Polyimide Resin For Fire-Resistant Moldings and Laminates

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Smoke and toxic gas generated match direct fire damage as hazards when plastics burn. Attempts to hinder burning by incorporating flame-retardant additives usually cause increased smoke and gas evolution from flammable synthetic materials. This is where the thermostable polymers can help.

A Thermostable Polymer

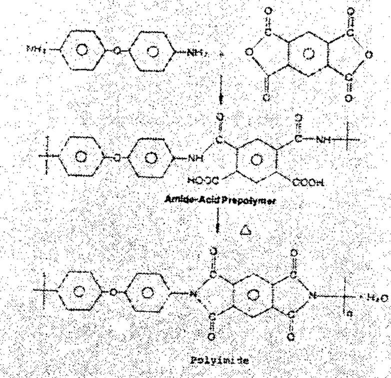
Polyimides, because of their fused heterocyclic ring structure and absence of hydrogen are inherently thermostable. The fused rings provide chain stiffness essential to high-temperature strength retention. Coupled with the fused rings, the low concentration of hydrogen in polyimides provides oxidative resistance by preventing fracture due to thermal degradation. The polyimides also have favorable cost-performance factors.

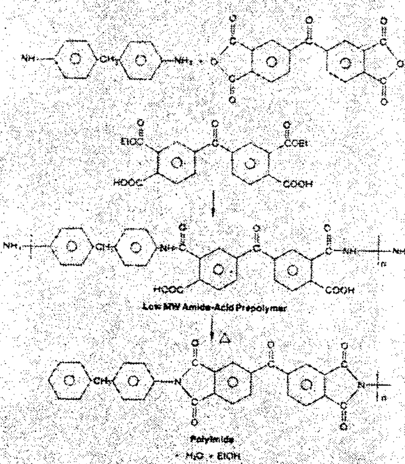
Fused rings, the result of the condensation of an aromatic amine with the aromatic dianhydride, are common to the commercially available polyimide resins (Fig. 1,2,3). However, the prepolymers and the routes to the cured polyimide vary considerably.

One system could be used for preparation of wire-coating enamels (Fig. 1). It is high-molecular-weight and consequently displays high viscosity at relatively low solid concentrations.

Another is an example of a typical condensation polyimide for laminating (Fig. 2). The low-molecular-weight prepolymer which results from using the diester provides a low-viscosity, high-solids varnish ideal for prepreg preparation. However, both water and alcohol are evolved during cure, which ends in laminates with voids.

One low-molecular-weight polyimide which differs from the other commercial resins can be processed in its ring-





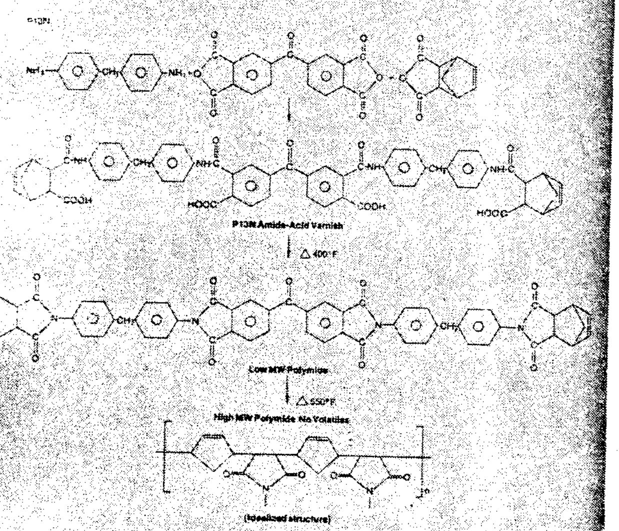


Fig. 1 (top right). High-molecular-weight polymer for wire-coating enamels. Fig. 2 (middle). Typical condensation polyimide for laminating. Fig. 3 (bottom). Low-molecular-weight polyimide for molding.

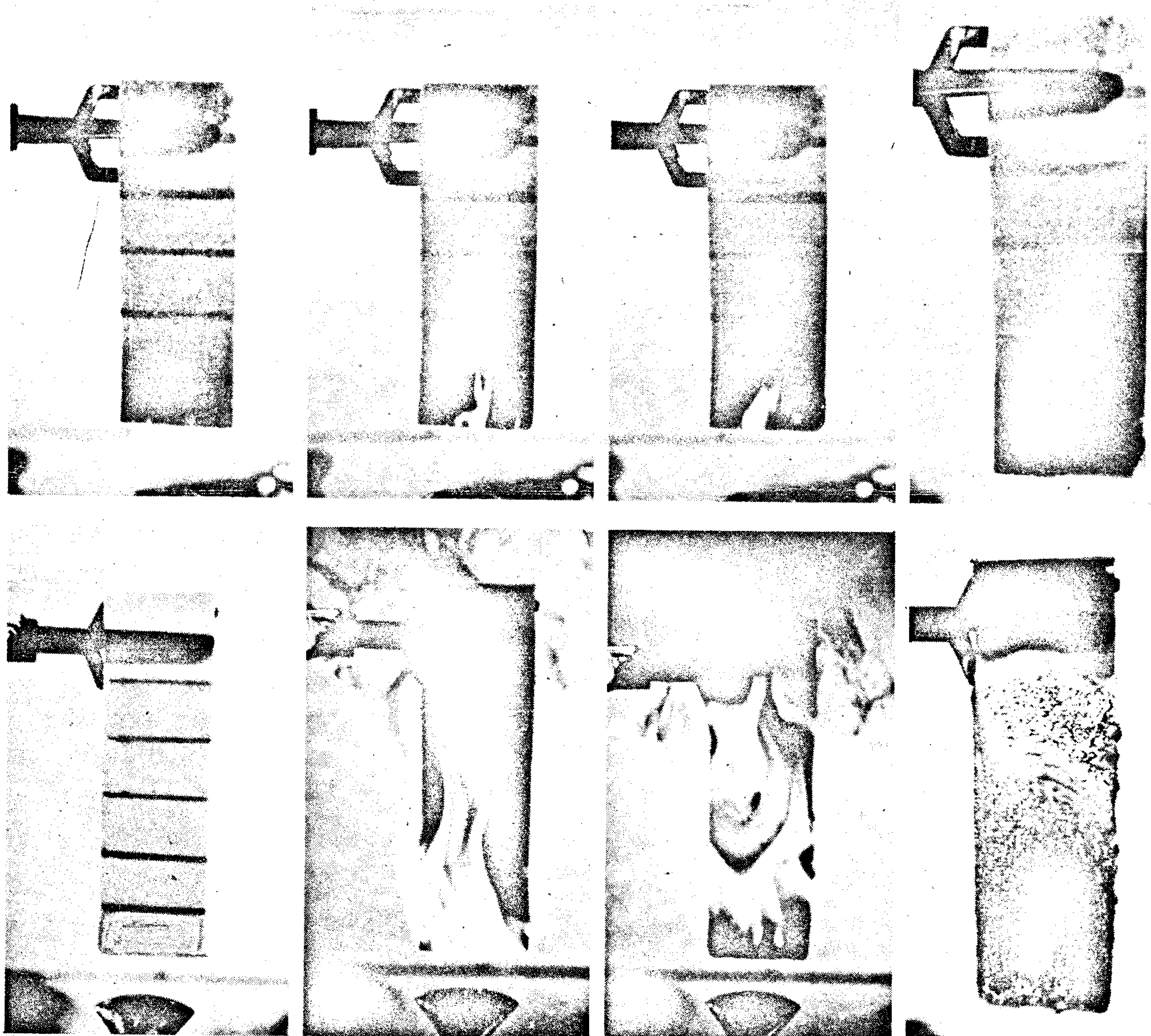


Fig. 4. Vertical test procedure (ASTM D 1692) of filled polyimide (top) and fire-retardant commercial resin (bottom). Times are (reading left to right) 1, 25, 55, and 285 sec.

Table 1 – Vertical Burn Test, ASTM D1692

Time (sec)	Filled-Polyimide Laminate	Flame-Retardant Resin Laminate
1	–	Edge ignition
3	1/4-in. burn	Edge propagation
5	1-in. burn	0.5-in. burn, some smoke; 3.5-in. flame ht
10	2-in. burn, slight flame	1.5-in. burn, mod. smoke; 4.0-in. flame ht
15	2.5-in. char; 2.5-in. flame ht	2.5-in. burn, mod. smoke; 5.5-in. flame ht
20	2.5-in. char; 4.5-in. flame ht	3.5-in. burn, mod. smoke; 5.0-in. flame ht
30	2.5-in. char; 4.5-in. flame ht	5.0-in. burn, hvy. smoke; 5.5-in. flame ht
50	2.5-in. char; 3.5-in. flame ht	5.0-in. burn, hvy. smoke; 7.0-in. flame ht
90	2.5-in. char; 2.5-in. flame ht.	6-in. flame ht gaseous combustion
120	2.5-in. char; 2.5-in. flame ht	As above, 4-in. resin burnoff.
135	2.5-in. char; 2-in. flame ht	As above, 5.4-in. destrt. distill. resin
180	Erosion only, no flame	5.0-in. resin burnoff
200	Erosion only, no flame	Slight flame
270	Erosion only, no flame	Flame-out, continued erosion
315	Erosion only, no flame	As above

Table 2
XP-2 Smoke Density Chamber

Time (sec)	Light Obscuration (%)	
	Filled-Polyimide Laminate	Flame-Retardant Resin
0	0	0
5	0	0
10	1	1
15	1	4
20	1	10
30	2	32
50	3	88
75	6	100
100	11	100
140	11	100

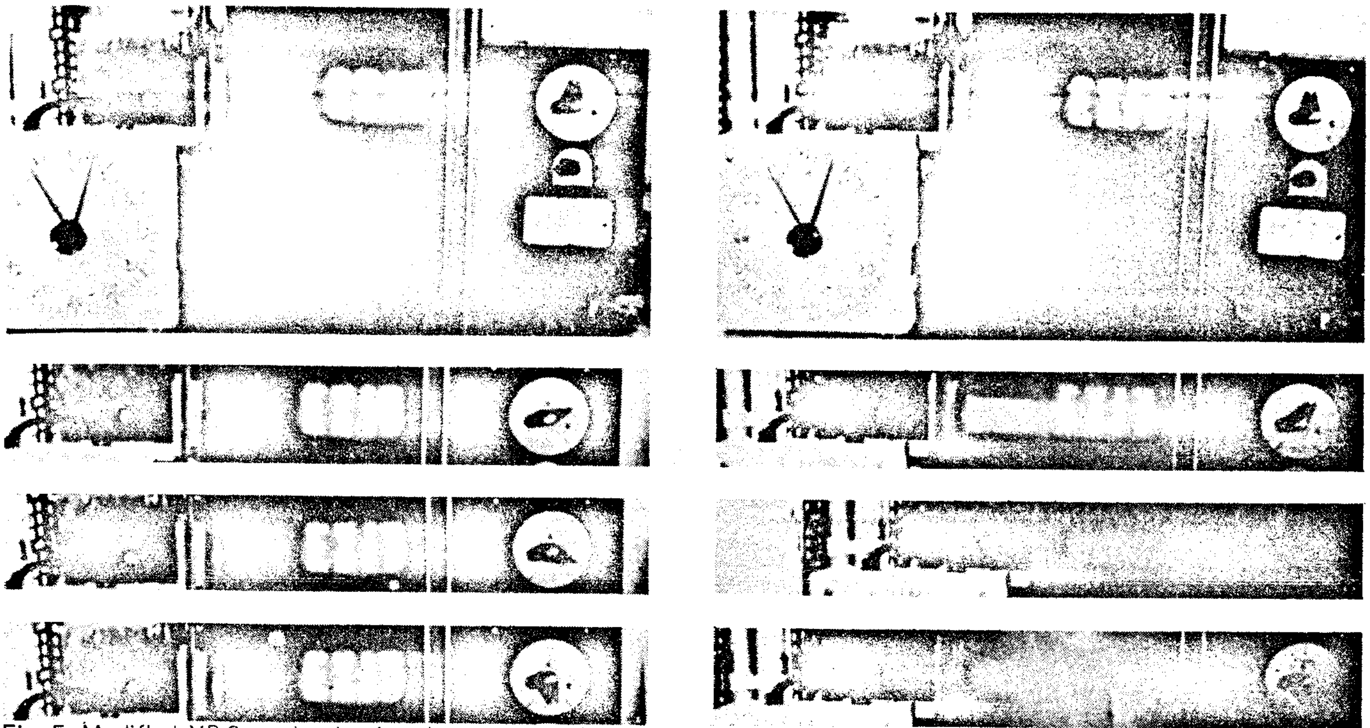


Fig. 5. Modified XP-2 smoke density chamber tests filled polyimide (left) times are (top to bottom) 5, 55, 95, and 135 sec. Fire-retardant commercial resin (right) times are 5, 35, 95, and 135 sec.

closed, imidized state, thereby providing void-free high-quality moldings (Fig. 3).*

Flammability

The flammability characteristics of polymers may be divided into six general categories according to the properties being measured: ease of ignition, combustion duration, flame propagation, fuel contribution, gas and smoke generation, and secondary effects.

The most widely accepted method of quantifying ease of ignition is the Limiting Oxygen Index. The L.O.I. test determines the minimum concentration of oxygen necessary to sustain combustion. These tests have been performed on both "neat" molded resin and the mineral-filled polyimide moldings. An oxygen content of 32% was determined as the L.O.I. for the 100% resin. Addition of a mineral filler of pulverized quartz (40 wt %) further reduced its flammability to L.O.I. of 39%. Similar L.O.I. values are achieved with resins containing retardants. These acceptable values alone, however, do not tell the complete story.

Flammability (combustion) and flame propagation were photographically recorded as a comparison of a commercial flame-retardant resin laminate and the filled polyimide (Fig. 4). A modified ASTM D1692-vertical test procedure was employed. As shown, the polyimide supports combustion only in the direct flame. Rapid char formation occurs with minimal smoke or gas generation. Flame propagation is essentially nil. Data from the test were recorded (Table 1).

Smoke

Since smoke and toxic gas are as dangerous as the fire itself, evaluation of resin flammability should include them. A modified XP-2 smoke density chamber was used to test smoke development characteristics (Fig. 5 and Table 2).

*P13N Polyimide—Ciba-Geigy Corp.

Smoke density was measured quantitatively by a Weston Barrier Layer photocell in the walls of the chamber 11 in. above the sample support. Time necessary to reach 100% light obscuration is normally used as a measure of the amount of smoke. For samples of the same material, the time to 100% obscuration can be measured within a standard deviation of 1.4 sec.

Important in gas or smoke generation are their secondary effects. In systems utilizing halogenated flame retardants, corrosion from HBr or HCl is important. The volatile products from the filled polyimide did not appear to present these corrosion problems.

Oxygen-Rich Atmospheres

In addition, filled-polyimide laminates passed FAA certification for nonflammability and were examined in conditions similar to those necessary for qualification in the Apollo and Skylab programs. Apollo and Skylab tests are conducted in oxygen-enriched environments. Four conditions were examined: 16.5 psia 100% O_2; 16.5 psia 60% O_2, 40%N_2; 6.2 psia 100% O_2; and 5.0 psia 70% O_2, 30% N_2.

In the 100% oxygen environment, flame propagation rate after ignition by flaming silicone sheeting was 0.04 in./sec at 16.5 psia and 0.026 in./sec at 6.2 psia. Both rates are acceptable, considering the atmosphere, but unacceptable in parts of the Apollo or Skylab vehicles. In the mixed environments, the laminate was self-extinguishing. These results appear to somewhat contradict the L.O.I. data. However, these are glass laminates which typically contain only 25 to 30 wt % resin. As mentioned earlier, mineral fillers can significantly reduce flammability.

It is expected that filled polyimides will be used in many applications where flame resistance is important. Potential fields for these applications are the aerospace, automotive, construction, and electrical/electronics. •