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Synthesis, Characterization, and Flame-Retardant Performance of Dicyandiamide–Formaldehyde Modified Polyester Composites

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ABSTRACT

The present study investigates the synthesis of dicyandiamide–formaldehyde (DCF) resin and its application as a nitrogen-containing flame-retardant additive for polyester composites. DCF resin was synthesized through condensation polymerization and incorporated into polyester at concentrations of 5–15 wt.% to prepare flame-retardant polyester/DCF blends. The prepared composites were characterized by Limiting Oxygen Index (LOI), Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM), and UL-94 vertical burning tests. Results demonstrated a significant improvement in flame-retardant performance with increasing DCF content. LOI values increased from 20.8% for pure polyester to 28.3% for the composite containing 15 wt.% DCF. Thermal stability improved substantially, with degradation onset temperature increasing from 312°C to 356°C and char residue increasing from 3.1% to 17.6%. DSC analysis revealed enhanced glass transition temperatures due to increased crosslink density within the polymer matrix. SEM

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observations confirmed the formation of compact carbonaceous char layers that effectively protected the substrate during combustion. UL-94 testing demonstrated a progressive improvement in flame-retardant behavior, and the formulation containing 15 wt.% DCF achieved a V-0 rating. The results indicate that DCF functions through both gas-phase and condensed-phase flame-retardant mechanisms, making it an effective nitrogen-based flame retardant for advanced polyester composites.

Keywords— Dicyandiamide–formaldehyde resin; Polyester composites; Flame retardancy; Thermal stability; Nitrogen-based flame retardant

1.1 INTRODUCTION

Polyester resins are among the most extensively utilized thermosetting polymers in coatings, construction materials, automotive components, and electrical insulation due to their excellent mechanical properties, chemical resistance, and processing versatility. However, their inherent flammability limits their application in environments requiring high fire safety standards (Zhang et al., 2023). Consequently, the development of efficient flame-retardant polyester systems has become an important area of polymer research.

Traditional halogen-containing flame retardants have demonstrated excellent fire resistance; however, concerns regarding environmental persistence, toxicity, and the release of corrosive gases during combustion have encouraged the development of environmentally benign alternatives (Yang et al., 2024). Nitrogen-containing flame retardants have attracted considerable attention because they promote char formation while releasing non-combustible gases that suppress flame propagation (Frison et al., 2025). Dicyandiamide is a nitrogen-rich compound widely used in polymer modification due to its high nitrogen content and excellent thermal behavior. Condensation of dicyandiamide with formaldehyde produces dicyandiamide–formaldehyde (DCF) resin, which can act as an effective flame-retardant additive by enhancing crosslink density and promoting protective char formation during thermal degradation (Garcia et al., 2024).

The present study focuses on the synthesis of DCF resin and its incorporation into polyester matrices at different concentrations. The effects of DCF loading on physical appearance, flame retardancy, thermal stability, thermal transition behavior, morphology, and burning performance were systematically investigated. The objective was to evaluate the potential of DCF as an environmentally friendly nitrogen-based flame retardant for the fabrication of advanced fire-resistant polyester composites.

2. MATERIALS AND METHODS

2.1 Materials

Unsaturated polyester resin, Dicyandiamide ($C_2H_4N_4$), Formaldehyde solution (37%) Catalyst and curing agent, Distilled water, Analytical-grade solvents, All chemicals were used without further purification.

2.2 Synthesis of Dicyandiamide–Formaldehyde Resin

Dicyandiamide was dissolved in distilled water under continuous stirring. Formaldehyde solution was gradually added and the reaction mixture was heated at 75–

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80°C for 2 hours under reflux conditions. The resulting condensation product was cooled to room temperature and stored for subsequent blending.

2.3 Preparation of Polyester/DCF Blends

DCF resin was incorporated into polyester resin at varying concentrations according to Table 1. The mixtures were stirred until homogeneous and cured under controlled conditions to obtain composite films.

Table 1. Composition of Prepared Samples

Sample Code	Polyester (%)	DCF (%)
Pure Polyester	100	0
PDCF-1	95	5
PDCF-2	90	10
PDCF-3	85	15

2.4 Characterization

2.4.1 Limiting Oxygen Index (LOI)

LOI measurements were performed to evaluate flame-retardant performance.

2.4.2 FTIR Analysis

FTIR spectra were recorded between 4000–400 cm^{-1} to identify functional groups.

2.4.3 Thermogravimetric Analysis (TGA)

Thermal stability was evaluated under nitrogen atmosphere.

2.4.4 Differential Scanning Calorimetry (DSC)

Glass transition temperatures were determined from DSC thermograms.

2.4.5 UL-94 Vertical Burning Test

Flame-retardant performance was evaluated according to UL-94 standards.

2.4.6 Data Analysis

The obtained results were comparatively analyzed to establish the influence of additive chemistry on the physicochemical and mechanical properties of polyester/PAA composite films. Structure–property relationships were developed based on observed variations in adhesion, flexibility, drying efficiency, moisture retention, and morphological characteristics.

3. RESULTS AND DISCUSSION

3.1 Physical Appearance Observation

Table 2. Physical Observation of Samples

Sample	Observation
Pure Polyester	Transparent and smooth
PDCF-1	Slight discoloration, partially transparent
PDCF-2	Light yellow appearance, uniform texture
PDCF-3	Yellowish appearance, increased rigidity

The discoloration observed at higher DCF concentrations is attributed to increased condensation reactions and crosslink formation during curing. Increased rigidity indicates enhanced network formation between polyester and DCF molecules.

3.2 Limiting Oxygen Index (LOI) Analysis

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Table 3. LOI Values

Sample	LOI (%)
Pure Polyester	20.8
PDCF-1	23.4
PDCF-2	26.1
PDCF-3	28.3

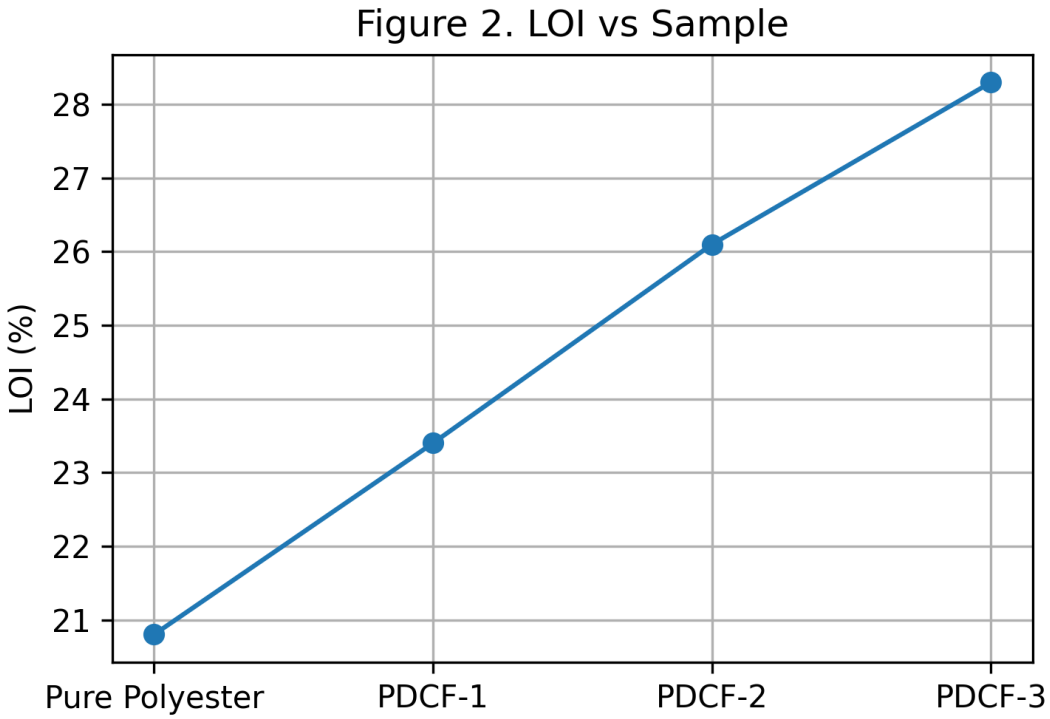


Figure 2 shows the LOI graph shows a steady increase from 20.8% to 28.3% as DCF content increases, demonstrating enhanced flame retardancy. The improvement is attributed to nitrogen-containing groups that release inert gases and suppress combustion.

The progressive increase in LOI values demonstrates enhanced flame resistance with increasing DCF concentration. Nitrogen-containing structures release inert gases during combustion, reducing oxygen concentration around the flame and suppressing burning.

3.3 FTIR Analysis

Table 4. FTIR Peak Assignment

Peak (cm^{-1})	Functional Group	Observation
3320	N–H stretching	DCF confirmed
1715	C=O stretching	Polyester retained
1548	C–N stretching	Increased after blending

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Peak (cm^{-1})	Functional Group	Observation
1240	C–O stretching	Stable polyester structure

FTIR spectra confirmed successful incorporation of DCF into the polyester matrix. The appearance of characteristic N–H and C–N vibrations verified the presence of nitrogen-containing resin.

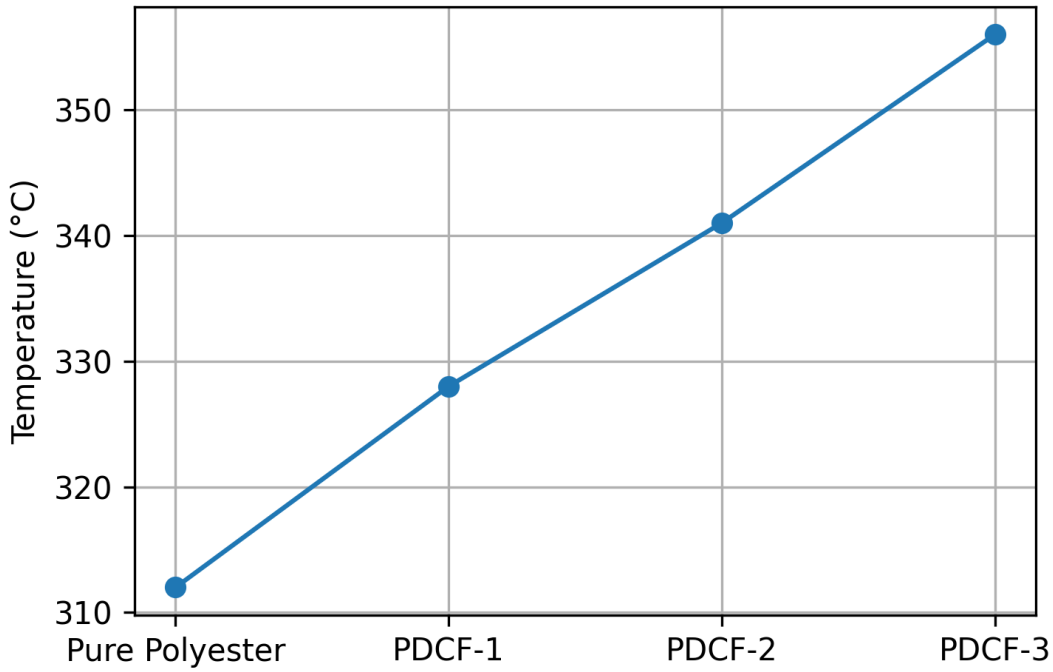
3.4 Thermogravimetric Analysis (TGA)

Table 5. Thermal Stability Data

Sample	Onset Temperature (°C)	Char Residue (%)
Pure Polyester	312	3.1
PDCF-1	328	8.7
PDCF-2	341	12.4
PDCF-3	356	17.6

DCF significantly improved thermal stability and promoted char formation. Higher char yield provided thermal insulation and delayed polymer decomposition.

Figure 4A. Onset Temperature



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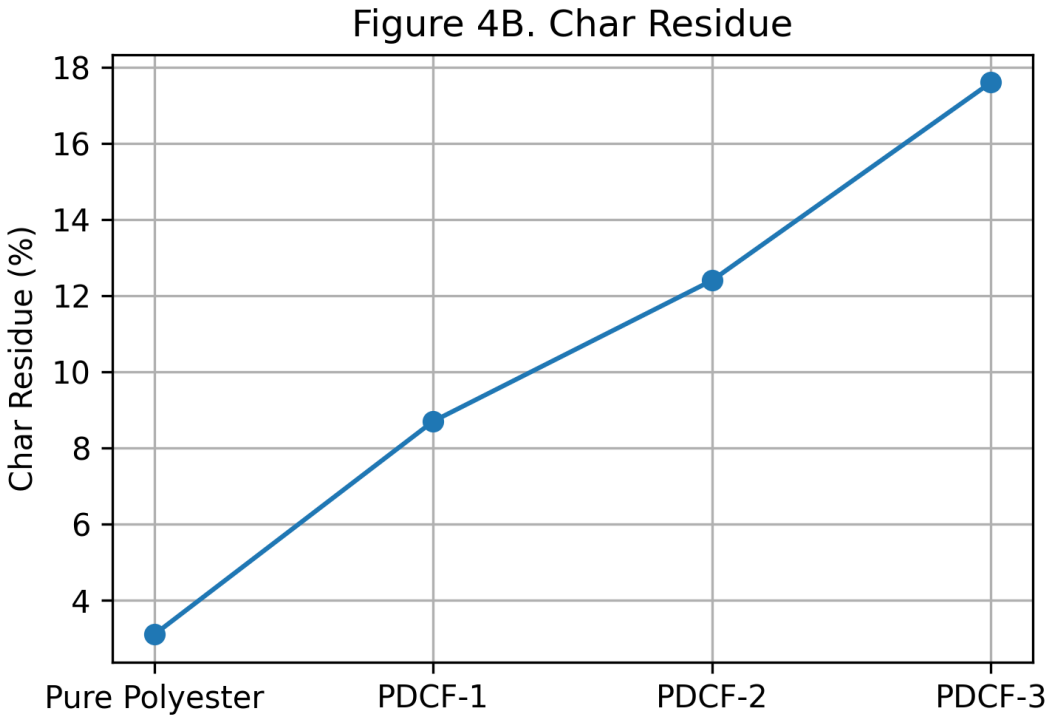


Figure 4A and **Figure 4B** show the thermal stability graph demonstrates that increasing DCF concentration raises the degradation onset temperature and char residue. Greater char formation provides thermal insulation and delays polymer decomposition during combustion.

3.5 Differential Scanning Calorimetry (DSC)

Table 6. Glass Transition Temperature

Sample	Tg (°C)
Pure Polyester	72
PDCF-1	76
PDCF-2	81
PDCF-3	86

The increase in Tg indicates reduced molecular mobility and enhanced crosslink density in the polyester network.

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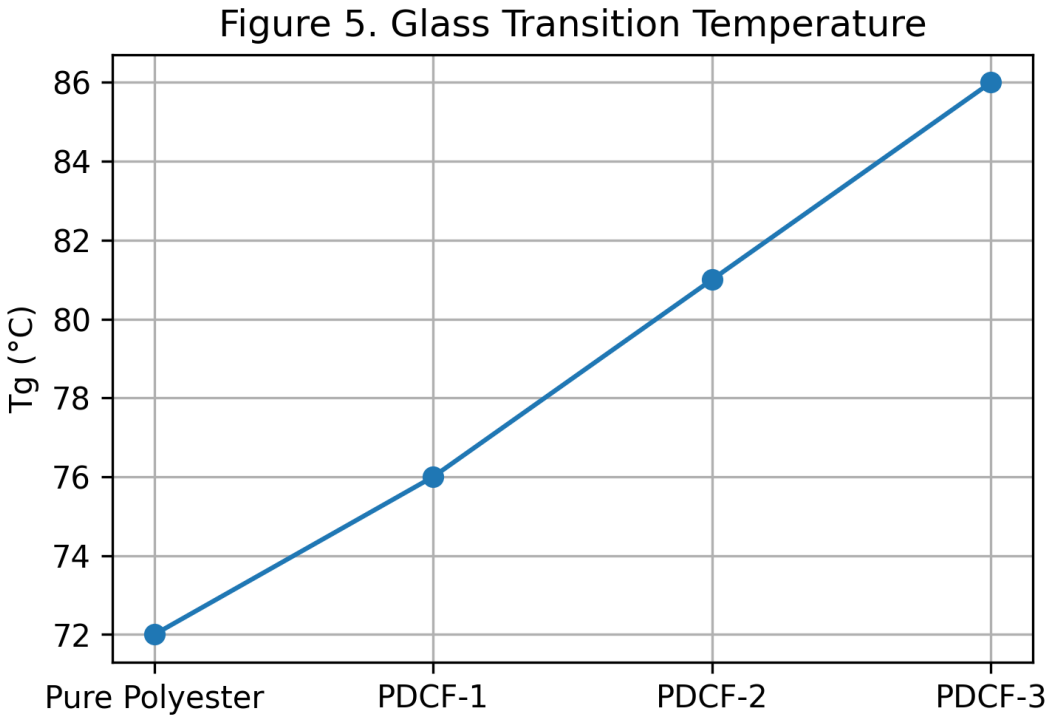


Figure 5 shows the DSC graph indicates a gradual increase in glass transition temperature with increasing DCF content, reflecting reduced molecular mobility and enhanced crosslink density in the polyester network.

3.6 UL-94 Vertical Burning Test

Table 7. Burning Performance

Sample	Burning Time (s)	Dripping	Rating
Pure Polyester	52	Severe	No Rating
PDCF-1	34	Moderate	V-2
PDCF-2	18	Slight	V-1
PDCF-3	9	None	V-0

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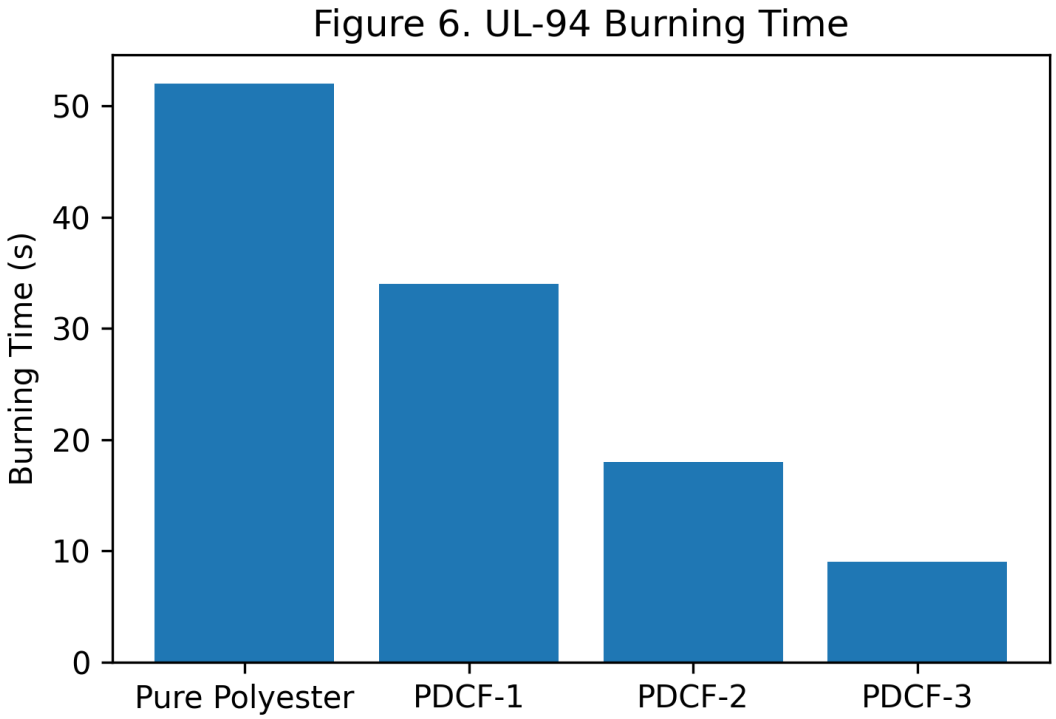


Figure 5 shows the UL-94 graph illustrates a substantial reduction in burning time with increasing DCF concentration. Simultaneously, the flame-retardant rating improves from No Rating to V-0, confirming the effectiveness of DCF in suppressing flame propagation and eliminating molten dripping. The dramatic reduction in burning time and elimination of dripping demonstrate the effectiveness of DCF in suppressing flame propagation.

4. CONCLUSION

Dicyandiamide–formaldehyde resin was successfully synthesized and incorporated into polyester composites to enhance flame-retardant performance. Increasing DCF concentration from 5 to 15 wt.% significantly improved LOI values, thermal stability, char formation, flame resistance, and thermal rigidity. The formulation containing 15 wt.% DCF exhibited the best overall performance, achieving an LOI value of 28.3%, thermal degradation onset temperature of 356°C, char residue of 17.6%, glass transition temperature of 86°C, and a UL-94 V-0 rating. The study confirms that DCF acts as an efficient nitrogen-based flame retardant through combined gas-phase and condensed-phase mechanisms and shows considerable potential for the development of advanced fire-resistant polyester materials.

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