

Melamine Polyimide Composite Fire Resistant Intumescent Coatings

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ABSTRACT

Components of intumescent coatings acid source, carbon source and blowing agent like melamine linked together by a binder provide cumulative fire retardant properties. When temperature of the coating surface reaches a critical temperature under the heat of flame, the surface begins to melt and is converted into highly viscous liquid. Simultaneously, reactions are initiated that result in the release of inert gases with low thermal conductivity. These gases are trapped inside the viscous fluid forming insulating char. The special composite of melamine polyimide, a C source and melamine a blowing agent showed high performance heat resistance in the present study. Polyimides have excellent heat and chemical resistance, excellent adhesion to a number of substrates and superior mechanical properties, such as high flexural modulus and compressive strength. Polyimides are also known to possess outstanding dimensional stability under loads, which allows their use in high temperature environments. Effect of the monomer on chemical reactivity between the binder and the intumescent additives has been studied by thermo-gravimetric analysis, differential scanning calorimeter and FTIR analysis. Thermal insulation studies by various intumescent composite coatings, applied on aluminium plates provided useful time temperature profiles.

Keywords: Bismellitimide carbonyl chloride biphenyl ether prepolymer, intumescent composite, poly bismellitimide melamide

1. INTRODUCTION

Thermal coefficient of expansion of steel and aluminium is much higher than polymers. Intumescent coatings represent an increasingly new way to provide passive fire protection¹ to the structural metals used in modern architectural designs. Intumescent coatings are designed to perform under severe conditions and to maintain the temperature and integrity of the metals when the temperature of the surroundings is more than their melting points². Intumescent produce a light char, which is a poor conductor of heat, thus retarding heat transfer and can significantly inhibit flow of heat from the gaseous combustion zone back to the substrate, thereby slowing the thermal decomposition process³.

The intumescent flame retardant system usually composed of three active ingredients: an acid source (catalyst) (generally ammonium polyphosphate-APP), a carbon source (such as (di pentaerythritol) and a blowing agent like melamine linked together by a binder⁴. Several studies⁵⁻⁷ have demonstrated that some polymers can participate in the intumescent phenomenon. If a binder acts in this way, it becomes a fundamental ingredient of the intumescent paint. Use of linear and cross-linked substituted styrene-acrylic copolymers has shown relationships between the polymer binder characteristics and the protective behavior of intumescent coatings⁸. Carbon-rich compounds are polyhydric, organic amine or amide, halogenated compound.

Typically, these materials also contain a significant amount of hydrates as binder. As the hydrates are spent, water vapour is released, which has a cooling effect. Once the water is spent, it is only insulation characteristics of the char that was produced, which can slow down heat transfer from the exposed side to the unexposed side of an assembly. Upon heating, the three active ingredients and the binder swell and form a thermal insulation multi cellular layer which can prevent heat from penetrating and flames from spreading. It does not modify intrinsic mechanical properties of the materials. When the temperature of the coating surface reaches a critical temperature under the heat of the flame, the surface begins to melt and is converted into highly viscous liquid. Simultaneously, reactions are initiated that result in the release of inert gases with low thermal conductivity. These gases are trapped inside the viscous fluid (formation of bubbles). Aromatic Polyimides due to stiff structure have exceptional thermal and oxidative stability. They are prepared from a variety of dianhydrides and diamines and characterised by the repeating imide structures (Fig.1). Polyamide-imide composite having following additive chemicals were used to formulate the intumescent coatings: Sodium silicate, potassium silicate, expandable graphite, melamine, borax, boric acid and silicon carbide.

2. EXPERIMENTAL

2.1 Reagents/Chemicals

Pyridine, acetic acid, 4,4'-diaminodiphenyl ether, hydrochloric acid, methanol, m-Cresol, n-Hexane were obtained from M/s Merck Chemical Co., Sisco and Fischer Scientific Co. trimellitic anhydride was Aldrich make. All reagents of GR grade were used.

2.2 Instrumentation

A microwave oven (M/s Raga's electromagnetic systems) of 700 W was used for poly-condensation reactions. The fourier transform IR spectra (FT-IR) were recorded with Shimadzu make spectrometer in the wave number range of 4000 and 400 cm^{-1} .

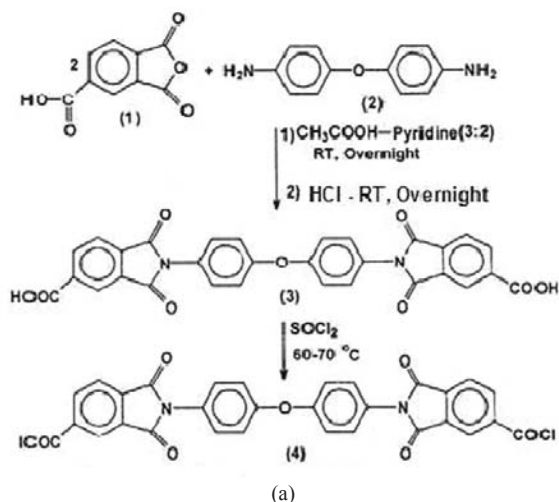
2.3 Procedure

The synthesis of melamine polyimide was done through microwave-assisted polycondensation reaction of the prepolymer N, N'-(4, 4'-diphenyl ether) bis-trimellitimide diacid chloride with melamine.

2.3.1 Prepolymer Synthesis

Into a 500 mL round bottom flask, 19.2 g of trimellitic anhydride, 10 g of 4, 4'-diaminodiphenyl ether and a 400 mL mixture of acetic acid and pyridine (3:2) was added. The mixture was stirred overnight at room temperature. Thereafter, 25 mL concentrated hydrochloric acid was added drop wise to the mixture. The mixture was stirred overnight at room temperature to form a yellow precipitate. The precipitate was filtered off under reduced pressure and then dried. This yielded 14 g of yellow crystals of bismellitimide carboxylic acid biphenyl ether. Pre-polymer synthesis reaction scheme is shown in Fig. 1(a).

The precipitate was mixed with 80 mL of thionyl chloride (SOCl_2) in a round bottom flask. The mixture was continuously stirred overnight in a water bath at 60 °C to give a clear solution. The mixture was then filtered under reduced pressure and the residue was washed with n-hexane. This yielded 8.5 g of yellow crystals of bismellitimide carbonyl chloride biphenyl ether.



2.3.2 Copolymerisation of Bismellitimide Prepolymer with Melamine

8.5 g of yellow crystals of bismellitimide carbonyl chloride biphenyl ether and 2.2 g of melamine were placed in a porcelain dish and ground to give a fine powder. 18 mL of m-cresol was added to the powdered mixture and it was stirred for 30 min to form a homogenous solution. The reaction mixture was then irradiated in a microwave oven at 80 % power for 10 min. The irradiated mixture was then poured into 100 mL of methanol and stirred for 10 min. The resulting precipitated polymer was then filtered off under vacuum and dried at 80 °C for 12 h, under 17 inches of vacuum. This yielded 12 g of solid polymer. The poly condensation reaction scheme is shown in Fig. 1(b).

2.3.3 Formulation and Development of Intumescent Coatings

These coatings were based on sodium silicate as its major constituent along with expandable graphite. Expandable graphite is known to have anti-oxidation and fire-resistant properties and it also improves water resistance of the coating. Coating compositions that were formulated and tested are given in Table 2. The viscous paste form was applied using a brush, on a 15 cm by 15 cm aluminium plate of thickness 2 mm. The coating was dried at room temperature (25-30 °C) for 24 hrs.

2.3.4 Coatings Modified with Melamine Polyimide

Intumescent coatings were prepared by the addition of melamine polyimide, which is a speciality polymer with high thermal stability. This was done to improve the mechanical properties and the efficiency of the coatings mentioned above. The formulations of the coatings are discussed in Table 1.

2.4 Thermal Analysis

Differential scanning calorimetric and thermo gravimetric analysis of the trimellitimide, trimellitimide carbonyl chloride and trimellitimide-melamine copolymer were conducted on Shimadzu DSC-60 and TGA-51 instruments at Auto Cluster Development & Research Institute, Pune. Thermo-gravimetric analyses were carried out at 10 °C/min under nitrogen

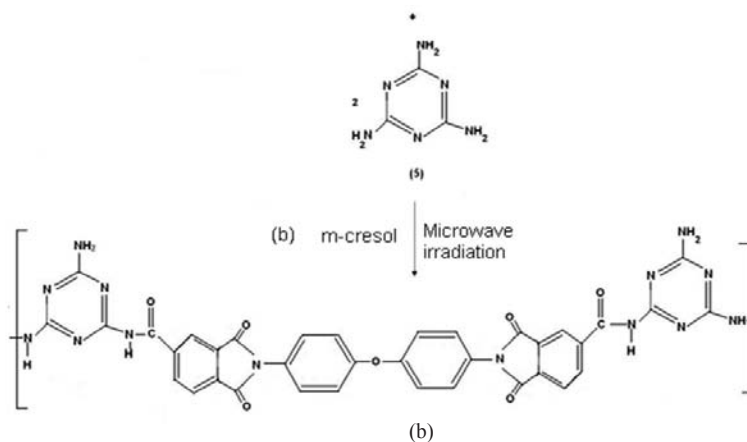


Figure 1. (a) Monomer synthesis, (b) Condensation reaction of bismellitimide carbonyl chloride biphenyl ether with melamine to synthesise polybismellitimide melamine.

Table 1. Composition of the intumescent coatings

Composition (in percentage)		Formulation				
		1	2	3	4	5
Sodium silicate	(30)	→	→	→	→	→
Potassium silicate	(30)	→	→	→	→	→
Expandable graphite	(20)	→	→	→	→	→
Boric Acid	(5)	→	→	→	→	→
Borax	(5)	→	→	→	→	→
Montmorillonite	(10)	→	-	-	-	-
Silicon Carbide	(10)	-	→	→	→	→
Magnesium Oxide	(5)	-	-	→	→	→
Magnesium Chloride	(5)	-	-	-	-	→
Melamine polyimide	(5)	-	-	-	→	-
Melamine polyimide	(6)	-	-	-	-	→

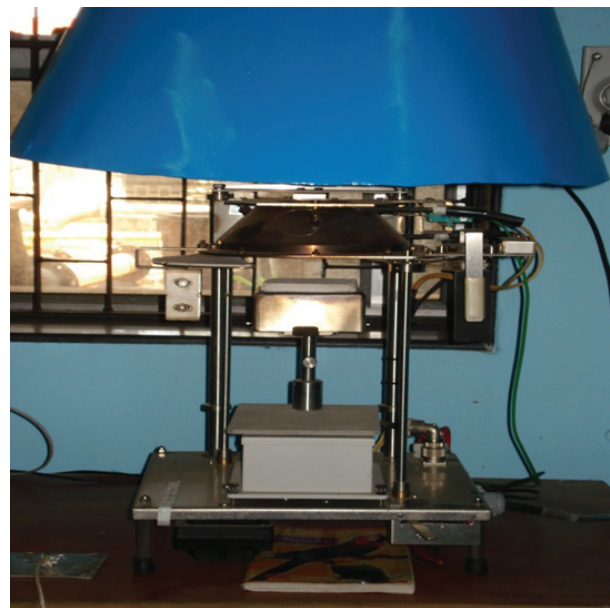
atmosphere (flow rate: 50 mL/ minute) using a Setaram MTB 10-8 microbalance. The samples (approx. 40 mg) in the form of powder were placed in open vitreous silica pans. The precision of the temperature measurements was 1.5 °C.

2.5 Fire Resistance by Intumescent Coating

Temperature profiles were measured at the interface between the intumescent coating and the metallic substrate for a sample exposed to a constant heat flux of 35 kW/m² under the conditions of the cone calorimeter presented in Fig. 2.

3. RESULTS AND DISCUSSIONS

The most widely practiced procedure in polyimide synthesis is the two-step poly (amic acid) process. It involves reacting a dianhydride and a diamine at ambient conditions in a dipolar solvent such as N, N-dimethylacetamide (DMAc) or N-methylpyrrolidinone (NMP) to yield the corresponding poly (amic acid), which is then cyclised into the final polyimide. The process enabled the first polyimide of significant commercial importance-‘Kapton™’, to enter the market. The process for most extensively developed Kapton polyimide utilises the monomer pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA)⁸. The rigid structure of polyimide provides high glass transition temperature ($T_g > 300$ °C) and gives good mechanical strength and high modulus. The linearity and stiffness of the cyclic backbone allow for molecular ordering and results in a lower coefficient of thermal expansion (CTE) than that of thermoplastics. Besides these properties, polyimides also have a low dielectric constant, high radiation resistance and high wear resistance. They have excellent heat and chemical resistance, excellent adhesion to a number of substrates and superior mechanical properties, such as high flexural modulus and compressive strength. Polyimides are also known to possess outstanding dimensional stability under loads, which allows their use in high temperature environments^{7,8}. Binding ability and thermal stability of Sodium silicate, makes it chief ingredients of intumescent coating⁹. Expandable graphite has an anti-oxidation and fire-resistant property. It

**Figure 2. Fire resistance study by cone calorimeter.**

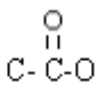
also improves water resistance of the coating¹⁰.

Melamine enables the creation of hard, glossy surfaces which are durable and hardwearing. Melamine surfaces and products are safe, hygienic, non-allergic and highly resistant to heat, chemicals and moisture¹¹. When melamine is exposed to heat and flames it decomposes, absorbing heat and creating a cooling effect. The time to ignition is delayed significantly as nitrogen, liberated by melamine during its decomposition, dilutes the oxygen which, in turn, inhibits the spread of flames and the generation of smoke¹¹. When melamine-based flame-retardant (intumescent) coatings are exposed to fire they swell with formation of inert N_2 gas. Melamine also acts as a blowing agent forming a stable, insulating charred foam layer. As a result the substrate material beneath the charred foam layer is protected from damaging heat (for example by delaying the time for a steel construction to collapse), thus extending potential escape time. Silicon carbide (SiC) has a specific gravity of 3.2, and its high sublimation temperature (approximately 2700 °C) makes it useful for bearings and furnace parts. It does not melt at any known pressure. SiC is chemically highly inert and has a very low coefficient of thermal expansion and experiences no phase transitions that would cause discontinuities in thermal expansion¹². It acts as a carbon source which gets decarburised giving rise to a carbonaceous char. Silicon carbide has high thermal remittance which results in radiation of incoming heat reducing the temperature at the back surface of substrate. Borax is not flammable and is not reactive. It loses 5 mol of water when heated to 100 °C, another 4 mol when heated to 150 °C, and the last mol at 400 °C. Boric acid releases chemically bonded water to reduce combustion.

3.1 FT-IR Analysis of Melamine Polyimide

The FT-IR spectral analysis results obtained for carboxylated-diimide and Melamine Polyimide are presented in Table 2.

Table 2. FTIR spectral results

Copolymer	Carboxylat-ed-diimide	Melamine Polyimide
Band assignment		Wave number (cm ⁻¹)
-NH- Amino stretching	3485.49	3475.84
C=O stretch overlap with imide	1780.36	1776.50
Five member ring with C=O group	1724.42	1716.70
N-H secondary amine aromatic	1508.38	1506.46
-C-N- stretching	1425.44	1284.63
 stretching	1116.82	--
C=O Stretching bond amide group	--	1633.76
C-O-C stretching	--	1246.06
Aryl -N- only sharp stretching	1388.79	1383.01

3.2 Thermal Analysis

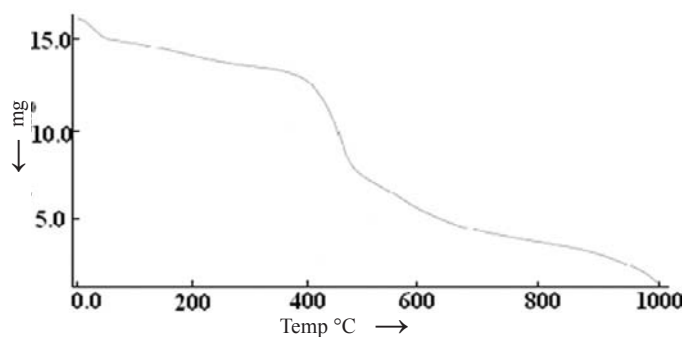
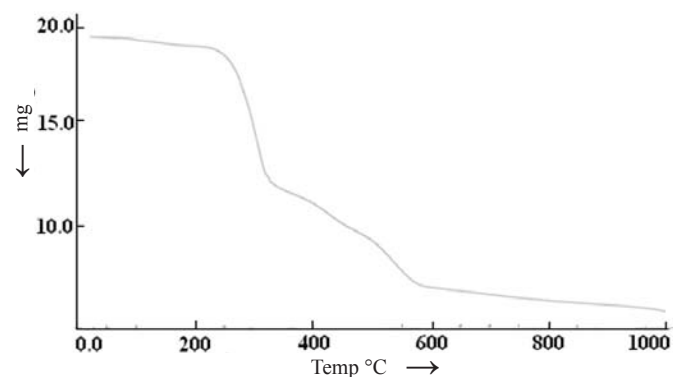
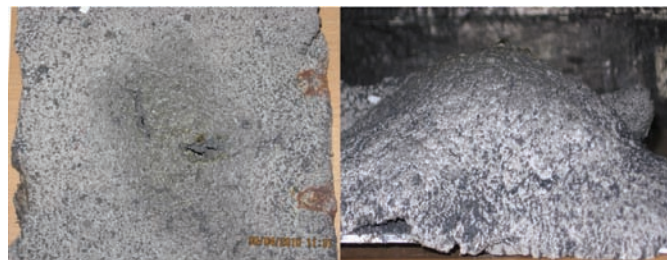
Thermo gravimetric analysis thermogram of the trimellitimide carbonyl chloride, trimellitimide-melamine (Melamine-polyimide) copolymer is depicted in Figs. 3 and 4 respectively. Fig. 3 shows onset of degradation from 35 °C due to removal of solvents and slow degradation from 100 °C onwards. There is rapid weight loss due to degradation of aromatic rings. Trimellitimide-melamine copolymer is stable up to 300 °C (Fig. 4), beyond 375 °C it shows fast degradation. After 375 °C it shows slow degradation representing further amide-imide linkages.

3.3 Fire Resistance by Intumescent Coating

A2 mm thick coating of formulation 5 (Table 1) was applied on aluminium plate and the fire test was carried out with thermo-coupled calorimeter. The coating thickness increased from 2 mm to 26 mm at the end of the experiment. Thus, the coating thickness increased by 13 times as a result of intumescence (Fig. 5). Also, the maximum temperature of coated aluminium substrate was observed to be 245 °C. The coating was able to maintain this temperature for 75 minutes. The formulation 5 coating showed the best results for thermal insulation as the temperature of other side of the plate remained below 65 °C for 5 minutes.

3.4 Time Temperature Profile Curves

The temperature of aluminium sheet was recorded against time during the fire tests. The recordings were carried out at time intervals of 30 s. These values were then plotted as time-temperature profile curves to understand the efficacy of the different intumescent coatings. Three specimens that were used to plot time temperature profile curves.

**Figure 3. TGA thermogram of trimellitimide carbonyl chloride.****Figure 4. TGA thermogram of trimellitimide-melamine.****Figure 5. Char formation for formulation 5: (a) Top view, (b) Side view.**

3.4.1 Time-Temperature Profile of Specimen I (Uncoated Aluminium Plate)

It was observed that specimen I which was an uncoated aluminium plate reached a temperature of 315 °C in 3 min and thereafter, the temperature increased to 525 °C within 6 min which led to softening of aluminium plate. The increase of the temperature of the plate was rapid and the metal lost its properties in a very short period of time.

3.4.2 Time-Temperature Profile of Specimen II (Aluminium Plate Coated with Formulation 3)

In the case of specimen II, the aluminium plate was coated with a 2 mm coating based primarily on silicates and expandable graphite. The coating was made as per formulation 3 given in Table 1. It was observed that the increase in temperature of

the aluminium substrate was much slower than the uncoated aluminium plate. It took about 25 minutes for the temperature to increase to 200 °C and the maximum temperature of the coated side of aluminium plate was restricted to 285 °C (Fig.6). However, the coating was able to sustain this temperature for only 55 minutes after which the char started to separate out from the plate and increase in temperature of plate was also observed.

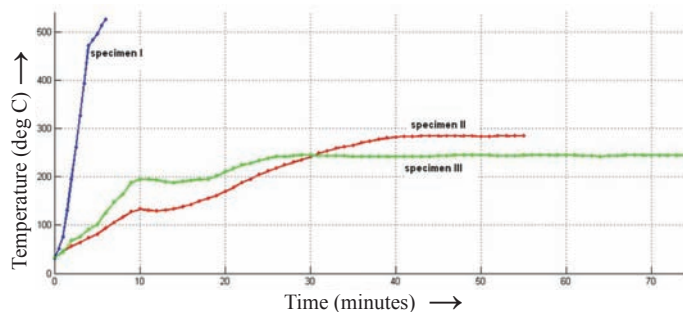


Figure 6. Time-temperature profile of specimen I, II and III.

3.4.3 Time-Temperature Profile of Specimen III (Aluminium Plate Coated with Formulation 5, Table 1)

For specimen III, the aluminium plate was coated with a 2 mm coating, having melamine polyimide. The initial increase in temperature of aluminium plate was faster than specimen II, with 200 °C being attained in 20 minutes as shown in time-temperature profile curve given in Fig.6. However, due to intumescence of the polymer coating and entrapment of gas between the surface and substrate, maximum temperature of coated aluminium plate was restricted to 245 °C and no further increase was observed. It produced good uniform char during the fire test. Stable temperature and fire protection for 75 minutes was maintained to the aluminium substrate.

In the intumescent process, two aspects have to be investigated carefully: the chemical aspect and the physical aspect, both demonstrated by the slow swelling and char formation. Thermally stable material presents a barrier effect to heat and to gases. In order to achieve this effect, a foamed charred layer has to be formed. A slow diffusion of gases in the structure during the intumescence allows the formation of an expanded structure as obtained in Fig.5.

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