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Effects of cell structure and density on the properties of high performance polyimide foams^{†,‡}

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Activity at the NASA Langley Research Center (LaRC) has focused on developing low density polyimide foam and foam structures which are made using monomeric solutions or salt solutions formed from the reaction of a dianhydride and diamine dissolved in a mixture of foaming agents and alkyl alcohol at room temperature. Monomer blends may be used to make a variety of polyimide foams with varying properties. The first foaming process developed consisted of thermal cycling the polymer precursor residuum and allowing the inflation of the particles to interact to create the foam. This process has resulted in foam structures with higher percentages of open cell content. Another innovative foaming process has been developed that begins with partially inflated microspheres, "friable balloons", with incomplete polymer molecular weight gain, which when fully cured into a foam results in more closed cell structures.

In a research study performed by NASA Kennedy Space Center (KSC) and LaRC, two closely related polyimide foams, TEEK-H series and TEEK-L series, (4,4'-oxydiphthalic anhydride/3,4'-oxydianiline and 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride/4,4'-oxydianiline) were investigated for density effects and closed versus open cell effects on the thermal, mechanical, and flammability properties. Thermal conductivity data under the full range of vacuum pressures indicate that these materials are effective insulators under cryogenic conditions. Contributing factors such as cell content, density, and surface area were studied to determine the effects on thermal conductivity. Cone calorimetry data indicated decreased peak heat release rates for the closed cell system, TEEK-H friable balloons, compared to the TEEK foams with higher open cell content. Mechanical properties including tensile strength and compressive strength indicated that the materials have good structural integrity. Foams with more open cell content resulted in greater tensile and compressive strengths than the closed cell foams. The maximum closed cell content achieved in the "friable balloon" system was 78% at a foam density of 0.048 gm/cm³. Published in 2005 by John Wiley & Sons, Ltd.

KEYWORDS: polyimides; foams; thermal properties; mechanical properties; high performance polymers

INTRODUCTION

The term polymer foams or cellular polymers refers to a two-phase gas-solid system in which the solid polymer is continuous and the gaseous cells are dispersed throughout the solid.¹ Foamed or cellular plastics may be classified according to the type of cells or cell structure: open-cell and closed-cell.² Open-cell foams have the solid phase as the cell edges with void space or gas phase connected

through the cell faces. The material is permeable since the cavities are connected. Closed-cell foams have cell faces with isolated cavities filled with trapped gas.³ Many types of foam contain a ratio or a percentage of open and closed cells. Carefully controlling the ratio of open or closed cell content allows for the fine tuning of foam properties. Foams in general have improved strength to weight ratios, thermal insulation, buoyancy, and energy dissipation in comparison to a non-foamed solid of the same material. Foams can be produced by several different methods including extrusion, compression molding, injection molding, reaction injection molding, and solid state methods. Despite the outstanding properties of common polymeric foams, these materials suffer from certain disadvantages, which include limited use at higher temperatures and poor fire resistance.⁴ Dimensional stability, thermal aging and degradation, friability, and

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susceptibility to thermal cycling, as well as ultraviolet light are other concerns.⁵

Based on a need for improved fire resistance, less smoke generation, and higher operating temperatures, NASA Langley Research Center (LaRC) and Unitika, Ltd of Japan have been developing the next generation of polyimide foam materials that will be used for cryogenic insulation, flame retardant panels, and structural sub-components. This new foam technology allows for the processing of different types of foams which include neat or syntactic foams, foam-filled honeycombs, and closed cell foams made from polyimide microspheres or "friable balloons".⁵ One foaming process developed consists of thermal cycling the polymer precursor solid residuum and allowing the inflation of the particles to interact to create a foam structure with higher open cell content. Another foaming process that has been developed begins with partially inflated microspheres, "friable balloons", which are partially polymerized. Thermal treatment of the microspheres results in complete imidization and a mostly closed cell foam.

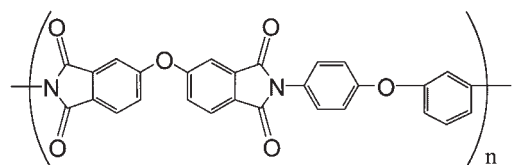
Densities of these foams can range from 0.008 to 0.128 g/cm³. Making subtle changes in chemistry, density and open or closed cell content, the physical properties of foams can be tuned to an application. It has been shown experimentally and theoretically that relative density is the most important parameter affecting physical properties.^{2,6} Less straightforward is the open-closed cell effects on physical properties of foams, however, closed cell content are known to affect the insulation characteristics of the foam. Closed cell foams can be thought of as composites with material stiffening gas trapped in pockets. The material derives its intrinsic strength from the cell walls and is reinforced with gas, thus closed cell foams typically are stiffer and stronger than open-celled foams, which derive their strength from struts. New materials that take advantage of the benefits of both closed and open-celled foams have recently been reported.⁷

Polyimide foams of varying densities and cell content were tested for mechanical, thermal, and flame resistant properties, with some of these data separately reported.^{5,8,9} This report includes the effects of density and cell content on properties such as thermal conductivity and thermal stability. Mechanical testing included compressive and tensile strengths under ambient conditions. The high performance polyimide foams tested in this study exhibited good flame retardancy in flammability experiments, excellent structural integrity, and superb thermal (cryogenic and high temperature) properties.¹⁰ It is important to emphasize that in comparing properties of the more open-celled foams to the closed-cell friable foams, that they were fabricated using two different processes, which is another important factor when interpreting experimental results.

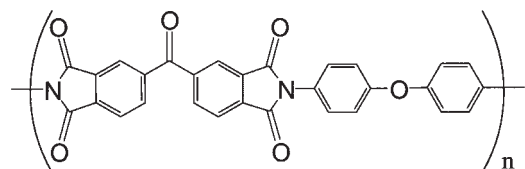
EXPERIMENTAL

Foam fabrication

The synthesis of the precursor polymer powders and the fabrication of the both the solid residuum foams and the "friable balloons" foams in this study were reported previously.^{5,9} Two different chemical formulations were used in the more open-celled solid residuum foams (Fig. 1), namely TEEK-H series



TEEK-HH (0.082 g/cm³) and TEEK-HL (0.032 g/cm³), ODPA/3,4'-ODA



TEEK-L8 (0.128 g/cm³), TEEK-LH (0.082 g/cm³), TEEK-LL (0.032 g/cm³), and TEEK-L5 (0.008 g/cm³), BTDA/4,4'-ODA

Figure 1. Chemical structures of TEEK polyimide foams.

and TEEK-L series.^{9–12} TEEK-H was the name given to ODPA/3,4'-ODA (4,4'-oxydiphthalic anhydride/3,4'-oxydianiline), and TEEK-L series to BTDA/4,4'-ODA (3,3',4,4'-benzophenonetetracarboxylic acid dianhydride/4,4'-oxydianiline). The name of TEEK foams designates the chemistry and density. For example TEEK-XY, the X indicates the functional groups in the main chain of the polyimide (see also Fig. 1) and the Y designates the density of the foam. The more closed cell foams were fabricated with the same chemistry of the TEEK-H series, designated TEEK-H friable, but utilized the partially cured polyimide microsphere termed, "friable balloons" to increase closed-cell content. The microspheres used to make the friable balloon samples were crushed to reduce the initial volume, which allowed densities higher than 0.04 g/cm³ to be attained. The fragmented friable balloons allow more material into the mold before the entire cavity is filled, and the density of the resulting polyimide foam is increased. A homogeneous size distribution of the balloon shards were obtained by uniformly mixing during processing.⁵

Characterization

Closed-open cell content

Closed cell content measurements were performed according to ASTM D6226 on a Quantachrome UltraFoam 1000. Open cell content is calculated from Boyle's Law. A known volume is pressurized in the Quantachrome chamber and the pressure change is correlated to the actual volume, thus allowing the open cell content of the sample to be calculated. Since foam content has to be unity, the closed cell content is considered the remainder.

Mechanical properties

Flatwise tensile and compressive strength were measured on a 9000 kg Instron test stand following ASTM D1623 test C and ASTM D-3574 test methods. Tensile specimens were cut to dimensions of 5.1 cm × 5.1 cm × 2.5 cm and bonded to support blocks using a low temperature epoxy adhesive. Specimens were placed in the Instron test apparatus and tested till the sample completely failed. All failures occurred within the foam and not at the bonded areas. Compression samples were also cut to 5.1 cm × 5.1 cm × 2.5 cm and tested till 50% deflection (50% initial thickness) was reached.

Thermal properties

Thermal conductivity. Thermal conductivity at ambient temperature and pressure was determined by a Netzsch Lambda 2300F heat flow meter using the ASTM C-518 standard protocol. The warm boundary temperature was approximately 307 K and the cold boundary temperature was approximately 286 K. The mean temperature was approximately 297 K (24°C).

A new patent-pending cryostat was used to determine apparent thermal conductivity (*k*-value). This device is based on the steady-state liquid nitrogen evaporation rate calorimeter method and tests the material under its actual-use, cryogenic-vacuum conditions.¹³ The cryostat test specimens were approximately 200 mm in diameter by 25 mm thick. Each specimen was evacuated (outgassed) for at least 48 hr after installation. The liquid nitrogen cold mass maintained the cold boundary temperature at approximately 78 K (−195°C). The warm boundary temperature was maintained at approximately 293 K (20°C) using an external heater. The temperature difference (delta temperature) was therefore 222 K while the mean temperature was 189 K. The cold vacuum pressures included the full range from high vacuum (1×10^{-5} torr) to soft vacuum (~1 torr) to no vacuum (760 torr). The residual gas within the vacuum chamber was nitrogen for all cryostat tests.

Thermal analysis. Thermal properties of the foams were performed on a TA Instruments 2950 using the TA Hi-Res[®] program. All the samples were run in air to a maximum temperature of 800°C. The parameters were set to a maximum heating rate of 50°C/min and a minimum heating rate of 5°C/min. The program slows down the heating rate of the sample as mass loss increases, which allows for improved sensitivity. Isothermal thermogravimetric analysis (iTGA) measurements used a heating rate of 50°C/min from room temperature to a temperature of 500°C and held there for 160 min. TA Instruments model 2920 was used for differential scanning calorimetry (DSC) analysis. DSC measurements involved heating samples 20.0°C/min to 350°C from room temperature, holding at 350°C for 10 min, rapidly cooling, equilibrating at 25.0°C, and reheating the sample to 350°C at 20°C/min. Glass transition temperature (T_g) results were determined from the second heating curve.

Flammability

Radiant panel testing followed the ASTM E162 test method. The radiant panel is 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 .¹⁴ Flame spread is how rapidly fire spreads across a surface. The radiant panel test was developed to provide an assessment of downward flame spread facing a 670°C radiant panel, with the sample inclined at an angle of 30° from the panel. Since radiation intensity decreases down the specimen, the time progress of ignition down the sample serves to measure the critical ignition energy.¹⁴ Per ASTM E162, each of the foams were cut into 15.2 cm × 45.7 cm samples and exposed to radiant panel testing. Radiant panel exposure was also used to calcu-

late the amount of shrinkage that occurred on exposure. The point of flame (3 inches from the top) was the reference point used for percent of shrinkage.^{9–11}

Cone calorimetry analysis was performed per ASTM E1354, with sample sizes measuring 10 cm × 10 cm × 2.54 cm. Cone calorimetry analysis utilizes the oxygen consumption principle during combustion as a measure of heat release. The rate of heat release is a major factor that determines the size of a fire. The oxygen consumption principle states that there is a constant relationship between the mass of oxygen consumed from the air and the amount of heat released.^{14,15}

RESULTS AND DISCUSSION

Cell content

For TEEK-L and TEEK-H series foams (solid residuum), it is clear that open cell content decreases as density increases (see Table 1). Designated densities and surface areas of these foams which have been previously reported^{9,11,16} are also listed in Table 1. TEEK-L series foams had a maximum closed cell content of roughly 30% at the highest density TEEK-L8 foam, 0.125 g/cm³ (Figs. 2 and 3). TEEK-H series had similar closed cell content at low densities, but diverges at densities greater than 0.032 g/cm³ (Fig. 3). In Fig. 3, the TEEK-H friable foams show a closed cell content maximum of approximately 80% in the range between 0.046 to 0.050 g/cm³ with respect to foam density. The closed cell content begins to decrease at density past 0.050 g/cm³ (Fig. 3). These friable balloon foams achieve high closed cell content when the balloons are allowed to expand and bond to each other. Thus these foams have a maximum density that they can achieve and in this case it is approximately 0.46 g/cm³. In order to obtain higher densities one must crush the balloons to increase the amount of material in the mold cavity. When this happens perfect

Table 1. TEEK foam density, cell content and surface area data

Sample foam	Designated density (g/cm ³)	Open cell content (%)	Surface area (m ² /g)
TEEK-HH	0.080	80.6	5.5
TEEK-HL	0.032	97.5	19.1
TEEK-L8	0.128	71.3	5.2
TEEK-LH	0.080	85.5	3.6
TEEK-LL	0.032	94.7	12.9
TEEK-L5	0.008	97.3	— ^a

^aSurface area not available.

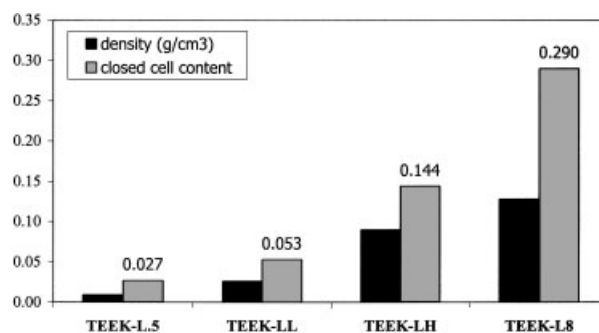


Figure 2. A correlation of closed cell content with density for TEEK-L series polyimide foams.

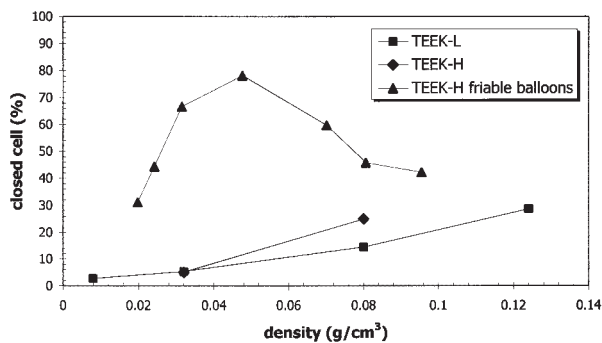


Figure 3. A comparison of how closed cell content percent changes with respect to density (g/cm^3) for TEEK-L, TEEK-H and TEEK-H friable.

spheres are no longer present and more potential pathways through the foams are created, thus the closed cell content is lowered as seen in Fig. 3. In order to maintain the high closed cell content and obtain higher densities new friable balloons need to be developed which have a smaller initial diameter so that a larger amount of material is present in the model cavity.

Mechanical properties

In this research polyimide foams are tested for tensile and compressive strength to verify the quality of these foams as a structural insulation, and to address the properties in terms of density and cell structure. Foams in general exhibit one of three characteristic traits when exposed to loading in either compression or tension. These traits can be described as being elastomeric, ductile or brittle. Most polymer foams will fail in either the elastomeric or ductile regime; however, under certain processing conditions one can have brittle polymer foam. In almost all cases foams tested in tension will fail due to a flaw that materializes as a crack and grows. Compression failure is more complex and is dependent on the open or closed cell nature of the foam. In general compression failure goes through three regimes; the first being a linear elastic region, this is followed by a plateau of elastic buckling or plastic yielding, and finally, a densification region where the cellular structure is compressed on itself.⁶ Figure 4 illustrates the typical compression curve for foams.¹⁷

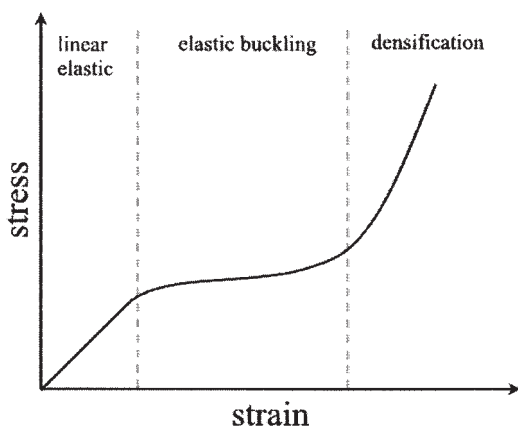


Figure 4. A typical compression curve for foam polymers.

Flatwise tension properties

Flatwise tension testing was performed on four different TEEK-L series and two TEEK-H series solid residuum foams. Foams were placed in a 9000 kg Instron test stand and loaded to failure. All foams failed due to an initial crack that propagated until failure occurred. Some of the foams failed at lower than expected tensile strengths due to poor specimen preparation or due to shear induced failures. Specimens at lower densities were more likely to fail due to shear because of the elongated cellular structure that was present. At the higher densities, crack propagation was more likely to dominate the failure than shear due to elongation of cells. This was apparent due to the much higher elastic modulus that was found in the higher density foams. Tensile modulus of the TEEK-LL and TEEK-L8 foams were 0.67 and 40.88 MPa, respectively. Figure 5 shows the tensile strength versus density for the TEEK-L series foams. The tensile strength increases with increased density and ranges from 0.11 MPa for the TEEK-L.5 foam to 1.98 MPa for the TEEK-L8 foam. The tensile strength of the TEEK-H friable foams also increases with increasing density, reaching a maximum tensile strength of 0.87 MPa at $0.08 \text{ g}/\text{cm}^3$. The tensile strength of the TEEK-H friable foam ($0.08 \text{ g}/\text{cm}^3$) was nearly half of the tensile strength of the same density TEEK-LH and TEEK-HH solid residuum foams, 1.66 and 1.44 MPa, respectively. The TEEK-L series had the highest tensile strength and TEEK-H friable foam had the lowest tensile strength, although it had the highest closed cell content of $\sim 46\%$ versus $\sim 14\%$ (see Table 1 and Fig. 3) for the TEEK-LH. The TEEK-H friable foams had consistently lower tensile strengths when compared to TEEK-H and TEEK-L series solid residuum foams at other densities. Although it is expected that increased closed cell content would have increased tensile strength, and thus the TEEK-H friable foams should have greater tensile strength. This result can be attributed to the foam process by which the powder foams and friable balloon foams are manufactured. The powder-based solid residuum foams have a distinct rib like cellular structure while, the friable balloon foams are similar to hundreds of spheres bonded together to form a closed packed network. The result is a rigid foam with high strength values for the powder based foams and a foam which can be more easily broken in the case of the friable balloons due to the small adhesion points at the radius of each sphere.

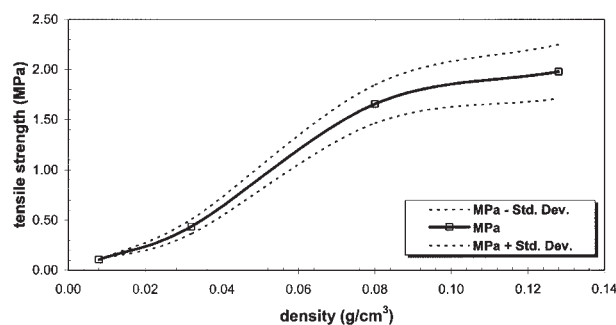


Figure 5. Tensile data for TEEK-L series with respect to density.

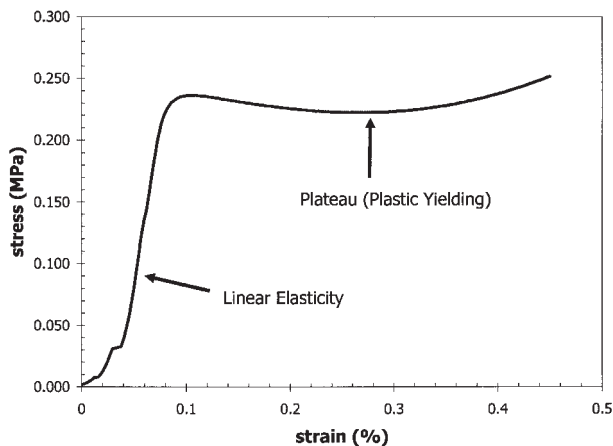


Figure 6. A typical compression curve for TEEK-LL polyimide foam.

Compression properties

Compression testing was performed on the same solid residuum TEEK-H and TEEK-L foams as described in the previous section. Figure 6 shows the compression properties of the TEEK-LL (0.032 g/cm³) foam and the apparent plastic yielding that took place. The TEEK-LL was the only one of the six foams tested which exhibited this elastic-plastic characteristic. The TEEK-HL, in Fig. 7, better represents the rest of the foams tested in compression. The only difference that was identified between these five polyimide foams was a steeper linear elastic region, which indicates a higher elastic modulus, and a steeper plateau as the density increased in the foams that were tested. Figure 8 shows the data for compressive strength versus density for all of the TEEK-L series foams tested. The values obtained in compression for this class of polyimide foam ranged from 0.026 to 2.28 MPa. Figure 9 is a comparison of compressive strength properties for the TEEK-H and TEEK-L series foams at 0.032 and 0.08 g/cm³. The data indicates a significant increase in compressive strength of the TEEK-L over the TEEK-H foams at 0.08 g/cm³. The modulus values for the 0.08 g/cm³ foams were 13.51 and 30.44 MPa for the TEEK-H and TEEK-L, respectively. The significant increase in modulus of the TEEK-L foam over the TEEK-H foam indicates that it is a major contributor in the difference in compression strength of these materials. Another reason

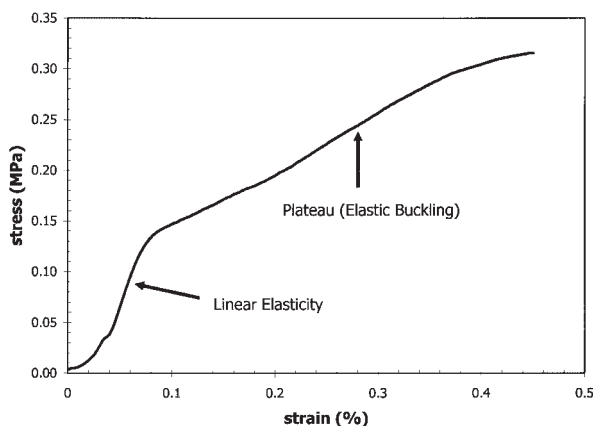


Figure 7. A typical compression curve for TEEK-HL polyimide foam.

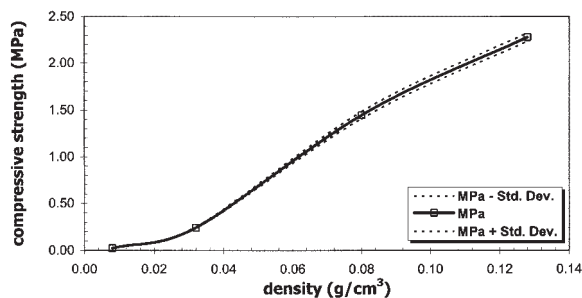


Figure 8. Compressive data for TEEK-L series with respect to density.

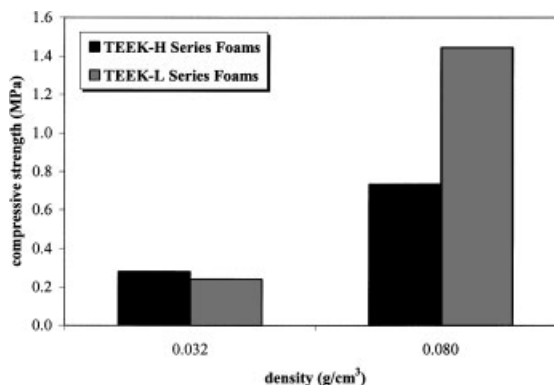


Figure 9. A comparison of compression strength between H series and L series TEEK polyimide foams with respect to foam density.

for the increase could be due to the cellular structure of the foams and the cell formation which will affect the final properties of the foams. In the TEEK-H friable foams, the compressive strength increases from 0.21 to 0.62 MPa as the density increases from 0.039 to 0.08 g/cm³ foams, respectively. However, as seen in the tensile strength data, the compressive strength is decreased over that of the solid residuum foams at the same density. The reason for the decreased compressive strengths in the TEEK-H friable foams are the same as that discussed for the reduction in tensile strengths in the previous section.

Thermal properties

Thermal conductivity

In general, thermal conductivity of foamed systems is among the lowest of any solid materials. The overall heat transfer in foams occurs through four mechanisms which in combination make up the thermal conductivity of any foam system. The four contributing factors are the conduction through the solid polymer, conduction through the gaseous cells, convection within the cells, and radiation through the cell walls and across the cell voids.^{6,18,19} Conduction through the gaseous cells is the largest contributor to the overall thermal conductivity as reported by Gibson and Ashby. In most situations where the blowing agent is a better insulator than air the thermal conductivity of the system can decrease over time. One must also take into account that in closed cell foams the heat transfer coefficient in the cell will change as the

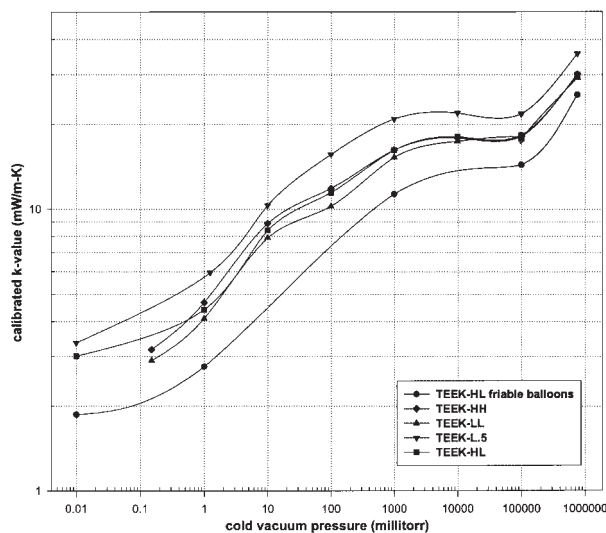


Figure 10. Apparent thermal conductivity of TEEK-H and TEEK-L series foams.

blowing agent is gradually replaced by air. For open cell foams the overall thermal conductivity of the system will increase if there is open transfer of air into the cells to promote convection within the cells.¹⁹

Thermal conductivity results at ambient conditions using ASTM C-518 for TEEK HH, TEEK-HL, and TEEK-LL foams are all ~ 38 mW/mK. The ambient thermal conductivity for TEEK-L.5 is significantly higher at ~ 50 mW/mK. The lesser density of the TEEK-L.5 contributes to an increase in thermal conductivity value. The apparent thermal conductivities (k -values) under cryogenic conditions including cold vacuum pressures from high vacuum to no vacuum are shown in Fig. 10 and listed in Table 2 for TEEK-H friable balloons (closed cell foam, 0.039 g/cm³) and the TEEK-H and TEEK-L series open celled foams in various densities. The closed cell foam TEEK-L friable balloons are seen to be the better insulator (lower k -values) under high vacuum cryogenic conditions. The TEEK-L.5 has the highest k -value for all

Table 2. Apparent thermal conductivity (k -value) under cryogenic-vacuum conditions: boundary temperatures are approximately 78 and 293 K; residual gas is nitrogen

Sample 200 mm diameter by 25 mm thick	High vacuum (1×10^{-5} torr) k -value (mW/mK)	Soft vacuum (1 torr) k -value (mW/mK)	Ambient (760 torr) k -value (mW/mK)
TEEK-HH	3.18	16.16	30.01
TEEK-HL	3.00	16.14	29.87
TEEK-HL friable	1.87	11.30	25.36
TEEK-LL	2.90	15.22	29.17
TEEK-L.5	3.36	20.82	35.41

Table 3. Thermal properties data for TEEK-H and TEEK-L solid residuum foams

Property	Test method	TEEK-HH	TEEK-HL	TEEK-L8	TEEK-LH	TEEK-LL
TGA ($^{\circ}$ C) (% weight loss)	10%	518	526	522	520	516
	50%	524	522	525	524	524
	100%	580	578	630	627	561
Glass transition temperature ($^{\circ}$ C)	DSC	237	237	283	278	281

conditions from high vacuum to ambient pressure. This is consistent with the results obtained under ambient temperature and pressure conditions. The major factor contributing to this reduced thermal performance (higher thermal conductivity and higher k -values) is the increased convection within the cells due to the high level of open cell content. Material factors affecting thermal performance include, for example, structure, composition, surface area, pore size, cell formation, and open cell content. The primary environmental factors include temperature, temperature difference, vacuum level, and residual gas composition. The interplay among material factors and environmental factors must be studied systematically to determine their relative importance for the overall thermal performance of a given material.

Thermal analysis

As expected, density or cell content does not appear to have a large effect on the thermal stability of the materials (Table 3). TGA data indicate that at 100% weight loss, the higher densities TEEK-L series have a slightly higher thermal stability compared to the TEEK-H series. The TEEK-L series has a higher T_g value ($\sim 280^{\circ}$ C), with the TEEK-H series having the lowest T_g value of 237° C.⁹ In Fig. 11, a comparison of the TEEK-L series (TEEK-L.5, TEEK-LH, and TEEK-L8) isothermal data at (500° C) show that density or cell content of the foams are not factors in thermal stability of TEEK foams. No significant differences in isothermal stability were observed in virgin foams before radiant panel exposure; however, after radiant panel exposed samples were compared isothermally, differences in degradation temperatures were observed, with the lowest density showing the most degradation and degradation temperatures decreasing as density increased in the same chemical series.^{11,16}

Flammability

Radiant panel

Radiant panel analyses reported previously⁹ indicated no significant flame spread for the polyimide foams. The panels did not propagate the flame, and only significant charring with some shrinkage occurred at and around the flame. Polyimides contain aromatic rings that can crosslink simultaneously with chain scission reactions and produce moderate to high amounts of char.²⁰ Since the critical ignition energy was not reached, the I_s value was reported as close to zero for all of the foams evaluated. These materials have excellent fire resistance properties. In Fig. 12, the percent shrinkage for each of the materials are seen. TEEK-LH (0.032 g/cm³) shows the greatest amount of shrinkage, and the TEEK-LH reveals the least amount. In the same chemical TEEK-H series, the higher density (0.08 g/cm³) has less shrinkage. However, in the TEEK-L series, the higher density

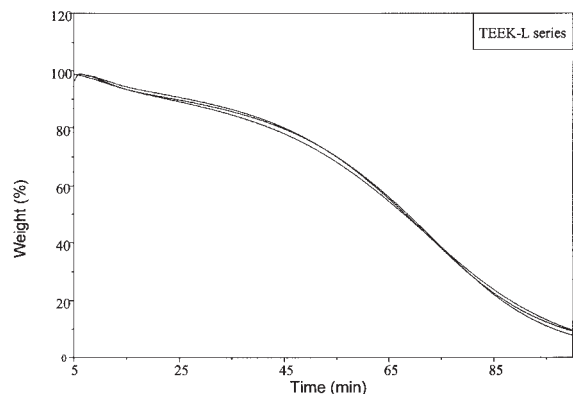


Figure 11. Isothermal curves at 500°C for TEEK-L.5, TEEK-LH, and TEEK-L8.

TEEK-L8 has more shrinkage than the medium density TEEK-LH, which can be explained only when surface area is addressed. As seen in Fig. 12, differences in densities do not explain the percent of shrinkage; however, in comparing surface area data (see Fig. 12 and surface area values given in Table 1) to the percent shrinkage, a direct qualitative correlation is observed.⁹

Cone calorimeter analysis

Critical heat flux, density, thermal conductivity, specific heat, and thickness (all samples the same thickness) are some of the factors influencing ignition properties of foams.²¹ Cone calorimeter analysis reports 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.¹⁵ Generally cone calorimetry on foams are run at 35 heat flux, however due to the high performance of these foams, the higher heat fluxes of 50 and 75 kW/m² were used. Table 4 provides the density, surface area, cell content and PHRR values for the more open-celled TEEK foams (solid residuum) listed.

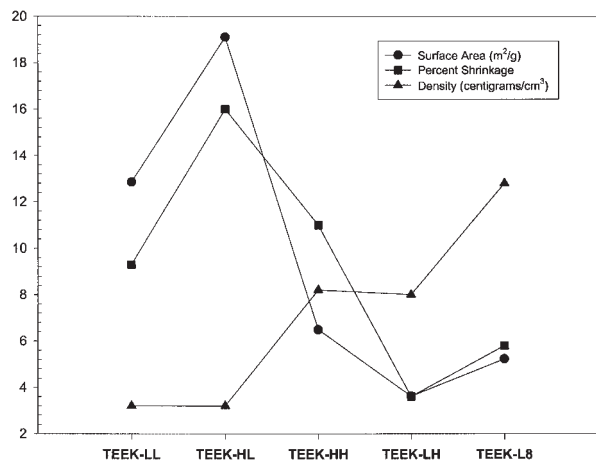


Figure 12. Radiant panel exposed samples, comparison of percent shrinkage, density and surface area (SA).

Table 4. Foams with density, surface area, cell content, and PHRR data

Sample	Theoretical density (g/cm ³)	Surface area (m ² /g)	Open cell content (%)	PHRR (75 kW/m ²)	PHRR (50 kW/m ²)
TEEK-HH	0.08	5.5	77.6	86 ^a	51 ^a
TEEK-HL	0.032	19.1	97.5	155 ^a	60 ^a
TEEK-L8	0.128	5.2	71.3	55 ^a	34 ^a
TEEK-LH	0.08	3.6	85.5	48 ^a	31 ^a
TEEK-LL	0.032	12.9	94.7	69 ^a	43 ^a
TEEK-L.5	0.008	— ^b	97.3	40 ^a	26

^a Notes average values of two data points.

^b Data not available.

Although the PHRR of the low-density polyimide foams are slightly lower than those of medium-density to higher density polyimide foams, no consistent correlation can be found between the PHRR and the foam density or open cell content (see also Fig. 13). It is clear that the PHRR is dependent upon something more than density or cell content. In comparing the same density foams (0.032 g/cm³) the TEEK-H series gives a comparable higher PHRR. As seen in the radiant panel data section, the surface area proves to have more correlation. It also appears that the actual chemical structure stability versus the surface area contribution is more distinguishable and differentiated at lower density and higher heat flux.¹⁶ Results in Table 4 shows that in comparing samples with similar surface areas but different chemical series, differences in PHRR shown are attributed to the lower thermal stability of the TEEK-H series. When the closed cell TEEK-HL friable is compared to more open-celled TEEK-HL of the same density, the PHRR rate is notably decreased as shown in Table 5. As expected, the THR values for the two samples are similar. Although surface area data are not available for this sample, due to it being closed cell, it is also expected to be low surface area which would follow the trend observed in the other samples where lower surface area values result in decreased PHRR values.

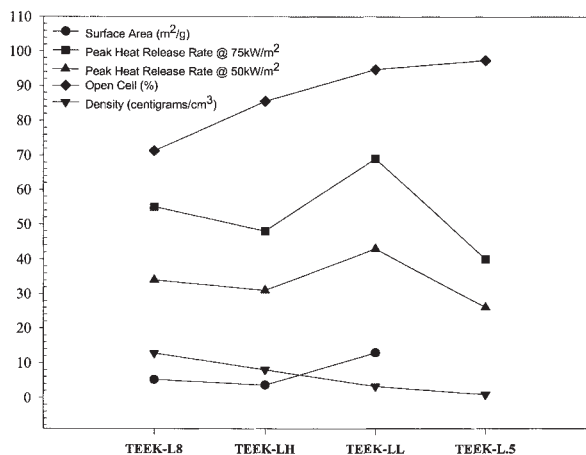


Figure 13. TEEK-L series comparison chart of density, surface area, open cell content and peak heat release rates.

Table 5. Cone calorimetry analysis data, time to ignition, and peak heat release rate

Sample	PHRR (kW/m ²)	THR (MJ/m ²)
TEEK-HL (35 kW/m ²)	11	2.3
TEEK-HL (50 kW/m ² avg.)	60	17
TEEK-HL (75 kW/m ² avg.)	154	21
TEEK-HL friable (50 kW/m ²)	24	30
TEEK-HL friable (75 kW/m ²)	65	34

CONCLUSIONS

As indicated in previous reports^{8,9,11,16} data presented validate that newly developed polyimide foams are high performance polymers with excellent mechanical, physical, and thermal properties and can also be classified as highly fire resistant materials.

Mechanical properties including tensile strength, compressive strength, and modulus indicate that the materials have good structural integrity. As expected, the tensile and compressive strengths of the foams increased with density; however, the more open cell solid residuum foams were stronger than the closed cell friable foams. This result can be attributed to the fabrication process of the foam. The powder-based solid residuum foams have a distinct rib-like cellular structure while, the friable balloon foams are similar to hundreds of spheres bonded together to form a closed packed network. Increased closed cell content also results in increased tensile and compressive strength in the solid residuum foams, however, the effect of closed cell content on the mechanical properties of the friable foams appear to not be as straight forward.

The radiant panel and cone calorimetry indicate that for flame retardancy, cell surface area along with the chemical structure play a larger role than the density of the materials. Cone calorimetry also indicated decreased PHRR values for the more closed cell system, TEEK-H friable balloons, compared to the TEEK solid residuum foams with higher open cell content.

Thermal conductivity data under full range of vacuum pressures indicate that these materials are good cryogenic insulators, and that increased closed cell content is a major factor for improving thermal performance. By carefully controlling polymer architecture, foam density, open-closed cell content, surface area, and cell structure, a custom designed foam can be fabricated for a specific application.

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