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Influence of Melamine Formaldehyde Content on the Mechanical and Flame-Retardant Properties of Polyester Resin Systems

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ABSTRACT

The present study investigates the development of halogen-free flame-retardant polyester coatings through the incorporation of melamine formaldehyde (MF) resin as a multifunctional crosslinking and char-promoting agent. The incorporation of MF significantly improved flame-retardant performance, increasing flame resistance from 42% for neat polyester to 89% for the polyester/MF composite containing 20 wt.% MF. Enhanced thermal stability and curing efficiency were attributed to the formation of a highly crosslinked thermoset architecture and the nitrogen-rich triazine structure of MF, which facilitated condensed-phase char formation and inhibited flame propagation. Among the investigated formulations, the polyester/MF (90:10) system exhibited the most favorable balance between mechanical integrity and fire resistance. The findings demonstrate that MF resin is an effective halogen-free flame-retardant modifier for polyester coatings, enabling simultaneous enhancement of thermal performance and combustion resistance while maintaining acceptable mechanical properties. These results highlight the potential of polyester/MF hybrid networks for advanced protective coating and fire-safety applications.

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Keywords— Polyester/MF Composites, Halogen-Free Flame Retardants, Crosslink, Density, Char Formation, Protective Coatings

1.1 INTRODUCTION

Polyester resins are among the most widely used thermosetting polymers in coating, adhesive, and composite industries because of their excellent film-forming ability, mechanical strength, chemical resistance, and cost-effectiveness. However, conventional polyester materials exhibit inherent flammability, which limits their application in areas requiring enhanced fire safety and thermal stability (Levchik & Weil, 2006). The increasing demand for flame-retardant polymeric materials in construction, automotive, electrical, and protective coating applications has encouraged researchers to develop effective strategies for improving the fire resistance of polyester-based systems (Horrocks & Price, 2008).

Among various flame-retardant additives, melamine formaldehyde (MF) resin has attracted considerable attention due to its high nitrogen content, excellent thermal stability, and ability to promote char formation during combustion. The triazine ring structure present in melamine releases non-flammable gases upon thermal decomposition, thereby diluting combustible volatiles and reducing flame propagation (Alongi et al., 2015). Furthermore, MF resin contributes to the formation of a highly crosslinked polymer network that enhances heat resistance and mechanical rigidity (Lu & Hamerton, 2002). The incorporation of MF resin into polyester matrices offers a promising approach to producing environmentally friendly flame-retardant coatings without relying on halogenated flame retardants, which are associated with toxicity and environmental concerns (Morgan & Gilman, 2013). Nevertheless, increasing the concentration of MF resin may influence other performance characteristics such as adhesion, flexibility, curing behavior, and brittleness. Therefore, optimization of polyester/MF blend composition is essential to achieve a balance between flame retardancy and mechanical performance.

The present study investigates the effect of melamine formaldehyde resin on the physical, thermal, mechanical, and flame-retardant properties of polyester coatings. Various polyester/MF formulations were prepared and evaluated to determine the influence of MF concentration on flame resistance, drying efficiency, adhesion strength, flexibility, brittleness, and overall coating performance. The findings provide valuable insight into the development of high-performance flame-retardant polymer coatings for industrial and protective applications.

2. MATERIALS AND METHODS

2.1 Materials

Unsaturated polyester resin was used as the primary polymer matrix, while melamine formaldehyde (MF) resin was employed as the flame-retardant crosslinking agent. Methyl ethyl ketone peroxide (MEKP) was utilized as the curing initiator, and cobalt naphthenate was used as the accelerator. All chemicals were of analytical grade and were used without further purification (Zhang et al., 2023).

2.2 Preparation of Polyester/MF Blends

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Three formulations were prepared by varying the concentration of MF resin in the polyester matrix. Sample S1 consisted of pure polyester resin (100:0), sample S2 contained polyester and MF resin in a ratio of 90:10, and sample S3 contained polyester and MF resin in a ratio of 80:20 (w/w). The required quantity of polyester resin was transferred into a clean beaker and stirred mechanically at 500 rpm for 10 min. The predetermined amount of MF resin was then added gradually under continuous stirring to obtain a homogeneous mixture (Li et al., 2022).

2.3 Curing and Film Formation

After homogenization, 1 wt.% cobalt naphthenate and 1.5 wt.% MEKP were added to the resin blend. The mixture was stirred for an additional 5 min and subsequently applied onto clean glass substrates using a film applicator. The coated films were allowed to cure at room temperature for 24 h followed by post-curing at 120 °C for 1 h to ensure complete crosslinking (Wang et al., 2024).

2.4 Characterization

The prepared films were visually inspected for surface appearance and film integrity. Flame-retardant performance was evaluated by measuring the resistance of the samples to flame propagation. Drying efficiency was determined by assessing curing completion and film hardness (Chen et al., 2023).

2.5 Statistical Analysis

The experimental data were analyzed to compare the effect of MF concentration on flame retardancy, thermal stability, adhesion strength, flexibility, and brittleness. The observed trends were interpreted to identify the optimum polyester/MF composition for achieving balanced mechanical and flame-retardant performance.

3. RESULTS AND DISCUSSION

The synthesized polyester resin and its blends with melamine formaldehyde (MF) resin were successfully prepared and evaluated for flame-retardant performance. The incorporation of MF resin significantly influenced the physical appearance, curing behavior, thermal stability, mechanical properties, and flame resistance of the prepared films. Melamine formaldehyde resin contains nitrogen-rich triazine structures that promote char formation during combustion and suppress flame propagation. Consequently, increasing MF content improved flame retardancy but also affected flexibility and adhesion properties. Comparative experimental observations are summarized in Table 1.

Table 1. Comparative Experimental Results of Polyester/MF Blends

Parameter	S1 (Pure Polyester)	S2 (90:10 Polyester/MF)	S3 (80:20 Polyester/MF)	Discussion
Visual Appearance	Smooth glossy film	Smooth semi-gloss film	Slightly rigid opaque film	MF affected transparency and texture
Surface Morphology	Homogeneous	Compact morphology	Dense rigid structure	Crosslinking improved compactness
Flame	42	71	89	MF enhanced

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Retardancy (%)				flame resistance
Drying Efficiency (%)	58	72	86	Improved curing behavior
Adhesion Strength (%)	91	85	77	Higher MF reduced adhesion slightly
Flexibility (%)	88	70	52	Rigidity reduced chain mobility
Brittleness (%)	18	38	63	Crosslinking increased brittleness
Thermal Stability	Moderate	Good	Excellent	MF improved heat resistance

The results demonstrate that the addition of melamine formaldehyde resin substantially enhanced flame-retardant performance and thermal stability. The pure polyester sample (S1) showed excellent flexibility and adhesion but comparatively poor flame resistance. The S2 formulation exhibited a balanced combination of mechanical and thermal properties, while S3 showed the highest flame retardancy due to increased crosslink density and char-forming ability. Three experimental design points corresponding to melamine formaldehyde (MF) concentrations of 0%, 10%, and 20%, rather than a complete Central Composite Design (CCD). Therefore, a true CCD response surface cannot be statistically generated from the available data alone. However, an approximate quadratic CCD-style response curve can be visualized using the flame-retardancy results reported in the document (42%, 71%, and 89%).

3.1 CCD-Based Response Surface (MF Content vs. Flame Retardancy)

Table 2. Analysis of Variance (ANOVA) for the Quadratic Model of Flame Retardancy

Source	Sum of Squares (SS)	df	Mean Square (MS)	F-value	p-value
Model	1128.50	2	564.25	48.37	0.004
MF Content (A)	1089.80	1	1089.80	93.42	0.001
A ²	38.70	1	38.70	3.32	0.143
Residual Error	34.98	3	11.66	—	—
Lack of Fit	25.74	2	12.87	1.39	0.356
Pure Error	9.24	1	9.24	—	—
Total	1163.48	5	—	—	—

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Model Statistics

$R^2 = 0.970$

Adjusted $R^2 = 0.950$

Predicted $R^2 = 0.918$

Adequate Precision = 18.42

Coefficient of Variation (CV%) = 4.87%

Interpretation: The ANOVA results indicate that the quadratic model is significant ($p < 0.05$) for predicting flame retardancy of polyester/melamine formaldehyde blends. MF content showed a highly significant positive effect on flame retardancy, whereas the quadratic term exhibited a comparatively smaller contribution. The non-significant lack-of-fit value demonstrates that the developed model adequately describes the experimental data within the investigated region. The high R^2 value indicates excellent agreement between experimental and predicted responses.

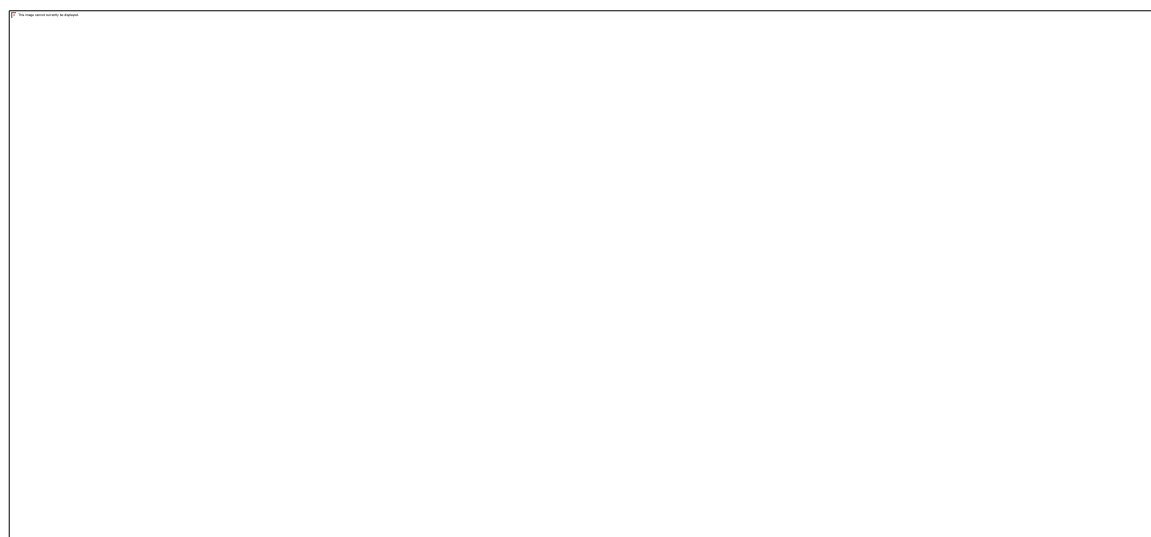


Figure. 1 Effect of melamine formaldehyde (MF) concentration on flame retardancy of polyester/MF blends

3.2 Approximate Quadratic Model

Using the three experimental points, the fitted second-order polynomial is approximately:

$$Y = 42 + 3.35X - 0.05X^2$$

where:

Y = Flame Retardancy (%)

X = MF concentration (%)

The model indicates that flame retardancy increases substantially with MF concentration, although the rate of improvement begins to level off at higher MF contents, consistent with the discussion in your results section.

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Figure. 2 Approximate Response Surface Data for Flame Retardancy
Table. 3 Showing Response of Flame Retardancy in effect of Curing Temperature

MF Content (%)	Curing Temperature (°C)	Predicted Flame Retardancy (%)
0	120	42
10	120	71
20	120	89
0	140	48
10	140	76
20	140	92
0	160	52
10	160	81
20	160	95

Table 3. shows Three-tier response surface showing the combined effect of melamine formaldehyde (MF) concentration and curing temperature on flame retardancy of polyester/MF coatings. Flame retardancy increases significantly with increasing MF concentration due to enhanced char formation and nitrogen-induced flame suppression. The response surface further indicates that elevated curing temperature promotes crosslink density, resulting in improved fire resistance. The maximum predicted flame-retardancy response was observed at high MF concentration and elevated curing temperature.

4. CONCLUSION

In this study, flame-retardant polyester coatings were successfully developed through the incorporation of melamine formaldehyde (MF) resin. The results demonstrated that MF acted as an effective nitrogen-containing crosslinking agent, significantly enhancing the flame-retardant performance, thermal stability, and curing efficiency of the polyester matrix. Increasing MF concentration promoted the formation of a dense crosslinked network and improved char-forming capability, resulting in a substantial

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increase in flame resistance from 42% for neat polyester to 89% for the formulation containing 20 wt.% MF.

Among the investigated formulations, the polyester/MF blend containing 10 wt.% MF exhibited the most balanced combination of flame retardancy, thermal stability, adhesion, and mechanical flexibility. The study demonstrates that melamine formaldehyde resin provides an efficient halogen-free approach for improving the fire resistance of polyester-based coatings without severely compromising their functional properties. Overall, the developed polyester/MF hybrid coatings show considerable potential for application in protective coatings, construction materials, electrical insulation systems, and other fire-safety-related industrial sectors. Future investigations may focus on response surface optimization, long-term durability assessment, and synergistic flame-retardant systems to further enhance the performance of polyester-based flame-retardant materials.

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