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A TGA study correlating polymer characteristics with smoke and flammability properties of polyester and phenolic resins *

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Abstract

Because of the unacceptable amount of smoke produced from styrene cross-linked polyester composites, when tested for specific optical density of smoke generated by solid materials (ASTM E662), phenolic resins are currently under investigation as an alternative to polyesters in marine applications. Thermogravimetric analysis (TGA), NBS smoke chamber tests, oxygen index tests, flame spread tests, and toxic gas production tests have been used to study the fire and flammability characteristics of two styrene cross-linked polyester resins, Vibrin F1029 and Hetron 692TP, and three resol phenolic resins, J2018L, OCFHJ1 and Plenco 11956.

Results of thermogravimetric analyses on the phenolic and polyester resins, in both air and nitrogen, indicate that the phenolic resins are superior to the polyester resins from a "smoke and flammability" point-of-view. That is, the phenolics are more stable thermally, produce less smoke, have a higher oxygen index, have a lower flame spread rating and produce less toxic gas than the polyester resins. The higher thermal stability and lower smoke release of the phenolic resins relative to the polyester resins is discussed in terms of the degradation mechanisms and degradation products of these resins.

INTRODUCTION

There are many thermoset resins which, when used in conjunction with glass or fibre reinforcement, yield composites with high strength to weight ratios, excellent corrosion resistance, and good electrical and ballistic properties. These properties make glass reinforced plastics (GRPs) attractive materials for the replacement of metallic alloys on board ships, where reductions in topside weight, improved corrosion resistance and better ballistic properties are particularly important. However, all polymeric materials will burn, and the fire hazards involved with the use of these materials on board ship are of great concern. Several factors determine the fire hazard involved with a particular polymeric material. These include the

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ignitability of the material, its flammability and smoke production, the rate of and total heat release of the material, and the toxicity of the smoke produced [1].

Several standard tests are used to assess the fire and flammability characteristics of polymeric materials, including GRPs. These tests include ASTM E162 [2], which provides a method for measuring the surface flammability of materials exposed to a set level of radiant heat energy, ASTM E662 [3], which measures the degree of light obscuration produced by the smoke released by a material under controlled exposure conditions using the National Bureau of Standards (NBS) smoke chamber, ASTM D2863 [4], which assesses the flammability of materials by measuring the minimum concentration of oxygen in an oxygen–nitrogen mixture that will just support flaming combustion of a material, and the Bombardier SMP800 test [5] for toxic gases including carbon monoxide, hydrogen chloride, hydrogen bromide, hydrogen fluoride, hydrogen cyanide, and oxides of nitrogen and sulphur.

Thermal degradation mechanisms, toxic and hazardous gas production and the thermal stability of polymeric materials have been studied using a number of analytical techniques. These include pyrolysis mass spectrometry [6], pyrolysis gas chromatography/mass spectrometry (pyr GC/MS) [7–10], low temperature thermal degradation GC/MS [11–13], thermogravimetric analysis (TGA) [8,14–19], and thermal volatilization analysis (TVA) [20–22].

In this paper, the results of thermogravimetric analyses, NBS smoke chamber tests, oxygen index tests, flame spread tests and Bombardier SMP800 toxic gas analysis tests on two styrene cross-linked polyester resins and three resol-type phenolic resins, in air and in nitrogen, are reported. The comparison and correlation of the degradation mechanisms, thermal stability, ignitability, smoke production, and flame spread of these materials to obtain an indication of how these materials might perform, in a relative sense, in a fire situation has been attempted.

EXPERIMENTAL

Thermogravimetric analysis

Thermogravimetric analysis was carried out on a DuPont Instruments Model 951 Thermogravimetric Analyzer in both the ramped and the isothermal mode. In the ramped mode the sample was equilibrated at 100 °C for 10 min, then heated at a rate of 20 °C min^{-1} to 1000 °C in an inert atmosphere (nitrogen) or to 800 °C in a reactive atmosphere (air). In the isothermal mode, the samples were equilibrated at 100 °C and then heated in a ballistic mode to final temperatures of 300 °C, 400 °C, and 500 °C in both inert and reactive atmospheres. The flow rate of nitrogen (inert) or air (reactive) was ≈ 100 ml min^{-1}.

Smoke production, toxic gas, flame spread and oxygen index tests

Smoke production, toxic gas, flame spread and oxygen index testing of the two polyester and three phenolic resins was carried out at an independent laboratory. The release of toxic gases, including carbon monoxide (CO), hydrogen chloride (HCl), hydrogen bromide (HBr), hydrogen fluoride (HF), sulphur dioxide (SO_2), and nitrogen oxides (NO_x), was monitored during the smoke production testing in the NBS smoke chamber.

Materials

Five thermoset resins were studied in this report: the two polyester resins Hetron 692TP (Ashland Chemical) and Vibrin F1029 (FibreGlas Canada Ltd.), and the three phenolic resins J2018L (BP Chemicals), OCFHJ1 (Owens Corning), and Plenco 11956 (Plastics Engineering Company).

Vibrin F 1029 is a phthalic acid-based polyester resin. Phthalic acid-based polyester resins are prepared by the condensation polymerization of phthalic acid or phthalic anhydride and unsaturated dibasic acids, such as fumaric acid, with diols.

Hetron 692TP is an isophthalic acid-based polyester that contains proprietary flame retardants. Isophthalic acid polyesters are prepared by the condensation polymerization of isophthalic acid or isophthalic anhydride and fumaric acid with diols.

Styrene was used as the cross-linking agent with the polyester resins at a concentration of 40% by weight. Cure was initiated with 1.0 part per hundred of resin by weight (phr) of methyl ethyl ketone peroxide (Lupersol DDM-9, Pennwalt) and 0.15 phr of cobalt naphthenate (Nuodex DMR, Nuodex Canada Ltd.).

The three phenolic resins investigated in this study were resol type. Resol phenolic resins are mixtures of mono-, di-, and trihydroxymethyl substituted phenols, mono-, di-, tri- and tetrahydroxymethyl substituted bis(hydroxyphenyl)methanes, and, to a lesser degree, methyl substituted ditolylbenzenes that are prepared from phenol and formaldehyde by controlling the ratio of the two reactants and the time and temperature of reaction. Resol formation is dependent upon maintaining an excess of formaldehyde in the reaction vessel, that is, keeping the ratio of phenol to formaldehyde (P/F) low.

The phenolic resins were obtained from cured glass reinforced panels, whereas the styrene cross-linked polyester resins were prepared as castings in-house. No attempt was made to separate the phenolic resin and glass fibre prior to analysis. Thermogravimetric analysis indicated that the J2018L GRP was approximately 55% glass by weight, the OCFHJ1 GRP was 80% glass by weight and the Plenco GRP was 75% glass by weight.

Resol phenolic resins can be cured at temperatures between 130 ° C and 250 ° C without the addition of a curing agent. Base or acid catalysis is often used to speed the curing reaction. Phenolics cured in the presence of ammonia have a yellow colour, which has been attributed to the presence of azomethine (–HC=N–) groups in the cured resin. Organic base catalyzed phenolics have also been shown to contain dibenzylamine and tribenzylamine structures, which under the proper conditions could be transformed into the azomethine group. Acid cure of resols will take place at room temperature in the presence of strong organic and inorganic acids such as *p*-toluenesulphonic acid, hydrochloric acid (HCl), and phosphoric acid (H_3PO_4). More recently hydroxybenzenesulphonic acids have been used, as they are incorporated into the polymer backbone and reduce corrosion problems associated with the migration of acid residues to the surface of the cured polymer, where they can interact with metallic components.

RESULTS AND DISCUSSION

Ramped thermogravimetric analysis

The results of the ramped temperature TGA for the two polyester and the three phenolic resins are shown in Figs. 1 and 2 respectively. For each resin the figures show the percentage weight loss versus temperature plot in either inert or reactive atmospheres.

The major difference in the weight versus temperatures plots for polyester resins Hetron 692TP and Vibrin F1029 was observed at temperatures above

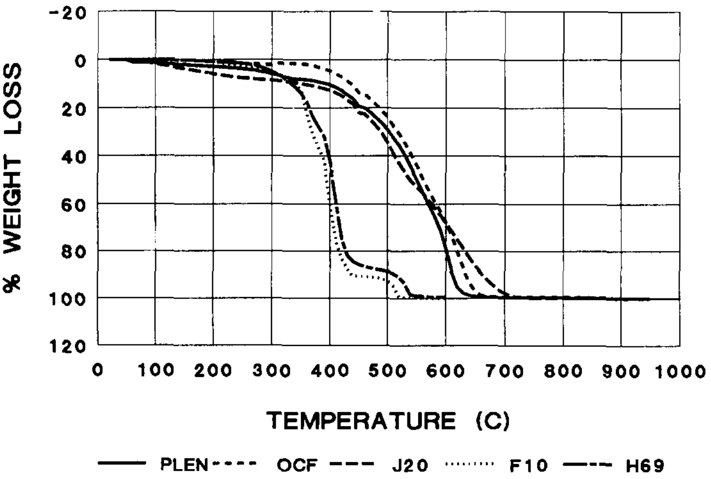

Fig. 1. Ramped temperature TGA plots in air for two styrene cross-linked polyester resins, Vibrin F1029 and Hetron 692TP, and three resol phenolic resins, J2018L, OCFHJ1 and Plenco 11956.

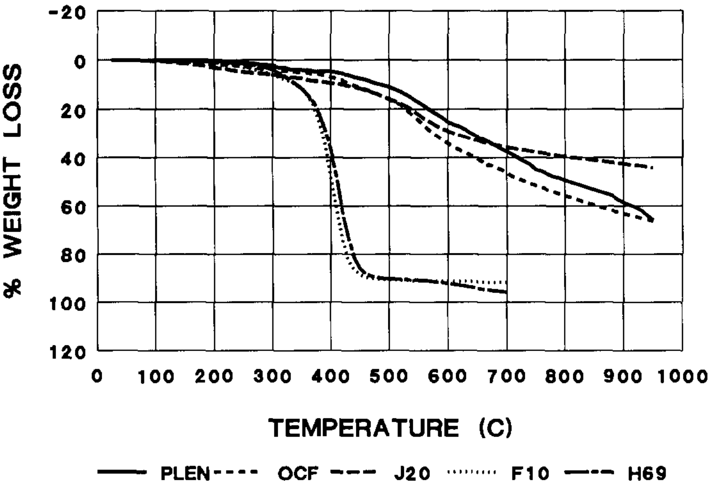

Fig. 2. Ramped temperature TGA plots in nitrogen for the two styrene cross-linked polyester resins and three resol phenolic resins as in Fig. 1.

450 °C. In air, Hetron 692TP was completely volatilized at 550 °C, whereas in nitrogen, 2.5% of the weight of the original sample remained at 700 °C. Similarly for Vibrin F1029, the sample was completely volatilized at approximately 550 °C in air, whereas 8% of the sample remained at 700 °C in nitrogen. This difference is due to the formation of char as the resins thermally degrade. The char that is formed can oxidize in air and is volatilized, whereas in nitrogen the char cannot oxidize and thus decomposes at a much higher temperature.

The weight versus temperature plots for the Plenco, J2018L and OCFHJ1 resins were also found to show a dependence on the nature of the atmosphere used. As the temperature was increased these phenolic resins decomposed more rapidly in air than in nitrogen. The observed change in the rate of decomposition as the temperature was increased is related to the degradation mechanism of phenolic resins.

The oxidation of phenolic resins has been studied by Conley [23–26]. In the inert atmosphere, no oxidative degradation can take place, and therefore any change in the weight of the sample is due to the thermal degradation of the resin. However, as the temperature is increased, the presence of oxygen accelerates the decomposition process. This can be related to the thermal degradation of phenolic resins by the interchain condensation mechanism, which is accompanied by the release of small molecules and the formation of a carbonaceous layer on the surface of the sample. The carbonaceous layer acts to retard the continued thermal degradation of the resin. In air, this layer can be oxidized and volatilized to expose the remainder of the resin. In an inert atmosphere the carbonaceous layer cannot be oxidized, breaks down more slowly and therefore slows the rate of weight loss of the resin.

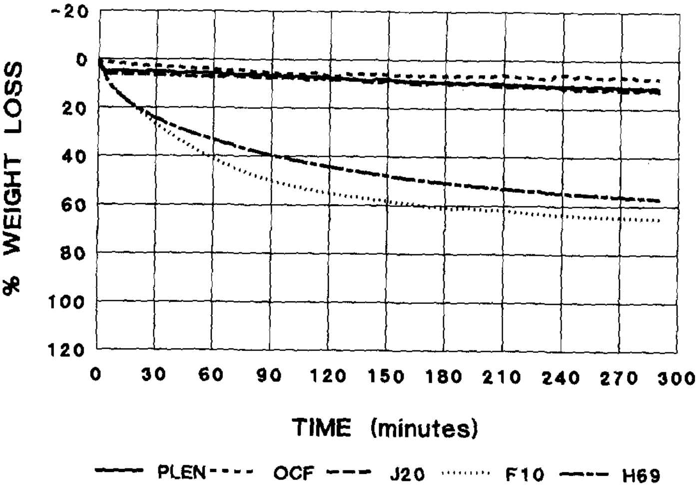

Fig. 3. Isothermal TGA plots in air at 300 ° C for the two styrene cross-linked polyester resins and three resol phenolic resins, as in Fig. 1.

The degradation products of the three phenolic resins examined in this study were similar and are characteristic of small molecules that would be released from the cleavage of bonds in a phenolic resin, that is, methyl substituted phenols and methyl substituted aromatics.

Isothermal thermogravimetric analysis

Figures 3, 4 and 5 show TGA plots of weight versus time for the two polyesters and the three phenolics in air at 300, 400 and 500 ° C respectively.

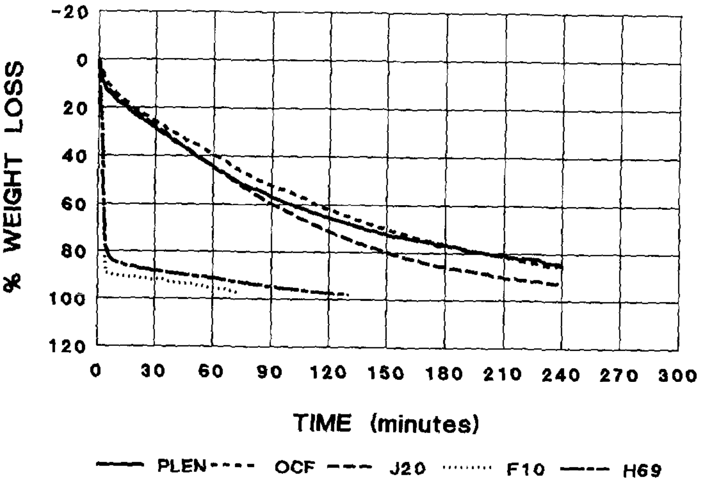

Fig. 4. Isothermal TGA plots in air at 400 ° C for the two styrene cross-linked polyester resins and three resol phenolic resins as in Fig. 1.

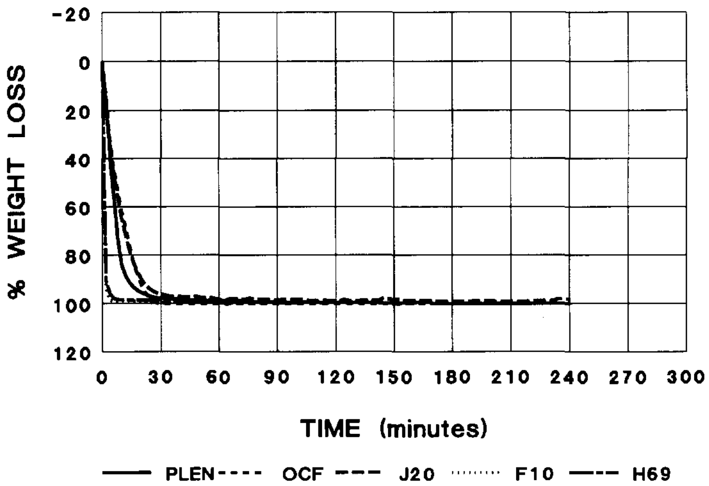

Fig. 5. Isothermal TGA plots in air at 500 °C for the two styrene cross-linked polyester resins and three resol phenolic resins as in Fig. 1.

Comparison of the plots at any given isothermal temperature indicates that the polyesters lose weight faster than the phenolics at equivalent times.

Isothermal analyses were also conducted at 300, 400, and 500 °C in an inert atmosphere, and the results are listed in Table 1. To allow for comparison of the weight loss of the resins and to give an indication of the thermal stability under that set of conditions, the percent weight loss of the resins at each temperature is given for the same duration of exposure.

It can be seen in Table 1 that the phenolic resins lose less weight than the polyester resins for a given temperature and time of exposure in either an inert or reactive atmosphere. For instance, at 400 °C and in an inert atmosphere, the polyesters lose ≈ 90% of their weight after 10 min, whereas

TABLE 1

Weight loss of two polyester and three phenolic resins at 300, 400 and 500 °C in both nitrogen and air following exposure at the times shown

Temp (°C)	Percentage weight loss (time, min)				
	F1029	692TP	Plenco	J2018L	OCFHJ1
In nitrogen					
300	65 (290)	51 (290)	15 (290)	17 (290)	12 (290)
400	91 (10)	88 (10)	21 (10)	20 (10)	22 (10)
500	97 (10)	93 (10)	33 (10)	33 (10)	42 (10)
In air					
300	65 (290)	57 (290)	12 (290)	13 (290)	08 (290)
400	90 (10)	85 (10)	17 (10)	16 (10)	15 (10)
500	99 (10)	98 (10)	84 (10)	65 (10)	62 (10)

TABLE 2

Results of the ASTM E662 (NBS smoke chamber) tests

Smoke production	F1029	692TP	OCFHJ1	J2018L	Plenco 11956
$Ds_{1.5}$	120	34	1	0	1
Ds_4	563	311	1	1	6
Ds_{Corr}	552	565	47	20	31

Ds, Smoke optical density at subscripted time (min).
Ds_{Corr}, Corrected smoke optical density.

the phenolics lose ≈ 20% of their weight after 10 min. At 400 °C and in air, the polyesters lose ≈ 88% of their weight in 10 min whereas the phenolics lose ≈ 16% of their weight after the same period.

ASTM E-662 (NBS smoke chamber) tests

The results of the NBS smoke chamber tests for the five resins are shown in Table 2. It is apparent from these results that the two polyester resins produce more smoke than the three phenolic resins. Comparison of the smoke production results for the two polyester resins shows that, although the corrected smoke optical density for these two polyester resins is essentially the same, F1029 produces smoke more quickly than the Hetron 692TP. That is, the smoke density readings for resin F1029 were 120 and 563 after 1.5 and 4 min respectively while the smoke density readings for resin Hetron 692TP at 1.5 and 4 min were 34 and 311 respectively. This was expected, since the results of the isothermal thermogravimetric analysis of these two polyesters shown in Table 1 indicated that Vibrin F1029 lost weight more quickly at a given temperature than Hetron 692TP.

Of the three phenolic resins, OCFHJ1 had the highest smoke density reading (Ds_{Corr}), 47, versus 31 for Plenco 11956 and 20 for J2018L.

The smoke production of polymers or particular organic compounds has been shown to be very dependent on the structure of those compounds. For instance, Table 3 lists the mass optical density (MOD) of smoke produced by some common polymers, styrene and paraffin wax. The mass optical

TABLE 3

Mass optical density (MOD) of several polymers and monomers [27]

Material	MOD ($cm^2\ g^{-1}$)
Polystyrene $[-(Ph)CH-CH_2]_n$	14300
Styrene $PhCH{=}CH_2$	9600
Polypropylene $[-(CH_3)CH-CH_2-]_n$	5250
PVC$[-(Cl)CH-CH_2]_n$	3400
Polyethylene $(-CH_2-CH_2-)_n$	2900
Paraffin wax $(-CH_2-CH_2-)_n$	2300
Polyoxymethylene $(-CH_2-O-)_n$	~ 0

density values are for equal masses of the various compounds. Polystyrene and styrene produce particularly large quantities of smoke, that is, the MOD values are 14,300 cm^2 g^{-1} and 9,600 cm^2 g^{-1}, whereas polyoxymethylene, which burns cleanly, has a MOD value of zero. The effect of changing the side group of a polymer chain on the smoke production of polymers is also illustrated by the data in Table 3. In going from polyethylene to polyvinyl chloride to polystyrene, where the side group on the chain changes from H to Cl to Ph, the smoke production as measured by the mass optical density increases from 2900 to 3400 to 14300 cm^2 g^{-1}.

Pyrolysis GC/MS indicated that the major degradation products of the styrene cross-linked polyester resins were styrene, methylstyrene, toluene and styrene dimer. These products are typical of the thermal degradation of a styrene-based polymer, which is known to proceed by a random chain scission mechanism followed by depolymerization to release styrene as the major degradation product. This suggests that the smoke production of the polyester resins can be attributed in large part to the presence of styrene cross-links in the cured resins. In addition, the polyester portion of the styrene cross-linked polyester resins contains aromatic compounds, such as phthalic acid and isophthalic acid in Vibrin F1029 and Hetron 692TP respectively, which are also good smoke precursors.

Although pyrolysis GC/MS indicates that a number of aromatic compounds, which are good smoke precursors, are released as the phenolic resins thermally degrade, the amount of smoke precursor released per unit mass of polymer is small relative to that for the polyester resins, as a result of the tendency of phenolic resins to condense and form char.

Toxic gas, flame spread and oxygen index test results

The results of the Bombardier SMP800 test for toxic gases, ASTM D2863 oxygen index test and ASTM E162 flame spread test for the polyester and phenolic resins are given in Table 4.

TABLE 4

Results of the Bombardier SMP800 test for toxic gases, the ASTM D2863 oxygen index test and the ASTM E162 flame spread test. Toxic gas (ppm)

Test	F1029	692TP	OCFHJ1	J2018L	11956
CO	1980	2545	476	950	635
HCl	8	150	86	3	24
HBr	8	16	<1	2	<1
HF	<1	<1	<1	1	<1
NO_x	1	<1	3	<1	<1
HCN	<1	<1	<1	<1	<1
SO_2	<1	<1	22	3	4
Oxygen index (% O_2)	20.4	30.4	65.0	45.4	55
Flame spread (kW min^{-1})	99	12	2	1	2

There was a considerable difference in the flame spread and oxygen index results for the two polyester resins. The flame spread for Vibrin F1029 was 99, whereas the flame spread for Hetron 692TP, which contained proprietary flame retardants, was 12. The oxygen index for Vibrin F1029 was also considerably lower than that for Hetron 692TP, that is, 20.4% for Vibrin F1029 versus 30.4% for Hetron 692TP. Further, more acid gas and more carbon monoxide were produced by the halogen-containing proprietary flame retardants in Hetron 692TP than by the phthalic acid based polyester. In the gaseous phase, halogens act to interfere with the free radical chain reactions that are responsible for the combustion process. The material burns inefficiently, and therefore has a higher oxygen index and lower flame spread index and produces more CO.

In general, the three phenolic resins produced less CO and had a higher oxygen index and a lower flame spread rating than either polyester resin. J2018L had the lowest oxygen index (45.4%) and produced the most CO (950 ppm) of the three phenolic resins tested. However, it produced less HCl than either Plenco 11956 or OCFHJ1, and had the lowest flame spread rating of the three phenolic resins tested. The low smoke production, low flame spread, and high oxygen index values of the phenolics are related to their thermal degradation mechanism. Interchain condensation leads to the formation of carbonaceous char and a significant reduction in the release of volatiles, as evidenced by TGA. The char layer acts to protect the underlying polymer from thermal degradation and reduces the release of volatiles required to initiate and propagate flaming combustion and the production of smoke.

CONCLUSIONS

The results indicate that the phenolic resins are superior, from a "smoke and flammability" point of view, to the styrene cross-linked polyester resins. Comparison of the smoke production, flame spread, and oxygen index results for two styrene cross-linked polyester resins, Vibrin F1029 and Hetron 692TP, and three resol-type phenolic resins, J2018L, OCFHJ1 and Plenco 11956, indicates that the phenolic resins produce less smoke, have higher oxygen indexes, and have lower flame spread ratings than either of the polyester resins.

TGA analysis shows that the polyester resins are less thermally stable than the three phenolics evaluated. The high smoke production of the styrene cross-linked polyester resins is related to the presence of approximately 40% by weight of styrene cross-links in these resins. Polystyrene degrades by a random chain scission–depolymerization mechanism, and the degradation products of polystyrene such as styrene, toluene and styrene dimer are excellent smoke producing materials. Although the proprietary flame retardants in Hetron 692TP reduced the flame spread and increased the oxygen index relative to Vibrin F1029, this resin system still has a higher flame spread rating and lower oxygen index than any of the three phenolic resins evaluated. The proprietary flame retardants in Hetron 692TP have little effect on the degradation of the styrene cross-links and result in the release of acid gases from this polymer.

REFERENCES

1 M.M. Hirschler, Fire Hazard and Toxic Potency of Smoke from Burning Materials, Advances in Combustion Toxicology, Vol. 2, Technomic, Lancaster, PA, 1989.
2 ASTM E 162-83, Standard test method for surface flammability of materials using a radiant heat energy source, 1987 Annual Book of ASTM Standards, American Society for Testing and Materials, Philadelphia, PA.
3 ASTM E 662-83, Standard test method for specific optical density of smoke generated by solid materials, 1987 Annual Book of ASTM Standards, American Society for Testing and Materials, Philadelphia, PA.
4 ASTM D 2863-77, Standard test method for measuring the minimum oxygen concentration to support candle-like combustion of plastics (oxygen index), 1987 Annual Book of ASTM Standards, American Society for Testing and Materials, Philadelphia, PA.
5 Boeing BSS 7239, Toxic gas sampling and analytical procedures using ASTM E 662 combustion modes (basis of Bombardier SMP800 specification), 1983.
6 L. Dean, S. Groves, R. Hancox, G. Lamb and R.S. Lehrle, Polym. Degradation Stab., 25 (1989) 143.
7 M.S. Chen, S.J. Chang, R.S. Chang, S.M. Chen and T.B. Tsai, Polym. Degradation Stab., 23 (1989) 239.
8 V. Mailhos-Lefivre, D. Saleet and B. Martel, Polym. Degradation Stab., 23 (1989) 327.
9 M. Blazso, E. Jakab, T. Szekely, B. Plage and H.R. Schulten, J. Polym. Sci., Part A, 27 (1989) 1027.
10 J.A. Hiltz and M.C. Bissonnette, Pyrolysis–gas chromatography/mass spectrometry of thermoplastic polymers, DREA Tech. Mem. 88/209, April 1988.
11 D. Price, G.J. Milnes, P.J. Taylor, J.H. Scrivens and T.G. Blease, Polym. Degradation Stab., 25 (1989) 307.
12 J.A.J. Jansen, W.E. Haas, H.G.M. Nautkens and A.J.H. Leenen, Thermochim. Acta, 134 (1988) 307.
13 J.A. Hiltz, Low temperature thermal degradation studies of styrene cross-linked vinyl ester and polyester resins, DREA Tech. Memo. 88/211, July 1988.
14 M.A. Iriarte, J.J. Irwin and J.I. Equiazabal, J. Mater. Sci., 24 (1989) 1021.
15 P. leParlorier, J. Therm. Anal., 33 (1988) 1085.
16 J.H. Flynn and B. Dickens, Thermochim. Acta, 15 (1976) 1.
17 B. Dickens, J. Polym Sci., Polym. Chem. Ed., 20 (1982) 1169.
18 B. Dickens, J. Therm. Anal., 27 (1983) 379.
19 E.A. Turi (Ed.), Thermal Characterization of Polymeric Materials, Academic, New York, 1981.
20 S. Zulfiqar, N. Akhtar, M. Zulfiqar and I.C. McNeill, Polym. Degradation Stab., 23 (1989) 299.
21 I.C. McNeill and M. Coskun, Polym. Degradation Stab., 25 (1989) 1.
22 I.C. McNeill and M. Coskun, Polym. Degradation Stab., 23 (1989) 175.
23 R.T. Conley, J. Appl. Polym. Sci., 7 (1963) 103.
24 R.T. Conley, J. Appl. Polym. Sci., 7 (1963) 171.
25 W.M. Jackson and R.T. Conley, J. Appl. Polym Sci., 8 (1964) 2163.
26 R.T. Conley, J. Appl. Polym. Sci., 9 (1965) 1117.
27 L.H. Breeden and M. Meisters, J. Fire Flammability, 7 (1976) 234.