based membranes with and without PEG content were recorded by the spectrometer (ALFA-Bruker) in the range of 4000–500 cm−1.

D. PEG Leaching Analysis

Leaching of PEG from PSf based membranes was done using water as leaching agent. The PEG containing membrane coupons of 3×3 cm in size were used in these investigations. Their weight and dimensions were measured carefully. These coupons were then dipped in beaker containing distilled water. Weight and dimensions of these coupons were measured periodically within the interval of 30 min. Leaching was analyzed at different temperatures of 25, 30, 40, and 50°C. After obtaining constant weight in repeated measurement, the samples were removed from beaker and dried in vacuum oven at 60°C for 48 hrs. After drying their dimensions and weight were measured and used in further calculations.

The percent weight change of the membranes during leaching was calculated by

$$\text{Avg. Change in wt. (\%)} = \frac{\text{Initial wt.} - \text{Final wt.}}{\text{Initial wt.}} \times 100 \quad (1)$$

The leaching of membrane was calculated by

$$\text{Avg. leaching (\%)} = \left(1 - \frac{\text{Final wt.}}{\text{Initial wt.}}\right) \times 100 \quad (2)$$

Removal of PEG from dense membrane can be represented by

$$\text{\% Removal of PEG} = \frac{\text{Avg. Initial wt. of PEG} - \text{Avg. Reduction in wt.}}{\text{Initial wt of PEG}} \times 100 \quad (3)$$

After removing of PEG from dense membrane by leaching process, the void space created in the membrane which is nothing but the porosity generated by the removal of PEG. The mathematical representation of porosity generated due to removal of PEG can be calculated as follows,

$$\text{Porosity generated due to removal of PEG} = \frac{\text{Initial wt.} - \text{Final wt.}}{\text{Density of PEG} \times \text{Volume of sample}} \times 100 \quad (4)$$

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After leaching of dense membrane, the dimensions of coupon was noted, and the change in volume is calculated by

$$\text{Avg. Change in volume (\%)} = \frac{\text{Initial volume} - \text{Final volume}}{\text{Initial volume}} \times 100 \quad (5)$$

III. RESULT AND DISCUSSION

A. *Selection of material*

The polysulfone (PSf) is excellent material for membrane preparation by phase inversion owing to its stability properties [26]. Additionally it has good solubility in solvents like *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, dimethylsulfoxide and *N*-methyl-2-pyrrolidone, which are preferably used for preparation of membranes by phase inversion with water as non-solvent [27]. Polymers especially poly(vinyl pyrroli-done) (PVP) and poly(ethylene glycol) (PEG) are widely used as additives in flat and hollow fiber polysulfone (PSf) membrane preparation. Property of easily and rapidly miscible in water, poly (ethylene glycol) (PEG) is a strong constant in the race of other additives. Molecular weight of additives also affects the leaching analysis. Selection of proper additive of specific molecular weight plays an important role in the selection process. PEG-6000 showed rapid and higher solubility in water as compare to PEG-9000 and PEG-20000. This made us to use PEG-6000 in current work.

B. *Formation of membrane*

The formation of membrane was studied for various concentration of PEG in PSf. A 2% PSf solution was prepared in DMAc and used in further discussion. The hydrophilicity was necessary and highly desirable property. Due to lack of hydrophilicity PSf has large fouling properties. PEG would act both a porogenic additive and provide hydrophilic characters [28]. For the optimization, 5-20 % (w/w of PSf) of PEG was used in current investigations. 5 and 10 % PEG containing PSf membranes showed good membrane formation. The membranes could be easily removed from glass surface and were elastic in nature. The membranes with 15 % PEG had rough skin layer and the surface was not uniform. 20% PEG containing membranes were sticky and could not be removed from petri dish. Hence the membranes with 15 and 20 % of PEG were not used in further investigations.

C. *FTIR analysis*

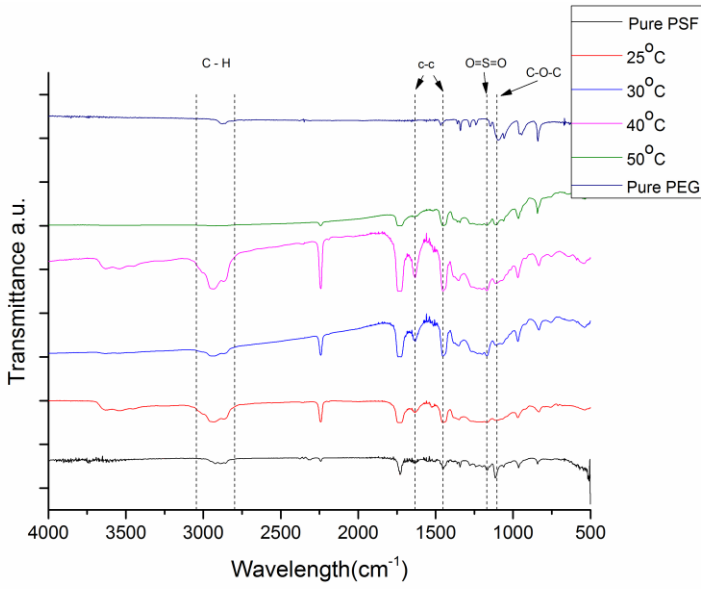

Fig. 1: FTIR spectra of PSf based dense and leached membranes

Formed membranes were analyzed by Fourier transform infrared spectroscopy (FTIR)[Fig.1]. The FTIR spectra showed complete removal of PEG from composites. The peaks at 1453 and 1632 cm^{-1} could be assigned for aromatics C-C stretching and 1279 cm-1 to the asymmetric O=S=O stretching [29, 30]. Peaks at 2772 – 3000 cm^{-1} shows for C-H stretching. The virgin polysulfone (PSf) and leached membranes shows symmetric stretching at 1132 cm^{-1} for stretch of sulphone (O=S=O) group. The peak at 1104 cm^{-1} related with for C-O-C stretching [31] which is not present in other graphs. This indicates complete removal of PEG from the membranes.

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D. Leaching Analysis

1) *Change in Weight:*The membrane samples were weighed periodically to analyze removal of PEG. A complete removal of porogenic material (PEG) was expected. Hence the weight was measured periodically till a constant weight was obtained for three sequential readings. This was followed by drying, to remove water from pores. This would provide void fraction generated from leaching of PEG. The leaching analysis was carried out at varying temperatures of 25, 30, 40 and 50 °C. The leaching results are summarized in TABLEI and plot of average change in weight versus temperaturt shown in [Fig 2]:

TABLE I
EFFECT OF TEMPERATURE ON LEACHING OF PEG-6000 (10 % w/w OF PSf) FROM PSf BASED MEMBRANES

Temperature(° C)	Avg. initial wt. (mg)	Avg. final wt. (mg)	Time for complete leaching (hr)	% change in wt.	% PEG removal
25	42.25	38.5	2	8.9	88
30	38.75	35	1.5	9.6	96
40	38.5	34.75	1	9.7	97
50	45.25	40.75	0.5	10	100

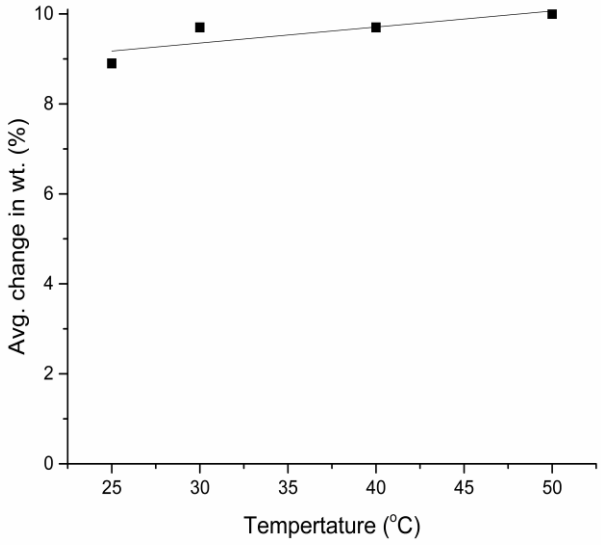

Fig 2: Effect of temperature on weight of membrane

The change in weight was mainly due to removal of PEG from PSf based membranes. A complete removal of PEG was observed in FTIR spectra. The same is supported from leaching analysis of PEG [TABLE I]. An almost complete ~ 90 % removal of PEG was observed at 25 °C [Fig 3], while it was almost 100 % for 30 °C and above. Thus, the temperature of 30 °C is enough to ensure complete removal of PEG [Fig 3].

2) *Change in volume:*As shown in TABLEII, percent removal of PEG was increased from 88 to 100 % with increase in temperature from 25 to 50 °C. Though the removal of PEG was increased, the volume of membrane samples was reduced by 4.29 %. Such reduction in volume could be attributed higher motion of polymer chains at higher temperature causing their realignment and pore collapse [32]. To avoid this, the leaching temperature was maintained at 30°C, which reduced possibility of such realignment. At the same time it gives 96 % removal of PEG from membrane matrix.

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TABLE II

EFFECT OF TEMPERATURE ON VOLUME CHANGE AND PEG REMOVAL.

Temperature (°C)	Avg. Change in wt (%)	Avg. Change in volume (%)	% Removal of PEG	Porosity generated due to PEG removal (%)
25	8.9	0	88	8.9
30	9.7	2.14	96	9.1
40	9.7	2.14	97	9.1
50	10	4.29	100	10.8

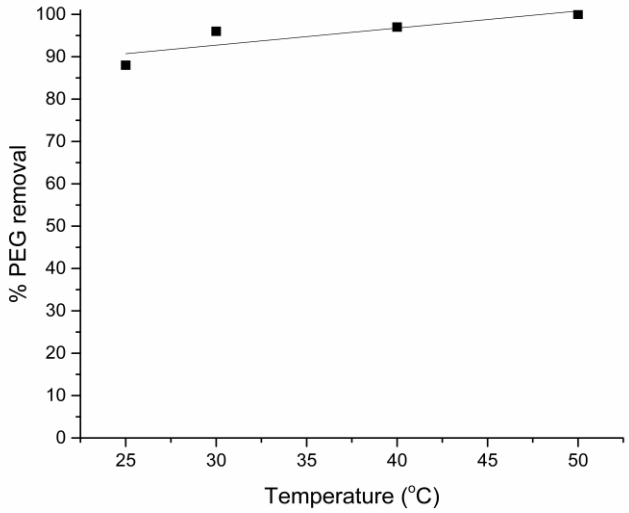

Fig 3: Effect of temperature on PEG removal

3) *Effect of Temperature on duration of leaching:* Rate of leaching of dense membrane depends on several factors where temperature is one of them. With increase in temperature, the rate of dissolution of PEG in water was expected to be faster. Thus it would ensure fast and quick removal of PEG. This was analyzed by leaching PEG at varying temperature 25 to 50 °C [Fig 4]. It was seen that, the time required for removal of PEG was reduced linearly with temperature. At 50 °C, the leaching was completed within half an hr as compared to 2 hr at 25 °C. The observation was as expected. The faster removal of PEG can be attributed to its faster dissolution in water used as leaching agent. The analysis was stopped at 50 °C, as the membranes became extremely delicate and difficult to handle after this temperature. This would reduce their usability in long term applications.

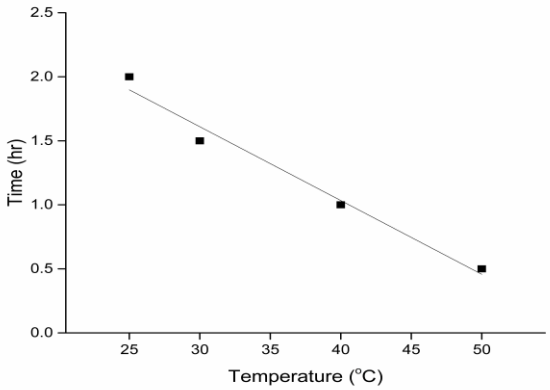

Fig 4: Effect of Temperature on Time of leaching

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IV. CONCLUSION

Various parameters affects leaching of porogenic material during porogen derived membrane preparation. Additionally these leaching parameters might induce the rearrangement of base polymer chains inducing realignment and pore collapse. To avoid this, the formation of PEG containing PSf based membrane and leaching of PEG from these membranes was optimized. The PSf based membranes showed good membrane formation for PEG-6000 content of 10 % or less. At higher PEG content, the membrane surfaces were not suitable for use. During leaching the temperature of 30°C provided comparatively faster leaching, without affecting membrane stability and structure. Formed membranes maintained its volume intact despite of removal of PEG from membrane matrix. Thus improving voids in the membranes, which would improve membrane transport properties.

V. ACKNOWLEDGMENT

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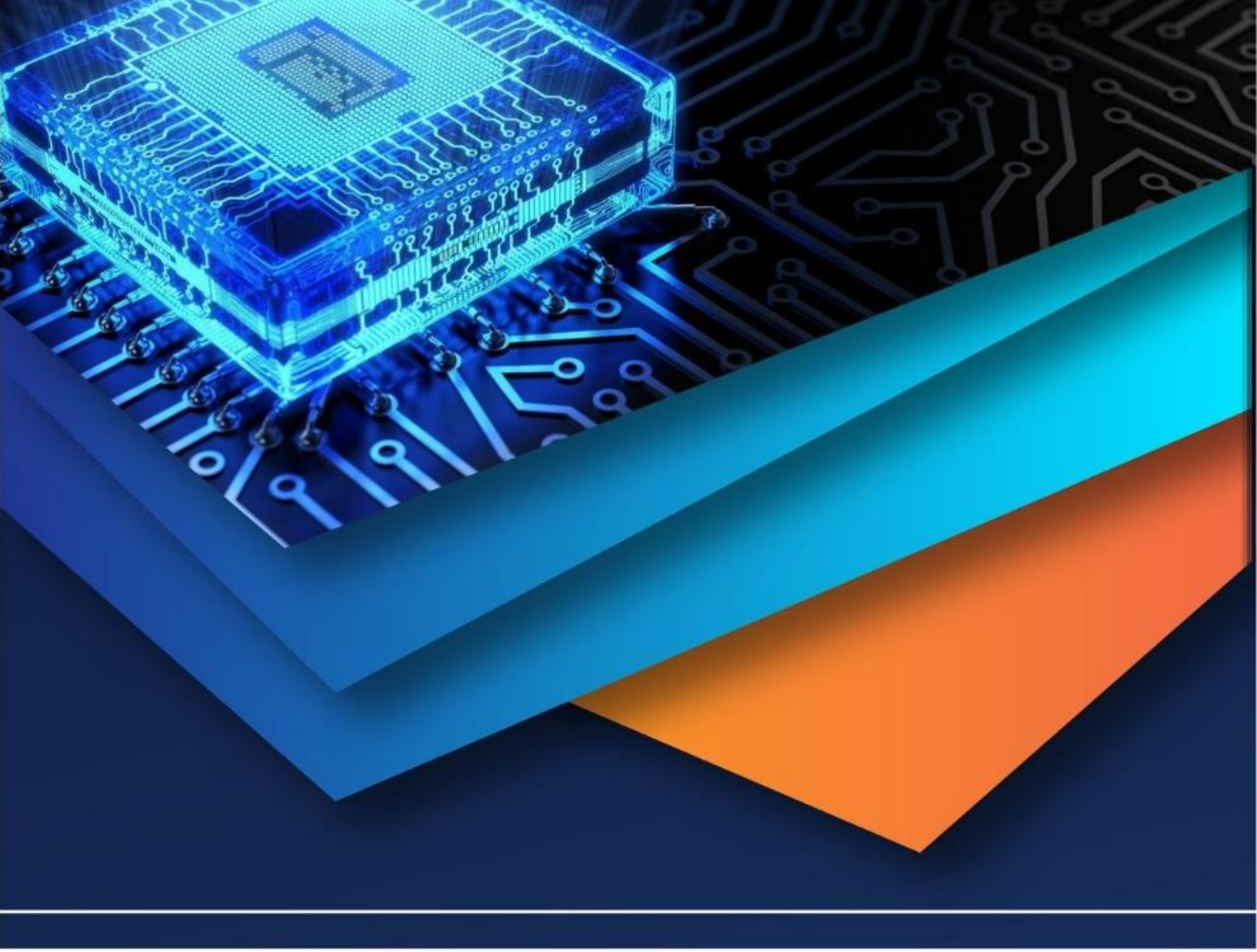

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