

Chapter 5

High Performance Polyimide Foams

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Aromatic polyimides have been attractive for applications in the aerospace and electronics industries. Unique properties such as thermal and thermo-oxidative stability at elevated temperatures, chemical resistance, and mechanical properties are common for this class of materials.¹ Newer to the arena of polyimides is the synthesis of polyimide foams.² In the present work, three different, closely related, polyimide foams are comparatively studied, including thermal, mechanical, surface, flammability, and degradation properties. In previous studies, the data relate to films³ and not foams. Foams have much higher surface areas and are a greater challenge to fire retard. Understanding degradation and properties versus structure, foam versus solid, is of interest. Data indicate that subtle differences in chemical structure result in large differences in surface area, which further result in large differences in heat release and other flammability properties.

NASA Langley Research Center (LARC) has been developing the next generation of polyimide foam materials that will be utilized for such things as cryogenic insulation, flame retardant panels and structural sub-components.² This new foam technology allows for the processing of polyimide neat or syntactic foams, foam-filled honeycomb or other shapes, and microspheres, all of which produce useful articles. These products can be used in a variety of ways: flame retardant materials and for fire protection, thermal and acoustic insulation, gaskets and seals, vibration damping pads, spacers in adhesives and sealants, extenders, and flow/leveling aids. This process can also produce polyimide foams with varying properties from a large number of monomers and monomer blends. The specific densities of these foams can range from 0.008 g/cc to 0.32 g/cc.²

Although certain physical and mechanical properties of some of these polymers have been previously studied and reported, the characterization and understanding of such properties as flame retardancy, fire protection, liquid oxygen (LOX) compatibility, and stability versus degradation of the foams are now of significant interest. The study of their respective properties (comparative) with regards to seemingly minor changes in chemical structure, density and surface area present a novel area of research. The information gained should be of significant value in the application of polyimide foams and polymeric foams in general.

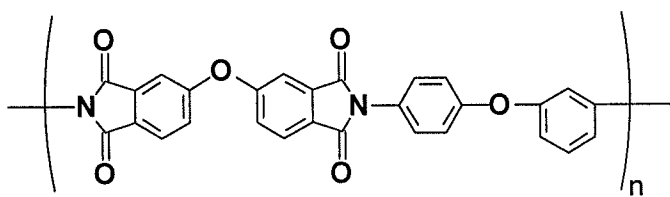
Figure 1 includes the chemical structures of the foams (see Table I for abbreviations). The last letter of each foam name designation identifies density values such as H for the higher density and L for the lower density foam.

Experimental

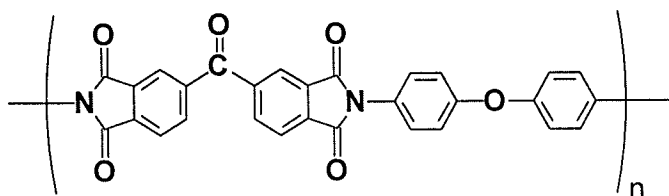
Material Synthesis

The salt-like foam precursor was synthesized by mixing monomer reactants of a dianhydride with a foaming agent (tetrahydrofuran) in methanol at room temperature. The dianhydride (e.g., ODP, 756g-2.4 moles) was dispersed in a mixture of tetrahydrofuran (THF-480g) and 280 g of methanol (MeOH) at room temperature. This solution was treated at 70 °C for 6 hours in order to convert the ODP into ODP-DEDA (dialkylester-diacid) complexed with THF by hydrogen bonding. Stoichiometric amounts of the diamine (e.g., 3,4'ODA, 488 g-2.4 mol) were added to the resulting solution of ODP-DEDA and stirred for 2 hours to yield a homogeneous polyimide precursor solution. The resulting

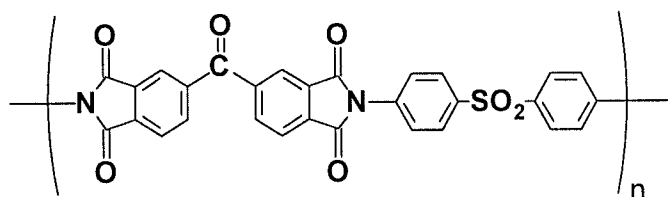
polyimide precursor solution had a solids content of 70 wt % and a viscosity of 20 poise at 20 °C. The solution was then charged into a stainless-steel vat and treated at 70 °C for 14 hours in order to evaporate the solvent (THF and MeOH). The resulting material was crushed into a fine powder (2 to 500 μ m) and sieved using a mesh, if needed. The polyimide precursor powder was then treated for an additional amount of time (0 to 300 minutes) at 80 °C to further reduce the residual solvents to around 1-10 wt% depending on the final density desired. Residual amounts of THF were determined by measuring the proton NMR spectra of the powders.⁴



TEEK-HH and HL (ODPA/3,4'-ODA)



TEEK-L8, LH and LL (BTDA/4,4'-ODA)



TEEK-CL (BTDA/4,4'-DDSO₂)

Figure 1. Chemical structures of foams.

Table I. Foam Materials Description

<i>Foam, Density</i>	<i>Description</i>
TEEK-HH (0.082 g/cc)	ODPA/3,4'-ODA (4,4 oxydiphthalic anhydride/3,4-oxydianiline)
TEEK-HL (0.032 g/cc)	ODPA/3,4'-ODA (4,4 oxydiphthalic anhydride/3,4-oxydianiline)
TEEK-L8 (0.128 g/cc)	BTDA/4,4'-ODA (3,3,4,4-benzophenone-tetracarboxylic dianhydride/4,4-oxydianiline)
TEEK-LH (0.082 g/cc)	BTDA/4,4'-ODA (3,3,4,4-benzophenone-tetracarboxylic dianhydride/4,4-oxydianiline)
TEEK-LL (0.032 g/cc)	BTDA/4,4'-ODA (3,3,4,4-benzophenone-tetracarboxylic dianhydride/4,4-oxydianiline)
TEEK-CL (0.032 g/cc)	BTDA/4,4'-DDSO ₂ (3,3,4,4-benzophenone-tetracarboxylic dianhydride/4,4-diaminodiphenyl sulfone)

Foam Fabrication

The amount of polyimide foam precursor powder necessary to completely foam a desired volume was placed in a chamber. The mold, shown in Figure 2, was heated to 140 °C for 60 minutes using heat plates on the top and bottom. The mold was then rapidly transferred to a nitrogen-convection oven set at 300 °C and held at 300 °C for 60 minutes. The mold was then cooled to room temperature. At this point the foam was post cured for several hours at 200 °C to remove all trace volatiles. The foam was removed from the mold and was ready for use.⁴ The foams were supplied by NASA Langley Research Center and Unitika LTD, Japan. Table I lists the abbreviations for the materials and densities of the foams studied.

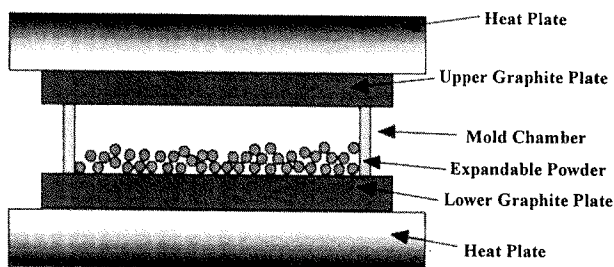


Figure 2. Mold Concept for TEEK Foaming.

Results

Mechanical Properties

Polyimide foams at varying densities were tested for mechanical and physical properties and reported.² Results are included in Table II. In the lower density materials, the TEEK-H and TEEK-L series have similar tensile strengths, with the TEEK-C series giving lower values comparatively. As expected, higher density increases both tensile strength and compressive strength for the same series of polymer.

Table II. Mechanical Properties

<i>Property</i>	<i>TEEK-HH</i>	<i>TEEK-HL</i>	<i>TEEK-LL</i>	<i>TEEK-CL</i>
Tensile Strength	1.2 MPa	0.28 MPa	0.26 MPa	0.09 MPa
Compressive Strength	0.84 MPa @10% Defl.	0.19 MPa @10% Defl.	0.30 MPa @10% Defl.	0.098 MPa @10% Defl.
Compressive Modulus	6.13 MPa	3.89 MPa	11.0 MPa	

Thermal Stability

Thermal properties of the polymers were studied in a comparative process using a TA Instruments Hi-Res Model 2950 Thermogravimetric Analyzer (TGA). TGA will measure the percentage of weight loss at different temperatures and the weight of residue at high temperature. Data reported in Table III were carried out in air, with a heating rate of 50.0 °C/min from room temperature to 800 °C with a resolution of 5 (associated with percent/minute value that will be used as the control set point for furnace heating). Analyses in nitrogen versus air indicate greater stability in nitrogen (agrees with previously reported data for polyimide films).³ A TA Instruments Differential Scanning Calorimeter Model (DSC) 2920 was used to determine glass transition temperature, T_g (see Table III), and other thermal changes.⁵ Results were obtained by heating foam samples 20.0 °C/min to 350 °C, holding at 350 °C for 10 min, equilibrating at 25.0 °C, and reramping at 20.0 °C/min to 350 °C, using the reramp curve to calculate T_g .

Data indicate that at 50% weight loss, the TEEK-CL series has the highest thermal stability, with the other series very similar in stability. It also has the

highest T_g . The TEEK-L series ranks next, with the TEEK-H series having the lowest T_g of 237 °C. Previous research on polyimide films indicates that although the dianhydride structure does not have a profound impact on the polyimide stability, some consistencies or trends in the ranking of the dianhydrides have been seen, depending upon whether thermal analysis was carried out dynamically or isothermally.⁶ Diamine structure appears to have a greater influence on the stability, with the ranking being $SO > SO_2 > CH_2 > O$.³

Table III. Thermal Properties for TEEK Polyimide Foams

<i>Property</i>	<i>Test Method</i>	<i>TEEK-HH</i>	<i>TEEK-HL</i>	<i>TEEK-L8</i>	<i>TEEK-LH</i>	<i>TEEK-LL</i>	<i>TEEK-CL</i>
Density G/cc	ASTM D-3574 (A)	0.08	0.032	0.128	0.08	0.032	0.032
Thermal Stability, Temp.°C	10% wt loss	518	267	522	520	516	528
	50 % wt loss	524	522	525	524	524	535
	100% wt loss	580	578	630	627	561	630
Glass Transition T_g , Temp.°C	DSC	237	237	283	278	281	321

Flammability Testing

Oxygen Index (OI), ASTM D2863, and Glow Wire Ignition, ASTM D6194

Table IV indicates the results of OI and glow wire testing at 960 °C. The OI measures the minimum amount of oxygen required for sustained combustion. Data range from 42 to 51, with higher densities slightly increasing the OI for the same series of materials (LL, LH, and L8).

In comparing different polymers, ASTM D6194, Glow-Wire Ignition of Materials, measures the ignition behavior of insulating materials using a glowing heat source. The samples did not ignite, but the depths of penetration are reported where contact with the heated source was made. The TEEK-HL indicated the most penetration when compared to the lower density materials, with the higher density TEEK-L series having the least amount of penetration.

Table IV. Oxygen Index and Glow Wire

	TEEK-HL	TEEK-HH	TEEK-LL	TEEK-LH	TEEK-L8	TEEK-CL
OI	42	49	49	51	51	46
Glow Wire Depth of penetration	most	Less than HL	Less than HH	Less than LL	Best, less than LH	Compares to HH

Radiant Panel, ASTM E162

The Radiant Panel was designed to measure both critical ignition energy and rate of heat release, the reporting value being the flame spread or radiant panel index, I_s .⁷ Analyses reveal that the flame spread index, I_s , is close to zero for all of the foams evaluated. However, the percentage of shrinkage (Figure 3) and the amount of charring are different. Considering the lower density materials, 0.032g/cc, TEEK-CL reveals the least amount of shrinkage, and TEEK-HL the most. In comparing the same chemical structure, more shrinkage and degradation are observed in TEEK-HL (0.032g/cc) versus TEEK-HH (0.08g/cc), see also Figures 4 and 5. Figures 4 and 5 are photographs of duplicate 6X18 inch foam samples exposed to Radiant Panel testing.

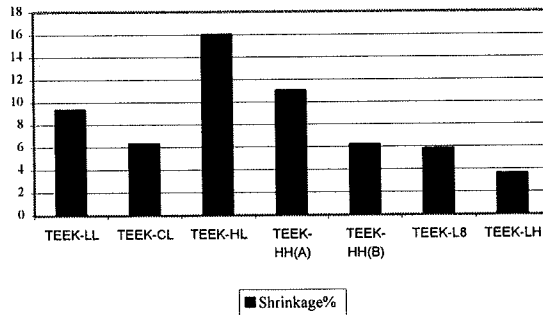


Figure 3. Shrinkage % from Radiant Panel samples.

As can be readily seen in the shrinkage data of the foams, chemical structure or density does not directly explain the differences observed. Given these results another correlation was investigated, namely surface area/porosity.

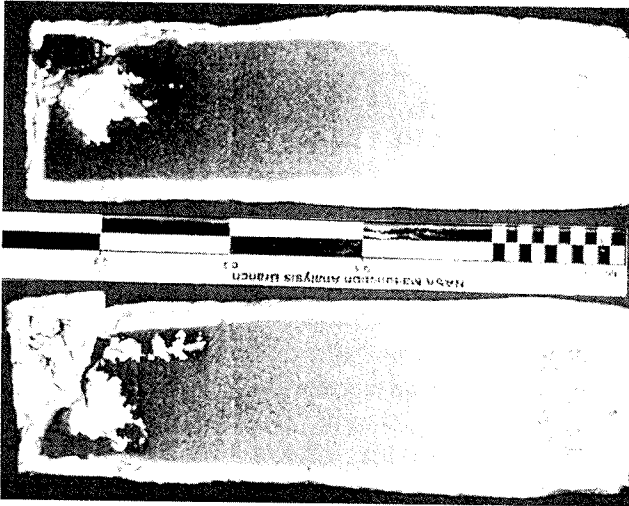


Figure 4. Duplicate samples, 6X18 inch foam TEEK-HL (0.032 g/cc) exposed to Radiant Panel.

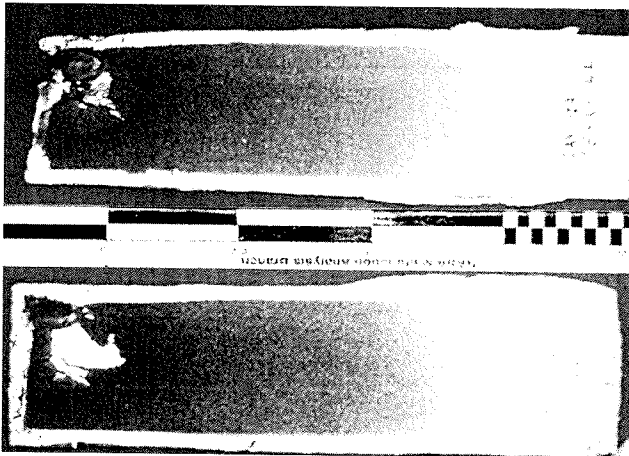


Figure 5. Duplicate samples, 6X18 inch foam TEEK-HH (0.08 g/cc) exposed to Radiant Panel.

Surface Area/Porosity

The surface areas were measured by the single point BET method using a Quantasorb Model QS-17 sorption analyzer.⁸ Foam samples were weighed and then inserted between plugs of Pyrex wool inside a 6 mm ID Pyrex U-shaped tube. The samples were pretreated by heating to 150 °C for 10 minutes using a heating mantle under flowing He (99.998%), at 200 cc/min (298 K, 1 atm) to remove any adsorbed moisture. Following pretreatment and cooling to room temperature under He, the adsorbate gas mixture of 29.3% N₂ in He was flowed over the foam. While the adsorbate mixture was flowing over the foam, the foam sample and enclosing Pyrex U-tube were submerged in liquid N₂ (77 K), and the thermal conductivity detector (TCD) signal was collected until a steady-state was achieved and integrated automatically. Duplicate experiments were performed, and the reported values are the averages. Surface area calculations and percentage of shrinkage gave a direct correlation as observed in Figure 6.

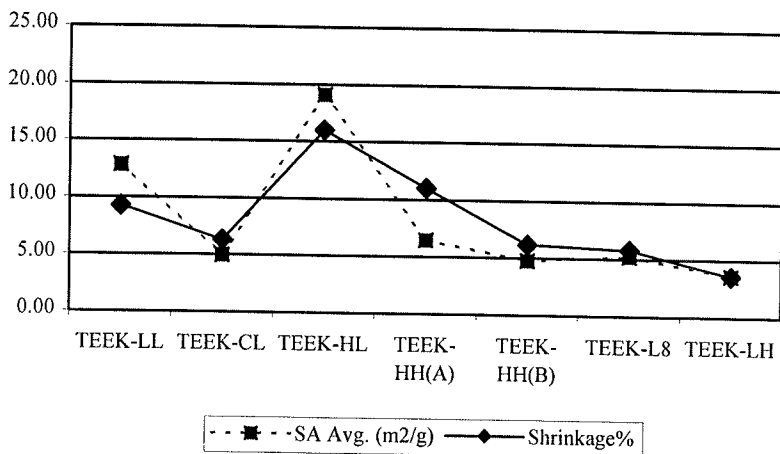


Figure 6. Correlation of Surface Area vs Shrinkage % from Radiant Panel.

Cone Calorimetry

Cone analysis was performed per ASTM E1354. Cone analysis utilizes oxygen consumption during combustion as a measure of heat release. Table V presents cone data, including time to ignition (Time ig), peak heat release rate (PHRR), average heat release rate (ave. HRR), total heat release rate (THR), smoke as specific extinction area (SEA), carbon monoxide production (CO), average mass loss rate (MLR), and initial and final masses.⁹

Table V. Cone Calorimeter Data

Sample	TIME ig (s)	PHRR (kW/m ²)	Ave. HRR (kW/m ²)	THR (MJ/m ²)	Ave. SEA (m ² /kg)	Ave. CO (kg/kg)	Ave. MLR (g/s/m ²)	Initial Mass(g)	Final Mass (g)
TEEK-HL 35 kW/m ²		11.5	3.10	2.3	530	0.31	0.35	9.2	7.5
TEEK-HL 50 kW/m ²	89.8	54.7	21	12.9	169	0.38	1.86	13.4	0.0
TEEK-HL 75 kW/m ²	13.8	154	28.9	22.5	160	0.13	1.22	14.1	4.7
TEEK-HH 35 kW/m ²		7.93	3.27	2.43	618	0.07	0.32	19.8	18.8
TEEK-HH 50 kW/m ²	55.0	50.5	24.8	37	261	0.19	1.18	24.6	6.7
TEEK-HH 75 kW/m ²	12.6	79.7	35.1	49.1	72.9	0.02	1.39	23.7	4.3
TEEK-LL 35 kW/m ²		17.3	1.43	5.25	32.9	0.00	3.80	9.4	7.2
TEEK-LL 50 kW/m ²	32.6	39.9	25.2	22.7	126	0.28	1.05	13.6	4.5
TEEK-LL 75 kW/m ²	8.8	53.4	26.3	21.2	117	0.03	1.12	13.6	4.7
TEEK-LH 50 kW/m ²	43.8	30.7	20.3	43.0	334	0.34	0.96	25.6	4.8
TEEK-LH 75 kW/m ²	17.5	43.7	25.4	53.9	6.14	0.14	1.07	26.0	3.8
TEEK-L8 50 kW/m ²	37.6	36.2	26.1	54.2	2.06	0.27	1.12	29.8	6.4
TEEK-L8 75 kW/m ²	15.5	58.3	30.1	68.3	33.5	0.15	1.75	34.2	4.3
TEEK-CL 35 kW/m ²		5.93	1.8	1.26	226	0.00	0.25	8.1	7.4
TEEK-CL 50 kW/m ²	133	26.2	17.9	15.4	55.8	0.28	0.92	12.1	4.9
TEEK-CL 75 kW/m ²	9.6	68.6	27	19	149	0.03	1.28	13.1	4.0

The cone analyses indicate that there is no ignition occurring at 35 W/m², with not even complete combustion at 75 kW/m². At 50 kW/m², TEEK-CL has the longest time to ignition at 133 seconds, followed by the TEEK-H series. However, at 75 kW/m², the times to ignition are similar. Table VI summaries the PHRR data observed at the different heat fluxes for the samples analyzed.

Table VI. PHRR and Ignition (Sec) Data From Cone Analysis

<i>Sample</i>	<i>Density g/cc</i>	<i>Surface Area</i>	<i>PHRR 75 kW/m²</i>	<i>PHRR 50 kW/m²</i>	<i>PHRR 35 kW/m²</i>
TEEK-HH	0.08	5.5	80 13ig	51 55ig	8
TEEK-HL	0.032	19.1	154 14ig	55 89ig	11
TEEK-L8	0.128	5.2	58 16ig	36 38ig	
TEEK-LH	0.08	3.6	44 18ig	31 44ig	
TEEK-LL	0.032	12.9	54 9ig	40 33ig	17
TEEK-CL	0.032	5.0	69 10ig	26 133ig	6

In Figures 7 and 8, the correlation between PHRR and surface area are presented in chart form. As observed in Figure 7, except for the TEEK-LL and TEEK-CL samples, surface area gives a fairly direct correlation with the PHRR rates at 75 kW/m². These data indicate that even with a significant increase in surface area for the TEEK-L series, the PHRR rates were not entirely proportional. However, as observed in Figure 8, the data collected at 50 kW/m² were more proportional. The average heat release data (ave. HRR) are similar for all the samples, with TEEK-CL slightly lower at the 50 kW/m² heat flux. The total heat release data (THR) appear to correlate well with densities of samples. The mass loss data (MLR) are similar throughout the samples. The specific extinction area (SEA, smoke) data for the samples at 35 kW/m² are a lot higher (due to the non-flaming pyrolysis), with the higher density materials giving lower values at 75 kW/m² (flaming).

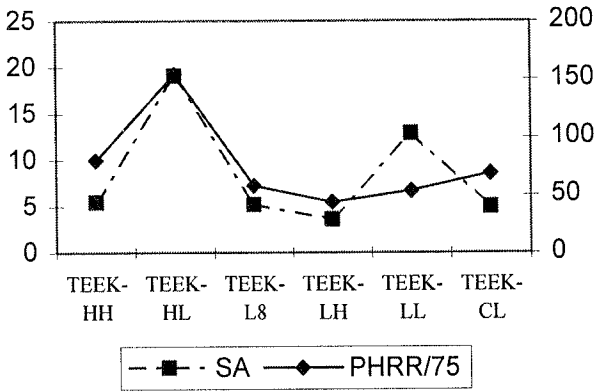


Figure 7. Comparison of PHRR at 75k W/m² and surface area.

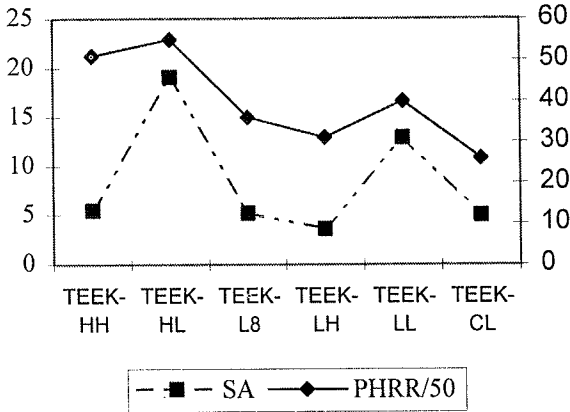


Figure 8. Comparison of PHRR at 50k W/m² and surface area.

Conclusions

Data presented validate that these newly developed polyimide foams are high performance polymers in mechanical, physical and thermal properties. Their intrinsic flame retardant nature also classifies them as fire resistant polymeric foams.

Although polyimide properties and stability versus degradation have been studied previously, the majority of the data related to films and not foams. Foams have much higher surface area and thus are a greater challenge to fire

retard. Because of the intrinsic flame retardant properties of polyimides, this research has given insight into the direct correlation of chemical structure, surface area and flame retardancy of foams. While subtle changes in chemical structure undoubtedly play a role, radiant panel and cone calorimeter performance indicates that differences in the surface area or cell size of the foams appear to have a larger effect than the densities or differences in chemical structure. Chemical structure, however, may dictate surface area or porosity in the formation of foams. For example, the TEEK-CL with its SO₂ linkage, shows the lowest surface area, the lowest heat release, and highest thermal stability.

Acknowledgements

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