New Method for Producing High-Performance Thermoplastic Polymeric Foams

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ABSTRACT: A new method for the production of foamed thermoplastic polymers from blends of a poly(aryl ether ketone) (PAEK) and polyetherimide (PEI) is presented. The blowing agent for the foaming process is water which is produced at elevated temperatures in an extruder, via an *in situ* reaction between an amine end group on the PEI, and a ketone functionality on the backbone of the PAEK chain. The effect of composition, mixing, time, and temperature are investigated. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1543–1550, 1997

Key words: foam; thermoplastic; polyetherimide; poly(aryl ether ketone); poly(ether ketone ketone)

INTRODUCTION

Often there is a need to increase the strength-to-weight ratio in polymer products in order to economize on resin, to lower the weight of the part, or to enhance thermal or acoustic barrier properties. This can often be achieved by foaming the polymer. Currently, the polymeric foam market primarily consists of gas-imbibed polystyrene, polyolefins, and polyurethanes used in consumer products, packaging, and construction.[1] Though these polymers perform well for their given applications, they cannot be used in high-performance applications where material properties must be maintained at elevated temperatures. However, there is a growing need for foamed products with higher temperature performance for the aerospace, electronics, transportation, and construction industries. The need for high-performance polymers, in general, is ever increasing. It has been estimated that the worldwide market for these more thermally stable polymers in 1988 was 90 million kilograms (49 million pounds) worth approximately \$2.3 billion.[2] Furthermore, this market is expected to double by the end of this decade. Polyimides are a natural material of choice for high-temperature foamed thermoplastic products due to their ease of processing, exceptionally high heat resistance, and general chemical stability.[1]

Considerable effort has been focused on the development of processing methods for polyimides for use in structural and insulative foam applications. A review of the literature reveals that the majority of the work has been in the area of flame-resistant, low smoke-generating, low-density polyimide foams. In these cases the methods for foam production involve an *in situ* foaming process whereby a volatile ingredient is generated through a "curing" of the polymer. For example, in the synthesis of polyimides from dianhydrides and diisocyanates,[3] the "curing" step involves the loss of carbon dioxide gas, $CO_2(g)$. D'Alelio was issued a patent for chain-extending polyimides

with aromatic polyisocyanates, wherein the foam was generated from $CO_2(g)$ emission.[4] In several patents issued to Gagliani and colleagues,[5–17] foaming was affected either through the loss of CO_2 in this manner or through the generation of a gaseous alcohol or water (at elevated temperatures) from an amide/ester or amide/acid, respectively, during imidization. The production of foams by this latter method results in open-cell structures which are limited with regard to their insulative and vapor barrier properties. Using an amine-terminated silicone, Lee[18] was able to produce closed-cell polyimide foams which had similar flame-resistant properties with enhanced thermal and vapor-barrier qualities. Potential applications for such foams can be found in aircraft cabins, space vehicles, and other transport environments where life or equipment might be endangered by the overheating of smoke-emitting materials; that is, these foams are designed to give off essentially no smoke or toxic fumes when exposed to flame. Their thermal, electrical, and acoustical insulative properties are, of course, essential to their application. As such they can be used in fire-containing walls and lightweight structures, to protect fuel tanks and heat-sensitive systems, and as "void filler" materials. Additionally, modifications have been developed in order to enhance flexibility and response to cyclical loads so that seat cushions may be manufactured which still possess the desirable flame-resistant properties.[16,17]

A common thread among the polyimide foams discussed thus far is their nonstructural nature. Though not always explicitly stated within the respective literature so far addressed, these materials are primarily intended for non-load-bearing applications. Structural polyimide foams have been made, however, using an *in situ* molding technique. Parker and Feldman[19] have developed a process by which a composite structure containing approximately 10% loading of chopped fiberglass and glass microballoons was produced in a closed-cell mold which was "a tough, extremely strong closed porosity foam" of density 1–12 lb/ft^3 (0.19–0.20 g/cc). The foaming action here was provided by the generation of $CO_2(g)$ through an isocyanate reaction, as discussed earlier. In order to cost-effectively fabricate structural foams of even minor complexity, one must employ an extrusion- or injection-molding technique. None of the foaming processes discussed thus far lend themselves to either of these operations. A review

of the literature reveals few examples of high-temperature structural foams made through these processes. Due to their thermoplastic nature and ease of processing, an obvious material of choice for this kind of production is the poly(ether imide) class of polymers. These polymers exhibit superior physical properties, including high heat and flame resistance and exceptional strength.[1,20,21] Polyetherimides are often used in high-performance applications where they are exposed to elevated temperatures and high mechanical loads. One of the leading, commercially available, thermoplastic polyimides is ULTEM®, which we designate in this paper as PEI.[22] This amorphous polyetherimide has a glass transition temperature (T_g) of about 220°C and, in general, has excellent heat and flame resistance with low smoke evolution.

The preferred method of production of polyetherimides is the "melt polymerization" process.[21,23] Here, a bis(ether anhydride) and an organic diamine (or a prepolymer thereof) is introduced into a heated extruder, wherein the reactants are melted. The components react in the molten state and are extruded and formed into pellets for future use in extrusion or injection molding. The processing temperatures associated with these production techniques can be on the order of 400°C. Furthermore, due to the high T_gs of these resins, processing must be conducted at similarly high temperatures.

Blowing agents used for conventional foamed polymers (polystyrene, polyethylene, polypropylene, polycarbonate, ABS, modified phenylene oxide, polyurethanes, and polyesters) are not ideally suited for processing at these elevated temperatures. Blowing agents such as inert gases require expensive gas metering devices and high-pressure processing equipment. Hydrocarbons such as pentane are explosive at these temperatures. Other typical blowing agents, such as *t*-alkylazoalkanes, simply decompose well below the necessary processing temperatures. In general, besides cost, a critical consideration affecting chemical blowing agents (CBAs) is their compatibility with the resin. The term "compatibility" has a twofold meaning in that the solubility of the agent affects its dispersion in the resin (and the subsequent uniformity of the cell structure), and the chemical reactivity of the gaseous product produced may affect its interaction with the resin.[24] An example of the latter concern is given by the high-temperature CBA 5-phenyltetrazole. In polyimide systems, the aromatic amine

decomposition products can deleteriously affect the polymer.[21] Smearing and Floryan[21] developed a foamable polyetherimide resin formulation based on the incorporation of dihydrooxadiazinone compounds which do not suffer from any of the above-noted problems. Examples of structural foams within Smearing and Floryan's report used ULTEM 1000 as the resin. The dihydrooxadiazinone CBA, also acting as a plasticizer, was incorporated at 30 to 50% loading into the polyetherimide at 188 to 199°C. This "concentrated" resin was then blended at a 2% concentration with pure ULTEM and extruded at 306 to 370°C to produce the structural foams. In nonreinforced (e.g., non-glass-filled) foams, densities of 0.90 g/cc were obtained. General Electric Plastics currently offers four grades of UL-TEM resins for structural foam production.[25] The recommended blowing agents are either nitrogen gas or FULC-20, a proprietary CBA incorporated in an ULTEM matrix. Using this CBA, up to 20% reductions in density are reported. The continuous service temperature (relative thermal index) for these foams (along with the neat resin) is stated to be 338°F (170°C).[26]

A series of nine patents issued to Krutchen and Wu[27] presents a simple procedure for the production of low-density polyimide foams. Here, a polyetherimide is imbibed with a chlorocarbon (methylene chloride, chloroform, 1,1,2-trichloroethane, and mixtures thereof) and subsequently extruded at elevated temperatures to yield foams which can be further thermoformed into "any desired shape." The imbibing process is achieved by exposing the resin to concentrated solvent vapors at room temperature for about 48 h. The densities of the resultant foams were less than 20 lb/ft^3 (0.32 g/cc). This is noted by the authors to be the first time that this has been achieved for polyetherimide-type foams. The lowest density foam demonstrated within these patents was a foamed ULTEM 1000 resin with a density of 2.5 lb/ft^3 (0.04 g/cc), which displayed a "fine closed cell structure."

The report presented here provides a new method for producing foams from blends of a polyetherimide (PEI) and poly(aryl ether ketone) (PAEK) based on a water-producing reaction between an amine and a carbonyl compound. This method has several attractive attributes which are discussed later.

EXPERIMENTAL

The polymers used in this study were obtained from commercial manufacturers. The specific

PAEK was poly(ether ketone ketone), which we designate as PEKK, supplied by the DuPont Corporation. The specific PEI was ULTEM 1000® which, as stated earlier, we designate as PEI. It was obtained from the GE Plastics Company. A Killion single-screw extruder fitted with a circular die with a length-to-diameter ratio of 10 was used for extrusion. Rheological analysis was performed on a Rheometrics Mechanical Spectrometer (model 800) equipped with 1-in-diameter parallel plates. The dynamic mechanical rate sweeps were conducted from 0.1 to 100 rad/s under nitrogen at a temperature of 360°C and a strain of 5%. Potentiometric titrations of amines in the PEI were performed using hydrogen bromide (HBr) on a CTI model CPA-80 auto titrator. Solutions of HBr were standardized using potassium hydrogen phthalate. Scanning electron microscopy (SEM) was used to investigate the fracture surfaces of samples via a Cambridge Instruments Stereoscan Model 200 SEM equipped with a secondary electron detector.

RESULTS AND DISCUSSION

During the extrusion of the blends of PEKK with the PEI at 335 to 350°C, it was noted that the melt viscosity increased with higher process temperature and longer processing times. This was evidenced by an increase in the pressure at the extruder head. This behavior of increasing melt viscosity with increasing time or temperature was found to depend upon the composition of the blend. At high concentrations of either polymer, the changes in melt viscosity diminished. In fact, no significant changes in melt viscosity were noted for either of the polymers in their pure state with repeated processing. At sufficiently high temperatures (>350°C), it was found that the blends began to foam while being extruded. In addition, the foaming process could be mitigated or stopped by either decreasing the process temperature or reducing the residence time in the extruder. In parallel with the noted changes in melt viscosity, the foaming was found to depend on composition as well. *Neither pure PEKK nor pure PEI foamed during extrusion.* For the particular system that was being studied at the time, it was found that the viscosity changes and foaming effects were maximized at a 70/30 (w/w) mix of PEKK/PEI.
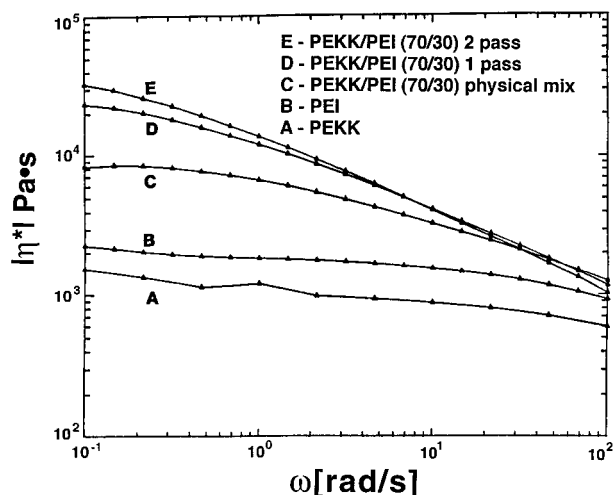
In order to quantify the viscosity changes in

Figure 1 Melt viscosity for the PEKK/PEI blends at 360°C under nitrogen at 5% strain.

the blends, a series of samples were extruded at 335°C in the composition of 70/30 (w/w) PAEK/PEI and analyzed via dynamic rheometry (see Fig. 1). Pure PEKK and pure PEI are labeled A and B, respectively. In a nonreactive system, one would expect that a miscible blend of these polymers would display a viscosity that is between that of the two pure polymers. This, however, is not what we observed. An extruded blend of the two polymers possesses a much higher melt viscosity (sample C). Further processing of the blend has the effect of increasing the melt viscosity even more. Samples D and E were taken from successively extruded samples of blend C. Clearly, a reactive process is occurring wherein there is chain extension and/or crosslinking.

In order to explain the changes in melt viscosity and foaming of the blends, there must also be functional groups in each polymer which react when combined. Furthermore, the reactive groups cannot be common to both polymers individually, since neither will undergo changes in viscosity nor will either one foam in their neat form. A view of the chemical repeat unit of each polymer shown in Figure 2 reveals no strikingly obvious candidates. The ketone, ether, and imide functional groups should not react with one another. However, it is generally known that free amine end groups are often present in polyimides due to the nature of the monomers and synthetic processes commonly used. With this in mind one can imagine an amine end group on the PEI reacting with some group on the PEKK, the obvious choice being the ketone functionality.

The key element to the presence of amine groups lies in the synthesis of the polyetherimide. It is known that the preferable method for polyetherimide production involves melt-extrusion of a dianhydride with a diamine. In order to control the molecular weight during this process, the stoichiometry of the reactants is typically offset, consistent with the Carothers relationship.[28] Thus, "a slight molar excess (about 1–5 mol %) of diamine can be employed resulting in the production of polyetherimides having terminal amine groups."[23] Indeed, titrametric analysis of the PEI used in this work revealed the presence of approximately one amine group per every 12.5 polymer chains (based upon the reported 12,000 number average molecular weight of the polymer[26]). Thus the terminal amine end groups in the PEI are clearly believed to react, at elevated temperatures, to form a ketimine molecular link.

This reaction is known to happen in other polymer systems and has been well catalogued.[29-35] The branched polymers of higher molecular weight would possess a much greater melt viscosity, reaching a crosslinked state in the case of extensive reaction. Furthermore, the by-product of this reaction is water. At the elevated temperatures of the extrusion processes under discussion here, water is a gas. Hence, the water acts as a pseudo-CBA. This reaction is diagramatically depicted in Figure 3.

Thus the ketimine reaction would easily account for the changes in the melt viscosities, the foaming of the blends, and the dependence of these phenomena upon the compositional ratio of
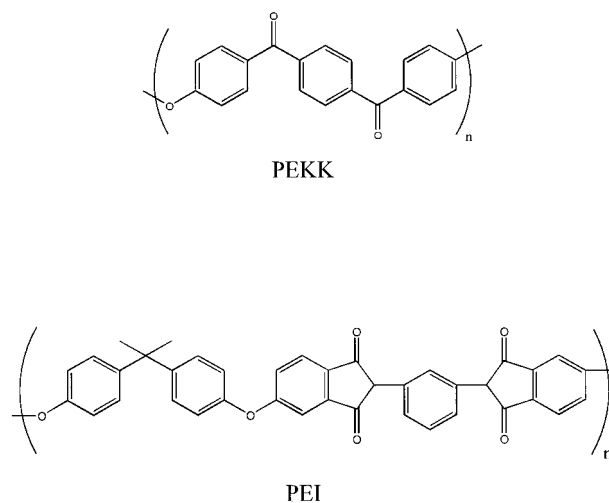

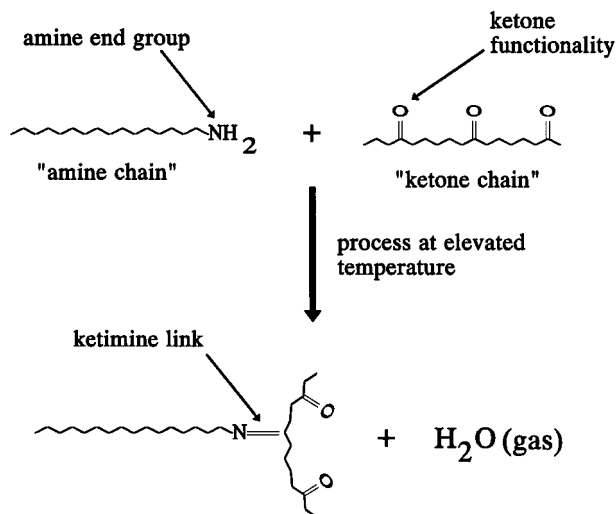**Figure 2** Chemical repeat units for PEKK and PEI.

Figure 3 Schematic showing the formation of a ketimine link with the production of gaseous water at elevated temperatures.

the blend. To take advantage of this phenomenon to produce high-temperature polymer foams, it is necessary to discuss the relevant factors that influence the foaming process.

The amount of water produced and, hence, the degree of foaming are directly proportional to the extent of reaction between the two reactive species (amine and ketone). In the blend under discussion here, PEKK is the ketone-containing polymer and PEI possesses the capability of having free amine groups on the ends of its chains. The probability of a reaction is dependent upon the following factors:

1. *Composition.* The likelihood of molecular contact and subsequent reaction is maximized when there is a high concentration of the reactive groups. As the relative concentration of either species decreases, the reaction probability decreases. Of course, at the extremes of either all amine or all ketone groups no reaction can occur, e.g., neither pure PEKK nor pure PEI will produce a ketimine foam. PEI polymer chains can be synthesized to contain practically any concentration of amine end groups desired: from zero to full end-group saturation. Thus the inherent degree of foaming in the PEKK/PEI blend at a given processing condition may be accurately controlled through variation of amine group

concentration within the PEI polymer and/or variation of the overall amount of PEI in the blend. Because the concentration of end groups is molecular weight-dependent, this variable is also potentially another controlling factor.

2. *Mixing.* The degree of mixing of the system will affect the extent to which the reactive species are brought within proximity of one another. Increasing the degree of mixing will tend to promote more reactions, thereby increasing the degree of foaming.

3. *Temperature.* The temperature of the polymer will affect molecular diffusion and thereby influence the degree of mixing on a molecular level. Hence, at high temperatures molecular diffusion is enhanced, favoring more reactions. Other effects of high temperatures are greater volumes for the gaseous water produced and low melt viscosity. Large gas volumes will result in increased expansion forces, causing rapid bubble growth. Ultimately, larger cell size will be observed at high temperatures. The reduced melt viscosity will also present less resistance to bubble growth.

4. *Time.* The time-dependent nature of chemical reactions (kinetics) dictates that longer times result in more reaction. The longer the system is at elevated temperatures, the more likely it is that the two reactive species will "encounter" one another amid the mass of other, nonreactive, species. Furthermore, bubble nucleation and growth are also a time-dependent processes. Though there are many other potentially important considerations for the control of foaming, they will not be addressed further in the present discussion. Clearly, however, it is possible that a variety of foamed polymer materials can be engineered through the control of these process and compositional variables, and through product design (geometry). The data presented in this article will specifically address the affects of composition and time. In order to gain a semiquantitative perspective of the effects of changing process variables, the densities of specific extruded materials were measured.

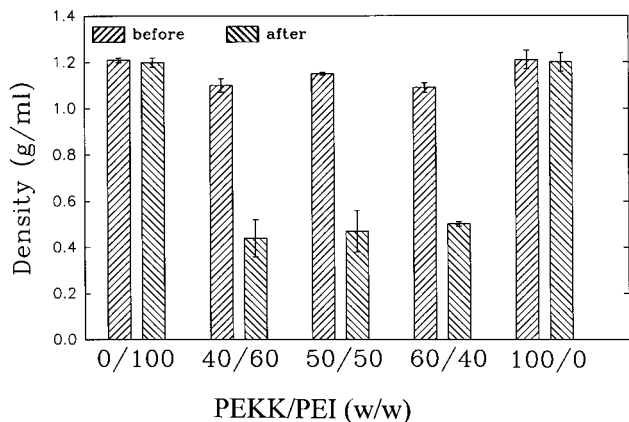As mentioned earlier, the PEI (ULTEM®) polymer used in this series of experiments was found

Figure 4 Densities of PEKK/PEI extruded blends before and after a 5-min residence time in the die.

to possess approximately one free amine group for every 12.5 polymer chains (based on titrametric data and reported molecular weight data). PEKK/PEI blends were produced by physically mixing the polymer pellets with subsequent extrusion in a single-screw extruder at 355°C with the final die temperature set at 275°C. Five different compositions of PEKK/PEI (by weight) were extruded: 100/0, 60/40, 50/50, 40/60, and 0/100.

The densities of the five compositions extruded at 10 rpm revealed only a nominal difference, about 4–8%, between the pure polymers and the blends. This indicates that under these conditions very little reaction occurred and/or that bubble nucleation and growth processes require longer times to occur in the blended samples. The extrusion process was halted and some material was allowed to remain in the die for 5 min before it was extruded. The densities of these samples held in the die were compared with their counterparts which were extruded without extra residence time. As expected, there was no significant difference in the densities of the pure PEKK and pure PEI samples before and after the 5-min residence time (less than 1% drop in density). For the blends, however, the density reduction was dramatic: over a 60% density drop in all cases. The density measurements of all the samples are shown in Figure 4. The clear presence of a cellular structure in a blended die-resident sample and the lack of a foam structure in its nonresident counterpart can be seen in the SEM shown in Figure 5. These micrographs were taken from the 40/60 blend and are representative of what is seen in the other two blended samples. SEM of the pure PEKK and pure PEI samples revealed

no foam structure either before or after the 5-min residence time, consistent with the density results. Thus it can be seen that both composition and process time have a significant impact on the degree of foaming in the extruded PEKK/PEI blends.

CONCLUSIONS

It is clear that the concept of controlling the foaming process in a high use-temperature polymer system via the ketimine reaction is possible. The data presented thus far show that composition, process time, and temperature greatly influence the foaming process in the PEKK/PEI blended system. What must be achieved in order to prop-
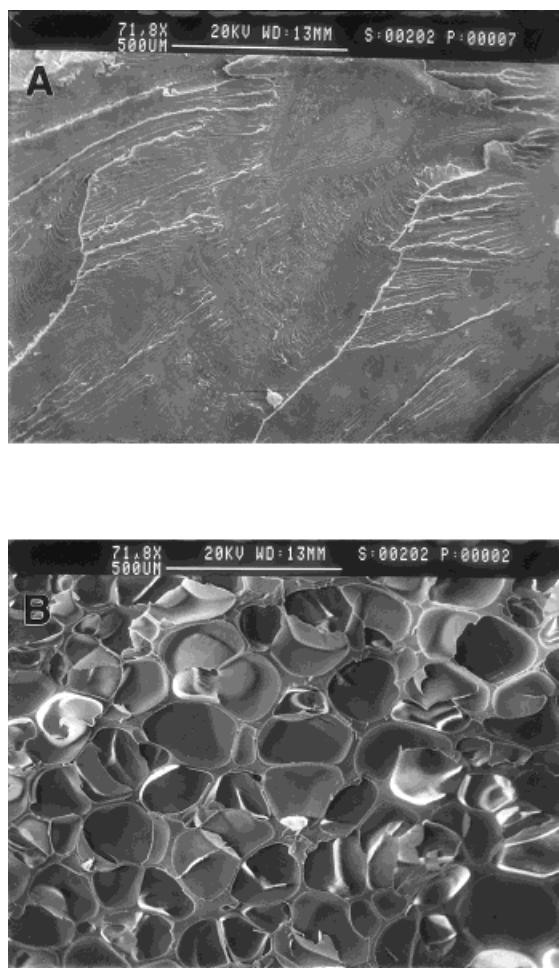

Figure 5 SEM micrographs of a 40/60 (w/w) blend of PEKK/PEI extruded at 10 rpm before (A) and after (B) a 5-min residence time in the die.

erly engineer useful PEKK/PEI foams is the actual *control* of the foaming process, as opposed to simply influencing it. This requires a complete understanding of the molecular and process variables involved in the foam production. Furthermore, the development of a quantitative relationship between processing parameters and product performance is required. The defining aspects of a project designed to address these issues must include three primary areas of effort. First, a considerable polymer synthesis thrust is necessary in order to manipulate molecular parameters such as molecular weight, reactive group concentration, molecular architecture, etc. Second, process engineering research is essential in understanding the foam system being developed. Last, the effects of changes in molecular and process variables must be quantified through characterization of the resultant products.

In comparing this high-temperature foam technology with the work done by others, it appears that there are several advantages offered by this process. The addition of blowing agent is unnecessary in this system. Furthermore, the compatibility issue is not a concern. The dispersement of blowing agent in the resin is already met. Furthermore, the gaseous water product presents neither a health hazard nor a polymer degradation problem. The process and product composition are completely tunable through simple process-controllable factors, e.g., polymer molecular weight, functional group concentration, process time, and temperature. No complex mixing or metering process would be necessary. Nor is there any need for a high-pressure extruder or injection-molding device. The tunability of this process may allow for the production of a wide range of materials, from very low density and highly insulative materials, to rigid structural foams. Furthermore, foamable resin pellets could be produced by extruding blends at low temperatures to prevent the imine reaction from occurring. It is likely that these pellets would possess a long shelf life. However, one potential disadvantage of water as a blowing agent is its possible corrosive effect on the process equipment. This feature is generally not a major problem because many of the newer endothermic CBA compounds depend on the use of water as the active blowing agent.[36]

It is fortunate that the ketimine foam process discussed here is reasonably simple, and it appears to lend itself to easy exploitation. It is probable that foams can be engineered to meet specific engineering requirements, such as product use temperature, mechanical strength, and thermal and acoustic insulative properties, through the control of polymer composition, cell size, foam density, and product configuration.

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