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Processing of microcellular foams from polybenzobisthiazole/polyetherketoneketone molecular composites

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This manuscript presents the results of a research project dealing with the processing of microcellular foams from molecular composites. The main goal of this work is the preparation, characterization, and evaluation of polymer-based foams. A variety of thermoplastic polymers have been evaluated with regard to the extent to which they can be formed into monolithic foams, and methods have been developed for toughening these foams. The primary mechanism for improving toughness and other mechanical properties is inclusion of rigid-rod polymers as dispersed phases. Both the thermoplastic host material and the molecular composites have been processed into the desired foams through extensions of the proprietary methods developed by Wright Materials Research Company. Part I of this series of papers presents the results of polybenzobisthiazole(PBZT)/polyetherketoneketone(PEKK) microcellular foams. The results show that the incorporation of the oriented rigid-rod polymers into a host thermoplastic matrix has given large improvements in mechanical and thermal properties of the foam. The properties of primary interest for optimization are of a mechanical nature, and for the anticipated structural applications include modulus, ultimate strength, maximum compressibility, impact resistance, and toughness. The microstructural details of the foams, which were monitored via standard microscopic techniques, were correlated with some of their properties.

1. Introduction

Many types of core materials are available today for sandwich constructions in aircraft and aerospace industry [1]. These include wood, polystyrene foams, polyurethane foams, PVC foams, poly(methacrylimide) foams, polyimide foams, and honeycomb cores. Among these core materials, PVC foams, poly(methacrylimide) foams, and aramid paper and aluminum honeycombs are most commonly used in the aircraft and aerospace industry.

PVC foams are based on the same chemical family as the familiar garbage bags, plastic pipe, and plastic films in common use and much information is available on the processing this polymer. Divinycell, Klegecell, Termanto are representatives of this class of foams. Poly(methacrylimide) foams such as Rohacell are manufactured by hot foaming of methacrylic acid-methacrylonitrile copolymer sheets. During foaming this copolymer is converted to poly(methacrylimide). Rohacell is recognized as a good-performance structural foam, but only for applications up to 350°F. In fact, the mechanical properties of all these polymeric rigid foams degrade significantly at elevated temperatures. As examples, the compressive strengths of Rohacell and Divinycell foams decrease to one-third of their original compressive strength at 350°F. Long-term applications at this temperature are therefore not recommended.

The results of a survey of the currently available foam cores reveal that Nomex aramid paper honeycombs are among the few that have acceptable ratios of extensional strength to weight. The drawbacks of these various honeycomb cores are their: (1) pronounced weakness in shear (a very important property in most applications of core materials), (2) moisture retention due to the open-cell constructions, and (3) high prices that limit their wide-spread utilization.

Foams from amorphous, glassy polymers such as polystyrene have been manufactured for decades. Most commercial polymer foams, however, are processed using a chemical blowing agent (CBA) which is decomposed during processing, or through the use of blowing gases such as the chlorofluorocarbons. The use of CBA's results in foams having cell size the order of millimeters. Thus, this project seeked to address these problems, by developing foams with good thermal stabilities and having well controlled densities (and hence desirable pore microstructures and mechanical properties).

To overcome the deficiencies of the conventional ("macrocellular") foams, Colton and Suh [2–4] reported a processing approach for the preparation of "microcellular" foams for amorphous polymers. Such foams are defined as those having cell sizes less than 100 μm, and bubble densities in the range 10^8–10^9 cells/cm^3.

In recent years, researchers at Wright Materials Research Co. have developed a number of proprietary foaming techniques to prepare microcellular foams based on the principle of thermodynamic instability [5–10]. These techniques have been used to process microcellular foams from molecular composites, as described below.

2. Experimental

2.1. Materials

Poly(etherketoneketone) (PEKK), with linear PEKK > 99% and density of 1.0 g/cm^3, was supplied by Fiberite. Two batches of Poly(p-phenylene-benzobisthiazole) (PBZT), with intrinsic viscosity of 21.4 and 14.0 dl/g, respectively, processed from PBT dope containing 82.85% P_2O_5, were synthesized and provided by Wright Laboratory (Wright-Patterson AFB). PEKK and PBZT were dried at 120°C in vacuum oven before use. Methanesulfonic acid (MSA) (99%), Ammonium hydroxide (28–30%) were purchased form Aldrich.

2.2. Preparation of PBZT/PEKK molecular composites (MC)

Both the PBZT and PEKK were dissolved in methanesulfonic acid. The solution was stirred at 70°C for about 24 h. After precipitation in distilled water they became fibrous materials. They were then neutralized in ammonium hydroxide and vacuum dried. The blending procedures are shown in Fig. 1. In this research, molecular composites with 5/95, 10/90, 30/70, and 50/50 percentage ratio of PBZT/PEKK were prepared. A PBZT/PEKK molecular composite with lower percentage of PBZT appears to be yellow. The color of the PBZT/PEKK molecular composites becomes darker when the percentage of the PBZT increases.

2.3. Characterization of molecular composites

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) were carried out under helium on a Universal V1.10B TA Instrument, using a heating rate of 10°C/min.

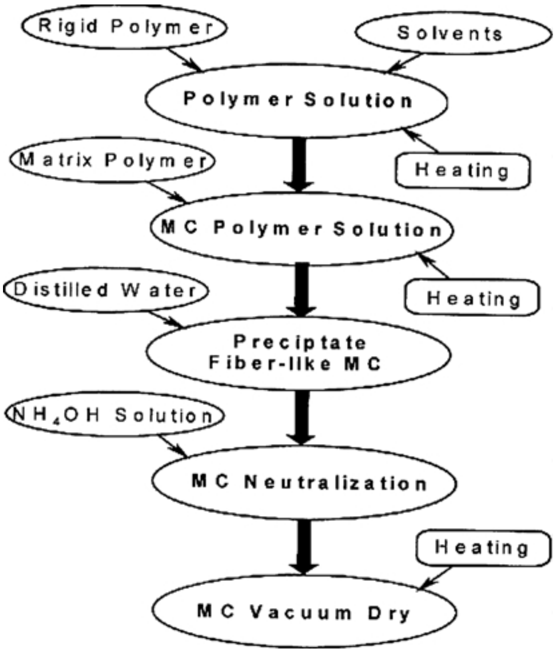


Figure 1 Preparative procedures for PBZT/PEKK molecular composites.

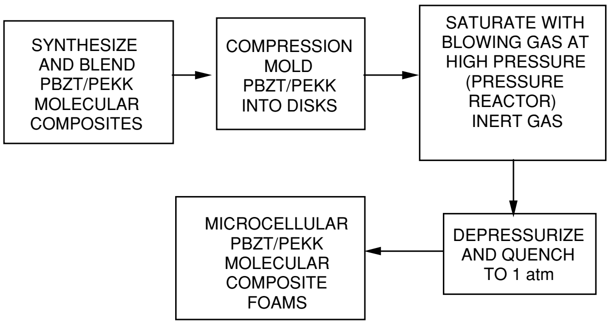


Figure 2 Schematic of WMR's proprietary foaming process.

2.4. Processing of microcellular foams from molecular composites

The rigid-rod molecular composites, PBZT/PEKK, were ground into fine powders and compression molded into disks. The disks were then foamed in a pressure vessel, using the foaming process developed by Wright Materials Research Co (WMR) as shown schematic in Fig. 2.

2.5. Characterization of molecular composite foams

The foam density was measured by water-displacement method, by measuring the volume of water displaced by the sample and dividing this volume into samples mass. The morphologies of the foamed samples were characterized by scanning electron microscopy (SEM). The samples were frozen in liquid nitrogen and fractured. The fractured surface was coated with gold and was examined with a Hitachi S-4200 SEM.

Samples for compression tests were cut with a diamond saw and had dimensions of approximately

$5.5 \times 6.0\ \mathrm{mm}^2$, with 5.5 mm in thickness. The compression tests were carried out at room temperature using an Instron Tester with a 1000lb load cell at a constant crosshead rate of 0.5 mm/min.

3. Results and discussions

3.1. Preparation and characterization of PBZT/PEKK molecular composites

By definition, molecular composites are formed if rigid rods are dispersed in a host matrix at the molecular level. Rigid-rod molecular composites are known to have superior thermal and mechanical properties, but foaming them is a challenging project. First, the blend of rigid-rod and thermoplastic random-coil matrix tends to give rise to phase separation problems. Second, rigid-rod polymers do not have an accessible T_g. The first problem has been solved recently by researchers at Wright Laboratory [11] using rigid-rod benzobisazole polymers functionalized with pendent sulfonic acid groups. These sulfo-pendent rigid-rods can form ionic associations with polar thermoplastic matrix polymers that have basic functionalities. The repulsion between ionically charged rigid-rods can prevent aggregation of the rods that normally leads to phase separation in the matrix. This approach provides a mechanism by which phase separation during the processing of the molecular composite can be prevented above the C_{cr} (critical concentration, 3–4 vol%). The second problem can be alleviated by blending rigid-rods with thermoplastic matrix which do have accessible glass transitions. Wright Laboratory's research results [11] show that up to 10 wt% of rigid-rod polymer can be incorporated in a thermoplastic polymer without loss of a glass transition.

The PBZT [12–15] rigid-rod polymer is a good candidate to form molecular composites as it can be obtained at relatively high molecular weights [11]. It typically has an intrinsic viscosity between 4.0 and 7.0 dl/g in methanesulfonic acid at 30°C, and no observeable T_g. A good candidate for the host matrix phase is a commercially available thermoplastic poly(etherketoneketone) (PEKK) which typically has a T_g about 156°C and a T_m around 310–350°C. Blending was carried out in methanesulfonic acid solution. Molecular composites with 5/95, 10/90, 30/70, and 50/50 weight percentage ratio of PBZT/PEKK were studied in this project. TGA analysis of PEKK polymer, Fig. 3, indicates that this material decomposes at about 525°C. TGA analyses of PBZT/PEKK with 10/90, 30/70, and 50/50 ratios reveal that they show a small decrease in weight between 330 and 380°C but are not decomposed up to the testing temperature of 600°C, as shown in Fig. 3. DSC analyses of the PEKK polymer show that its T_g is about 156°C, Fig. 4. DSC results of 10/90 PBZT/PEKK molecular composite, Fig. 4, indicates that its T_g is about 230°C. Therefore, the addition of rigid rods to a molecular composite does increase the T_g of its matrix material.

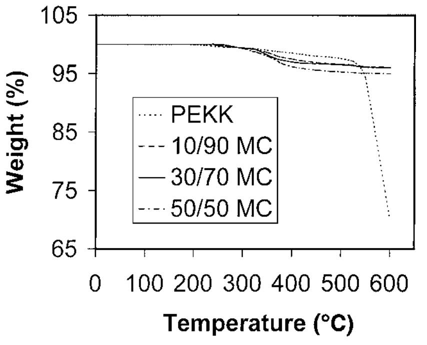


Figure 3 TGA analysis of the PEKK, 10/90 PBZT/PEKK, 30/70 PBZT/PEKK, and 50/50 PBZT/PEKK polymer.

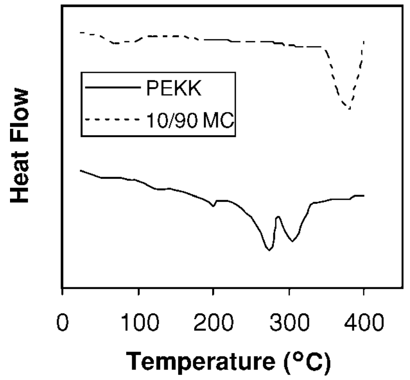


Figure 4 DSC analysis of the PEKK, and the 10/90 PBZT/PEKK polymer.

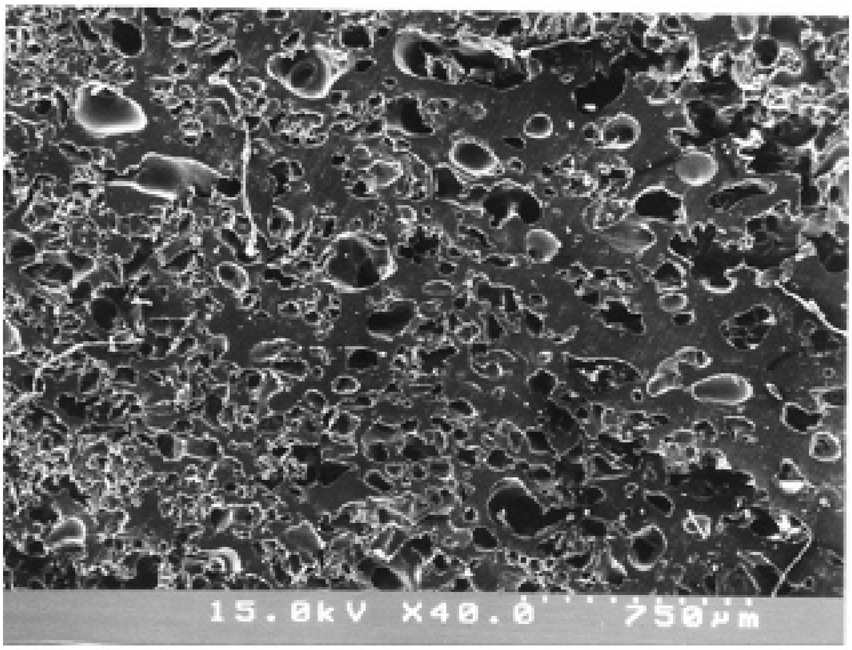
3.2. Processing of microcellular foams

Microcellular foams were processed using the method developed by WMR. During the course of this research, we found that PBZT/PEKK molecular composites were very rigid and very difficult to foam. Observations indicated that this class of molecular composite soften very little at elevated temperatures. We have tried to foam this family of materials at various temperatures and pressures and obtained only high-density foams with densities ranging from 0.92 to 1.1 $\mathrm{g/cm}^3$ as the materials remain quite rigid at elevated temperatures. To increase the "softness" of the MCs at elevated temperatures we blended the 10/90 MC (10% of PBZT and 90% of PEKK) with various amounts of PEKK powders. This did give foams with lower densities. The number of bubbles in the samples increase and the density depends on the processing conditions. We have also blended PBZT fibers with PEKK powders and processed them into foams. Among the three categories of polymeric composite foams mentioned above, this one is the easiest to process. Foams with very low densities can, in fact, be achieved.

3.3. SEM analyses

The SEM micrographs of the PEKK foams are shown in Fig. 5. Their densities are 0.65 and 0.52 $\mathrm{g/cm}^3$ for the top and the bottom part of the figure, respectively. The pore size ranges from 10 to 100 μm, depending on the processing conditions. The foams from the blend of 10% PBZT fibers with 90% PEKK powders have been processed with conditions chosen to attempt to reduce the density. SEM analyses show that the diameters of the bubble ranges from 100 to 700 μm.

SEM photomicrographs for the 10/90 PBZT/PEKK molecular composite foams show that the bubbles are 20–60 μm in diameter and the foam density is about



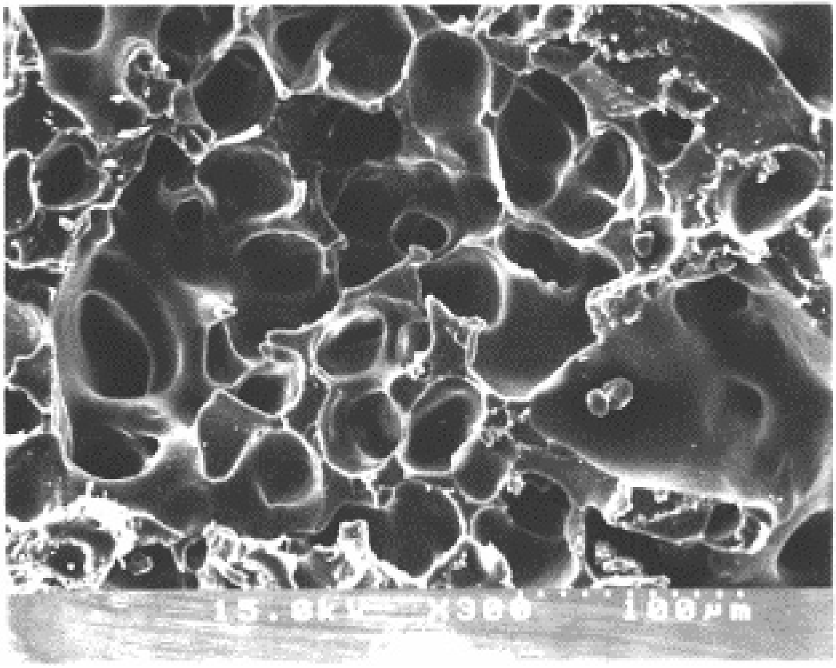


Figure 5 Microcellular PEKK foams having densities of: 0.65 g/cm^3 (top) and 0.52 g/cm^3 (bottom).

1.1 g/cm^3, as shown in Fig. 6. After increasing the gas saturation pressure the density of the MC foam was reduced to about 0.92 g/cm^3, as shown in Fig. 7. We have also prepared PBZT/PEKK composites with 5% PBZT rods. This rod content was significantly lower then the 10–30% used in previous cases. The reason for reduction of rod percentage is to reduce the rigidity of the MC making it easier to foam. Initial trials using this 5/95% MC resulted in microcellular foams with densities about 0.92 g/cm^3 as compared to 1.1 g/cm^3 that we obtained earlier for the 10/90 MC foam under the same foaming conditions.

3.4. Mechanical properties

Compression testing was performed to evaluate the stress-strain relationships of the microcellular foams processed from the PEKK and PBZT/PEKK molecular composites. The results are plotted together to facilitate comparisons. For purpose of comparisons, we plot specific mechanical properties versus the applied strain where specific mechanical properties are defined as mechanical properties (such as modulus and strength) divided by the density of the material. Fig. 8 shows the specific compression strength of various foams as a function of the strain. The results include microcellular foams of PEKK, 10/90 PBZT/PEKK MC, 50% of 10/90 PBZT/PEKK MC, blended with 50% of PEKK, 10% of PBZT fibers blended with 90% of PEKK, and a Divinycell HT110. The densities of the PEKK foams are 0.71 and 0.65 g/cm^3 for the upper and the lower curve, respectively. The result indicates that Divinycell HT110 reaches a plateau after the applied strain is about 4%. In contrast, the PEKK and molecular composite foams do

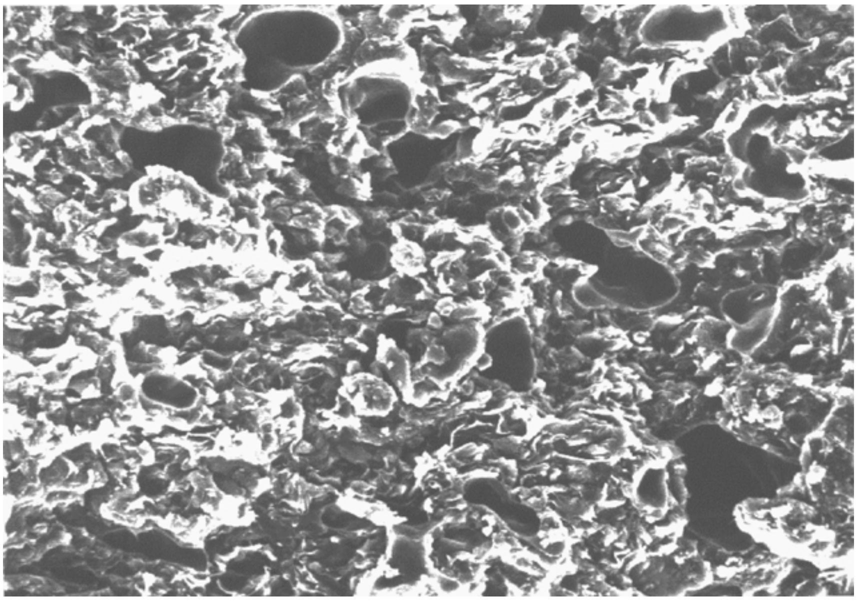


Figure 6 High-density 10/90 PBZT/PEKK molecular composite foam (1.1 g/cm^3).

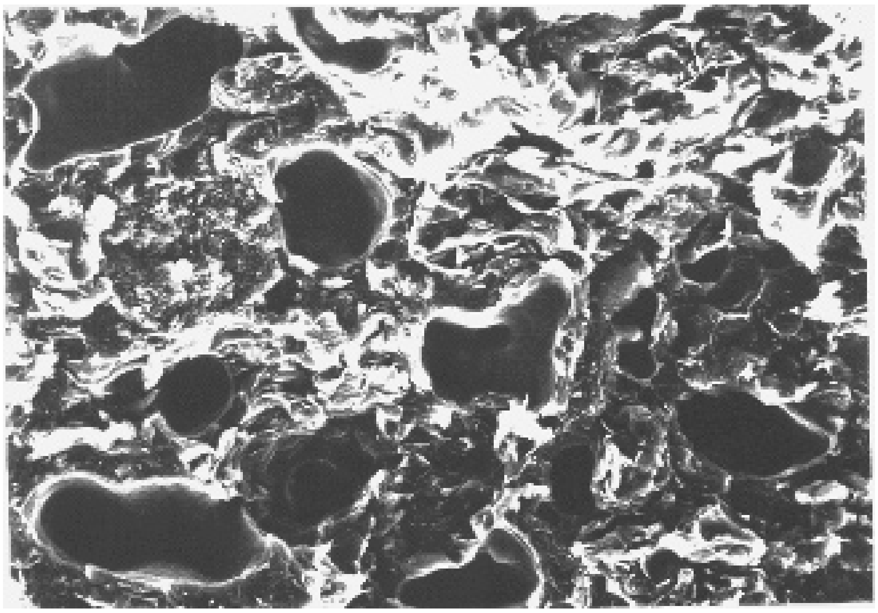


Figure 7 The 10/90 PBZT/PEKK molecular composite foam, the density of which was reduced to 0.92 g/cm^3.

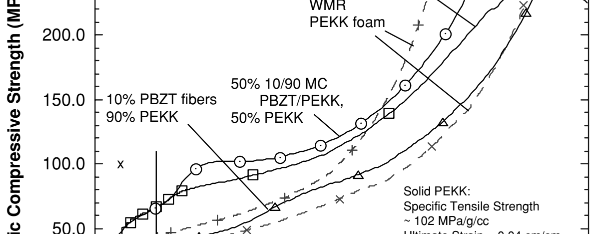


Figure 8 Comparisons among specific compression strengths of PEKK, PBZT/PEKK MC, and a Divinycell foam.

not have a plateau. The specific compression strength increases monotonically as the applied strain increases. There is no distinct fracture behavior after the foams were loaded to about 76% strain. This shows that our microcellular foams are very "ductile" and have very high fracture toughness. This should help tremendously in a variety of structural applications.

The material vendor for the PEKK could not provide compression properties, but did supply value of the tensile strength. The specific tensile strength of a solid PEKK sample is 102 MPa/g/cm^3 which is the same as the yield strength value of the PBZT/PEKK molecular composites. The solid PEKK sample has a clean fracture whereas our foams did not show any sign of fracture after they were loaded to 300 MPa/g/cm^3. Apparently, the great improvement in mechanical behavior is due to the unique morphologies of the foams.

TABLE I Comparisons of specific mechanical properties of PEKK, PBZT/PEKK MC, and Divinycell foams at 10% applied strain

	Divincell	PEKK foams	10% PBZT/PEKK MC foams	50% 10/90 PBZT/PEKK MC 50% PEKK	10% PBZT fibers 90% PEKK
Specific modulus (Mpa/g/cm^3)	117.2	375.7	688.5	892.5	384.1
Specific compressive strength (Mpa/g/cm^3)	11.7	37.6	66.5	89.1	38.3

TABLE II Comparisons of specific mechanical properties of PEKK, PBZT/PEKK MC, and Divinycell foams at 30% applied strain

	Divincell	PEKK foams	10% PBZT/PEKK MC foams	50% 10/90 PBZT/PEKK MC 50% PEKK	10% PBZT fibers 90% PEKK
Specific modulus (Mpa/g/cm^3)	40.7	214.2	333.3	329.1	229.1
Specific compressive strength (Mpa/g/cm^3)	12.2	64.3	96.4	98.8	68.6

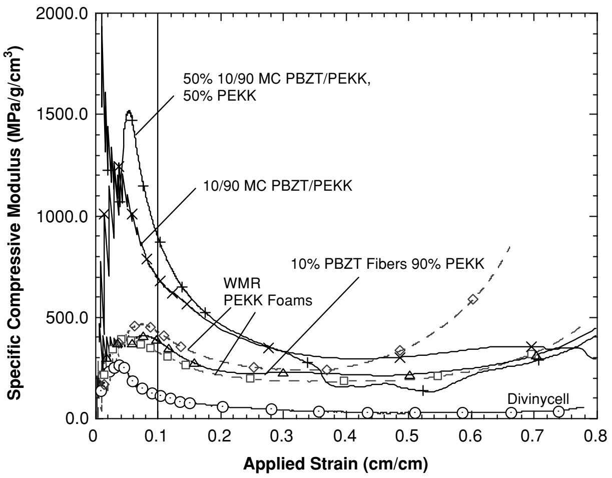


Figure 9 Comparisons among specific compression moduli of PEKK, PBZT/PEKK MC, and a Divinycell foam.

The specific compression modulus is plotted as a function of the applied strain in Fig. 9. The results, similar to the specific compression strength, are significantly higher than that of Divinycell. At 10% strain, the values of PEKK foams are about 2.5 times those of Divinycell whereas the values of PBZT/PEKK are about 5 times those of the Divinycell. It should be noted that specific modulus is normally calculated at a point or points rather than the entire stress-strain curve.

The numerical comparisons of the specific compression strength and modulus are listed in Tables I and II at 10% strain and 30% strain, respectively. Considerable improvement in properties are clearly in evidence.

4. Summary and conclusions

A number of summary and conclusions can be drawn from this research effort:

(1) The specific modulus of the 5/95 PBZT/PEKK MC foam at 10% strain is 2.5 times that of the PEKK foam.

(2) The specific compression strength of the 5/95 PBZT/PEKK MC foam at 10% strain is 1.9 times that of the PEKK foam.

(3) The specific modulus of the 5/95 PBZT/PEKK MC foam at 10% strain is 8.2 times that of the Divinycell foam.

(4) The specific compression strength of the 5/95 PBZT/PEKK MC foam at 10% strain is 6.2 times that of the Divinycell foam.

(5) The foam density of the PBZT/PEKK molecular composites processed by the technique described above are relatively high, from 0.92 to 1.11 g/cm^3.

(6) The technique described in this paper for molecular composite foams has been included as part of a patent application recently filed by WMR.

Microcellular composite foams processed from molecular composites exhibit very intriguing morphologies and superior mechanical properties. It would be a challenging job to further reduce their densities while maintaining their high desirable mechanical properties.

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