Plackett–Burman experimental design to facilitate syntactic foam development

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ABSTRACT: The use of an eight-experiment Plackett–Burman method can assess six experimental variables and eight responses in a polysiloxane-glass microsphere syntactic foam. The approach aims to decrease the time required to develop a tunable polymer composite by identifying a reduced set of variables and responses suitable for future predictive modeling. The statistical design assesses the main effects of mixing process parameters, polymer matrix composition, microsphere density and volume loading, and the blending of two grades of microspheres, using a dummy factor in statistical calculations. Responses cover rheological, physical, thermal, and mechanical properties. The cure accelerator content of the polymer matrix and the volume loading of the microspheres have the largest effects on foam properties. These factors are the most suitable for controlling the gel point of the curing foam, and the density of the cured foam. The mixing parameters introduce widespread variability and therefore should be fixed at effective levels during follow-up testing. Some responses may require greater contrast in microsphere-related factors. Compared to other possible statistical approaches, the run economy of the Plackett–Burman method makes it a valuable tool for rapidly characterizing new foams. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42892.

INTRODUCTION

Syntactic foams, consisting of hollow pore formers (such as microballoons or microspheres) incorporated in a polymer matrix, are an area of broad research interest and commercial importance. They are common in marine and aerospace applications, where their ability to insulate, reduce mass, provide buoyancy, increase strength, or enhance dimensional stability have both functional and economic benefits. Their closed-cell structure contrasts with the open or closed cells of gas-blown foams, as it is determined largely by the choice of matrix and pore-former rather than the generation and transport of polymerization reaction products. The purpose of this study is to propose a general protocol for the initial stages of syntactic foam development.

The model foam used in these studies is based on a poly(dimethylsiloxane) (PDMS) network. The pore-formers, glass microspheres ("beads"), are a common additive to a variety of matrices.[1] They have been studied in many syntactic foams based on numerous types of polymer matrices.[2–8] Other microsphere materials, such as carbon, may be preferred over glass to further reduce density or enhance thermal or electrical conductivity.[9] Microsphere systems may be additionally reinforced by nanoclay to improve tensile strength[10] or carbon nanotubes to improve compressive strength.[11]

A key aspect of this study is the implementation of a Plackett–Burman experimental design (Table I) to screen for significant variables by assessing many experimental factors simultaneously. Plackett–Burman designs, first described in 1946,[12] reduce the number of experiments needed to screen for main effects when compared to full factorial experimental designs. The number of experiments required for a full factorial design can be calculated using eq. (1):

$$N = l^f \tag{1}$$

where N is the number of experiments, l is the number of levels (the number of discrete values for the variables being assessed, commonly two), and f is the number of experimental variables, or factors. For example, a two-level, seven-factor experiment would require 128 experiments. Such a 2^7 design would assess

Table I. Plackett–Burman Matrix for Eight Experiments Screening Seven Factors, X1–X7

Exp #	X1	X2	X3	X4	X5	X6	X7
1	−1	−1	−1	−1	−1	−1	−1
2	1	1	1	−1	1	−1	−1
3	−1	1	1	1	−1	1	−1
4	−1	−1	1	1	1	−1	1
5	1	−1	−1	1	1	1	−1
6	−1	1	−1	−1	1	1	1
7	1	−1	1	−1	−1	1	1
8	1	1	−1	1	−1	−1	1

"high" and" low" levels of all seven factors as well as interactions, including those of multiple factors. Carrying out this design would certainly be extremely time-consuming. For seven experimental factors, N is greatly reduced to eight experiments using a Plackett–Burman experimental design. By limiting the time allotted to a screening design, it is then possible to sequentially build informed, subsequent experiments based on what has been learnt.[13]

An important advantage of Plackett–Burman experimental designs is orthogonality. When comparing any two columns of Table I, all four possible combinations of +1 and −1 appear an equal number of times. As a result the calculated effects on the responses are uncorrelated, and the main effects of the factors can be evaluated independently of one another.[14] Orthogonality is a property of numerous potential design matrices, some of which can accommodate more than two factor levels. A detailed treatment of the subject is available in Chapter 7 of Ref. 14. The Plackett–Burman method is appropriate for this current work because the designs, such as Table I, can be produced from standard generator rows[14,15] and analyzed with the straightforward calculations described in the Results and Discussion section. These features make the method readily accessible to non-statisticians.

One constraint of the Plackett–Burman approach, however, is that N must be a multiple of four, thus requiring the number of factors to be $N - 1$. If the number of experimental factors to be screened is $<N - 1$, one or more *dummy* factors (i.e., factors which are known to have no influence on the experimental result) can be used. While not required to implement the Plackett–Burman method, dummy factors are useful in assessing whether real factors have a significant impact on the experimental result, as they provide an estimate of standard error for the calculations described subsequently. While a thorough review of statistically derived experimental designs is beyond the scope of this introduction, an informative overview is provided by Brereton.[15]

The Plackett–Burman method is well suited to the development of syntactic foams as well as other composites.[16] When considering the properties of each phase independently, and the manner in which the two are combined, factorial designs may be unwieldy due to the large number of possibly active factors. Ease of preparation, however, is a distinct advantage for

syntactic foams. Numerous formulations can be produced and tested in a relatively short time, often without the need for custom synthesis or elaborate processing. The result is a rapid yet statistically rigorous approach to screening variables and developing materials.

This work demonstrates that a model syntactic foam, consisting of glass beads in a polysiloxane matrix, can be studied with great run economy using the Plackett–Burman method, particularly when compared to other more resource-intensive statistical approaches. Gel point and foam density are strong candidates for future predictive modeling. Results do not support further efforts to control thermal and mechanical properties without first assessing greater contrast in the experimental levels. Processing conditions introduce significant variability and should therefore be controlled at the earliest opportunity. Such observations made early will later lead to greater confidence in more detailed characterization of material properties and the subsequent study of variable interactions.

EXPERIMENTAL

Materials and Formulations

Sylgard® 184 two-part elastomer kit and DC-3-6559 cure accelerator from Dow Corning were used as received. The two-part elastomer kit is a proprietary platinum-catalyzed mixture containing vinyl end-capped oligomeric dimethyl siloxane and a methyl hydrosiloxane crosslinking agent. Both resin and curing agent contain dimethylvinylated and trimethylated silica filler (30–50% and 10–20%, respectively). The cure accelerator contains a platinum compound and dimethylvinylsiloxy-terminated dimethylsiloxane.[17,18]

Glass microspheres provided by 3M™, grades S22 (0.22 g cm⁻³, 50th percentile diameter of 35 μm), S38 (0.38 g cm⁻³, 50th percentile diameter of 40 μm), and S60 (0.60 g cm⁻³, 50th percentile diameter of 30 μm) were also used as received.

Appropriate amounts of base resin and cure accelerator were mixed according to the levels prescribed in Tables I and II. Microspheres were then added to obtain the appropriate final volume percentage, and briefly hand mixed to incorporate. The curing agent was added rapidly by syringe immediately before

Table II. Plackett–Burman Experimental Levels

Factor		Low level (−1)	High level (+1)
X1	Resin composition (wt % base resin/wt % cure accelerator)	91/9	99/1
X2	Bead distribution (vol % X3 bead/ vol % other bead)	25/75	100/0
X3	Bead density (g cm⁻³)	0.22	0.38
X4	Bead loading (vol %)	25	35
X5	Dummy		
X6	Mixing rate (rpm)	1000	2000
X7	Mixer pressure (kPa)	78	20

machine mixing. The amount of curing agent was held constant at 10 wt % of the combined resin-accelerator mass. Formulations were mixed for 1 min in a model ARV-310 vacuum-type planetary centrifugal mixer (THINKY, USA). The specimen cup simultaneously rotates (analogous to the earth about its axis) and revolves (earth about the sun). The instrument automatically sets the rate of revolution at one-half of the rate of rotation, and applies a programmable degree of vacuum with an internal pump. After mixing, a small amount of sample was taken for immediate rheological analysis, while the remainder was poured into molds and allowed to cure at room temperature.

Experimental factor levels (Table II) were chosen after informal scoping to develop familiarity with the system. These experiments included assessing the ability to incorporate volume loadings up to 60% of S60 beads into Sylgard® 184. The levels in Table II avoid extremes of microsphere density and volume loading in order to ensure that all Plackett–Burman samples could be prepared in the vacuum mixer. There is also an experimentally achievable midpoint (such as 30 vol % beads) for each factor which is not tested in this two-level design. Based on the concept of sequential experimentation described in the Introduction, these traits allow Plackett–Burman results to support quantitative follow-up analysis. After the factors of interest have been reduced, the midpoints may be tested in replicate runs. Factor levels may be broadened or narrowed from the current values. By this route, a central composite design,[15] for example, may be assembled using some results already acquired combined with new data. Once completed, such a design, having greater than two levels per factor, is appropriate for studying higher-order effects such as interactions.

Selection of Responses

The responses studied represent a variety of techniques to simulate a range of possible applications. The goal in selecting such a range is to identify properties for potential tunable materials. Viscosity at 1 h is considered an indication of the uncured material's ability to flow, as pertains to an encapsulant filling a gap without entering adjacent areas. Similarly, gel point is considered an indication of network formation and a surrogate for pot life. Microscopy was performed to assess uniformity of the foam, including bead dispersion, quality of mixing and the bead–matrix interface. Density is a commonly addressed foam property directly related to weight savings and the corresponding application advantages. Indentation hardness is a rapid empirical method for comparing the foams' resistance to deformation. Although the measurements are related to viscoelastic properties, they do not themselves directly represent those fundamental properties.[19] The coefficient of thermal expansion (CTE) addresses dimensional stability in applications involving heat generation, or having insulation requirements,[20] in which case minimal dimensional change is desirable.

The glass transition temperature (T_g) is an important feature for applications because it involves changes in the elastic properties of the network and thus influences service temperature. The effects of fillers on a polymer system T_g cannot be predicted *a priori*, and may result in an increase, decrease, or negligible change.[21,22] Although the T_g of PDMS is quite low (150 K),[23] T_g is measured to ascertain if limiting service temperatures are influenced by foam formulations. Dynamic mechanical analysis measures the foams' viscoelastic responses to sinusoidal force. The ratio of the loss modulus (energy dissipated), to the storage modulus (energy absorbed), is termed tan δ, or the damping parameter. It is measured to address the ability of the foam to absorb mechanical energy.[22,24]

Rheology (Viscosity and Gel Point)

The initial curing process was monitored with an AR-G2 rheometer (TA Instruments, New Castle, DE) at 25°C using 25 mm electrically heated parallel plates and a time sweep at 5.0% strain and an oscillation frequency of 1 Hz. The gel point was defined as the crossover of the storage modulus and the loss modulus. Dynamic viscosity was evaluated at 60 min, below the minimum observed gel point across all runs, for the Plackett–Burman analysis. Rheological values were corrected for the elapsed time to transport the sample to the rheometer and initiate measurement (3.7 ± 0.5 min) so that reported time intervals begin at the cessation of mixing.

Microscopy

Scanning electron micrographs of foam cross-sections were obtained using an Inspect F50 scanning electron microscope (FEI, Hillsboro, OR). The extent of bead dispersion within the sample was characterized by the distance from the bottom of the foam that did not contain microspheres (the "no-bead-band," or NBB).

Physical Properties (Density and Hardness)

Density measurements were conducted via an Ultrapyc 1200e (Quantachrome Instruments, Boynton Beach, FL) pycnometer, using helium displacement and sample mass. Hardness was evaluated with a handheld durometer (Fowler, 30D Sharp D scale). Three density and hardness measurements were taken per sample, and the averages reported.

Thermal and Mechanical Properties (CTE, T_g, and Tan δ)

Linear thermal expansion was measured with a Netzsch DIL 402 C vacuum-tight horizontal pushrod dilatometer (Netzsch Instruments North America, Burlington, MA) on cylindrical samples ~5 mm in diameter × 13 mm in height. Samples were cooled from ambient temperature to −55°C, held for 15 min, and then heated to 125°C at 1°C min⁻¹. The coefficient of thermal expansion (CTE) was derived from the slope of the best-fit line to the data between −55°C and 125°C.

Differential scanning calorimetry (DSC) was performed on a TA Instruments Q2000. Calibrations were performed with sapphire and indium standards. Samples were cooled to −180°C at 20°C min⁻¹ and then heated to 40.0°C ± 0.1°C at 20°C min⁻¹, with a nitrogen purge flow of 50 mL min⁻¹. T_g was determined by TA Instruments Universal Analysis 2000 software from the inflection point of the heat flow signal. Two replicates were performed, and the averages reported.

Dynamic mechanical analysis (DMA) was performed in a compression clamp on a TA Instruments Q800 with molded cylindrical samples 15 mm in diameter and 5 mm in height. A frequency sweep was performed between 1 and 200 Hz, at 40°C

Table III. Experimental Results

Exp #	Visc. (Pa s^{-1})	Gel point (min)	NBB (μm)	Density (g cm^{-3})	Hardness (shore D)	CTE 1/°C ($\times 10^{-4}$)	T_g (°C)	tan δ
1	41.0	88.7	89.3	0.853	15.0	2.193	−121.5	0.101
2	10.1	433	262	0.883	14.1	2.330	−120.8	0.135
3	325	63.4	0	0.787	21.7	1.763	−121.4	0.135
4	83.2	80.5	0	0.815	17.3	1.938	−121.3	0.111
5	18.7	423	83.3	0.810	16.0	1.798	−121.2	0.213
6	22.5	122	119	0.930	13.0	2.190	−120.3	0.139
7	8.77	569	786	0.895	10.3	2.326	−120.0	0.146
8	12.6	531	286	0.804	16.1	1.949	−120.6	0.139
Avg	65.3	289	203	0.847	15.4	2.061	−120.9	0.140
RSD(%)	165	76.1	127	6.05	21.6	11.0	0.46	23.6

and an amplitude of 10 μm. The damping (tan δ) value at 5 Hz was extracted for the Plackett–Burman analysis. This frequency was selected because it avoids the prolonged run times involved with very low frequencies and the possibility of instrument limitations at very high frequencies.[24] Three replicates were tested, and the averages reported.

RESULTS AND DISCUSSION

Interpretation of Plackett–Burman Coefficients

The Plackett–Burman design for the development of syntactic foams is displayed in Table I. As is common with these experimental designs, the high and low levels (l) of the factors are coded as +1 or −1, respectively. The experimental factors (X1-X7) and the values of the levels (high and low) are displayed in the columns of Table II. The responses (r) of each characterization technique are shown in the columns of Table III. A Plackett–Burman coefficient (b) for a factor on a response can then be calculated using eq. (2), where n is the individual experiment number, and N is the total number of experiments.

$$b_{X1,r} = \left[\left(l_{X1,n1} r_{X1,n1} \right) + \left(l_{X1,n2} r_{X1,n2} \right) \ldots + \left(l_{X1,n8} r_{X1,n8} \right) \right] / N \quad (2)$$

For example, the Plackett–Burman coefficient (also called an "effect") for resin composition (X1) affecting viscosity (Table III) is calculated below by substituting values into eq. (2). It assesses the effect observed by changing the resin composition from the low level to the high level. Note that, although units do not cancel in eq. (3), Plackett–Burman effects are

commonly discussed as dimensionless. Therefore, units are included in Table IV, but are omitted from the text.

$$b_{X1} = [(-41.0) + (10.1) + (-325) + (-83.2) + (18.7) + (-22.5) + (8.77) + (12.6)]/8 = -52.7$$

Plackett–Burman coefficients for each factor and experiment number are displayed in Table IV. The first step in evaluating the Plackett–Burman coefficients is to compare the coefficients of the experimental factors to the coefficient of the dummy factor.[15] Any coefficient with a magnitude exceeding that of the dummy may initially be considered significant. For example, resin composition (X1) and mixer pressure (X7) yield Plackett–Burman coefficients of 200 and 36.8, respectively, for the gel point response (Table IV, second column). These are the only two values whose magnitudes exceed the Plackett–Burman coefficient for the dummy factor (X5) of −24.2. Therefore, first inspection indicates that resin composition and mixer pressure significantly affect the gel point of the syntactic foam, whereas the three bead-related properties (X2, X3, X4) and mixing rate (X6) have no significant impact on this experimental response.

Although Plackett-Burman designs can be constructed for N up to 100 experiments, typically N is much smaller, and the effects are assumed to follow a t distribution. The effects may then be further prioritized using a t-test.[25] This is helpful if it is difficult to determine if the magnitude of a real factor's effect differs meaningfully from that of the dummy. The dummy effects (E_d)

Table IV. Plackett–Burman Effects

	Visc. (Pa s^{-1})	Gel point (min)	NBB (μm)	Density (g cm^{-3})	Hardness (shore D)	CTE 1/°C ($\times 10^{-4}$)	T_g (°C)	tan δ
X1	−52.7	200	151	0.000875	−1.31	0.0399	0.238	0.0184
X2	27.4	−1.48	−36.5	0.00388	0.788	−0.00287	0.113	−0.00288
X3	41.6	−2.35	58.8	−0.00213	0.413	0.0284	0.013	−0.00813
X4	44.7	−14.4	−111	−0.0431	2.34	−0.199	−0.238	0.00963
X5	−31.7	−24.2	−87.1	0.0124	−0.338	0.00313	−0.013	0.00963
X6	28.6	5.53	43.9	0.00838	−0.188	−0.0416	0.163	0.0184
X7	−33.5	36.8	94.6	0.0139	−1.26	0.0399	0.338	−0.00613

Table V. t statistics for Plackett–Burman Effects[a]

	Visc.	Gel point	NBB	Density	Hardness	CTE	T_g	tan δ
X1	8.27				−3.89	12.8	19.0	
X2					2.33		9.00	
X3							9.08	
X4				−3.48	6.93	−63.6	−19.0	
X5								
X6						−13.3	13.0	
X7				−3.74		12.8	27.0	

[a] Absolute values ≤1.96 removed for clarity. Critical values are 1.96 (70%), 3.08 (80%) and 6.31 (90%), 12.7 (95%), and 63.7 (99%).

and the number of dummy factors (n_d) are used to assess the variance of an effect, as in eq. (3).

$$\sigma^2 = \frac{\Sigma E_d^2}{n_d} \quad (3)$$

The standard error of the effect (SE_{eff}) is then determined according to eq. (4).

$$SE_{eff} = \sqrt{\sigma^2} \quad (4)$$

The t-statistic for a given effect on a given response is determined by eq. (5).

$$t = \frac{effect}{SE_{eff}} \quad (5)$$

In the case of a design with one dummy factor, this process simply consists of normalizing each coefficient to the magnitude of the dummy coefficient. Using one degree of freedom and a two-tailed t-test, critical t-values (t_{crit}) can be obtained.[26] The results of calculations using eqs. (3)–(5) are shown in Table V, along with several critical t-statistics at different confidence levels. If the magnitude of a given t statistic is greater than t_{crit} we reject the null hypothesis that the effect causes the same amount of change in the response as the dummy factor causes.

By rejecting the null hypothesis we conclude that a factor has a significant main effect. Because this is a screening design, a level of 70% is a useful guidepost for significant effects.[27]

Evaluation of Responses

Representative rheological data is shown in Figure 1 (all rheological data is provided as Supporting Information, as Figures S1 and S2). Viscosity has four effects with magnitudes greater than the dummy (X5, −31.7). The negative effect on viscosity of resin composition (X1, −52.7) may indicate a reduction in viscosity by changing to a resin containing less cure accelerator. The positive effects on viscosity of bead density (X3, 41.6) and bead loading (X4, 44.7) may indicate that increasing the bead loading from 25 vol-% to 35 vol-% and the bead density from 0.22 g/cm^3 to 0.38 g/cm^3 increases the viscosity, consistent with increased drag forces from additional beads. The negative effect of mixer pressure (X7, −33.5) only slightly exceeds the magnitude of the dummy. Because the t-statistics for these four variables are below the 70% significance level, however, 60-minute viscosity would not likely be selected as a property for future tuning. It is also notable that experiment 3 has an extreme value for viscosity (325 Pa*s, Table III) related to its gel point of 63.4 minutes. This value contributes a high relative standard deviation for viscosity values, yet does not contribute to the identification of statistically significant Plackett-Burman effects.

The gel point may be the more readily controlled and practical rheological property, as resin composition (X1) is clearly the dominant factor. The effect of 200 indicates that the high level of resin composition, containing less accelerator, prolongs the gel point. The t-statistics in Table V show that resin composition is significant to greater than 90%, and that the only other factor having a magnitude greater than the dummy (mixer pressure, X7, 36.8) has a t-statistic (1.52) below 70%. For rheological properties, therefore, the Plackett-Burman analysis indicates that resin composition is the most significant factor for further study, and that gel point is the more tunable property.

None of the three factors in the NBB response having magnitudes greater than the dummy (resin composition, bead loading, and mixer pressure) have a significance level exceeding
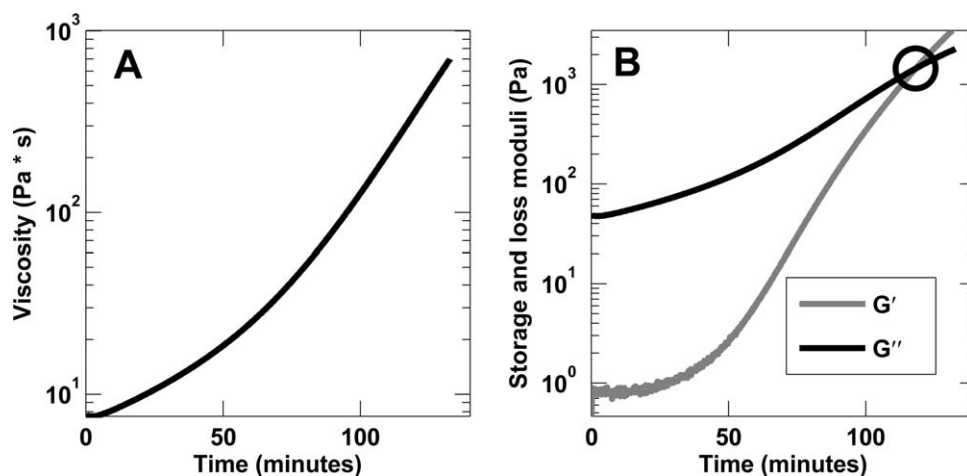

Figure 1. Representative rheology data for experiment 6. Data illustrates viscosity profile (A) and the determination of the gel point (B, circled) at the intersection of the storage modulus (G′) and loss modulus (G″).
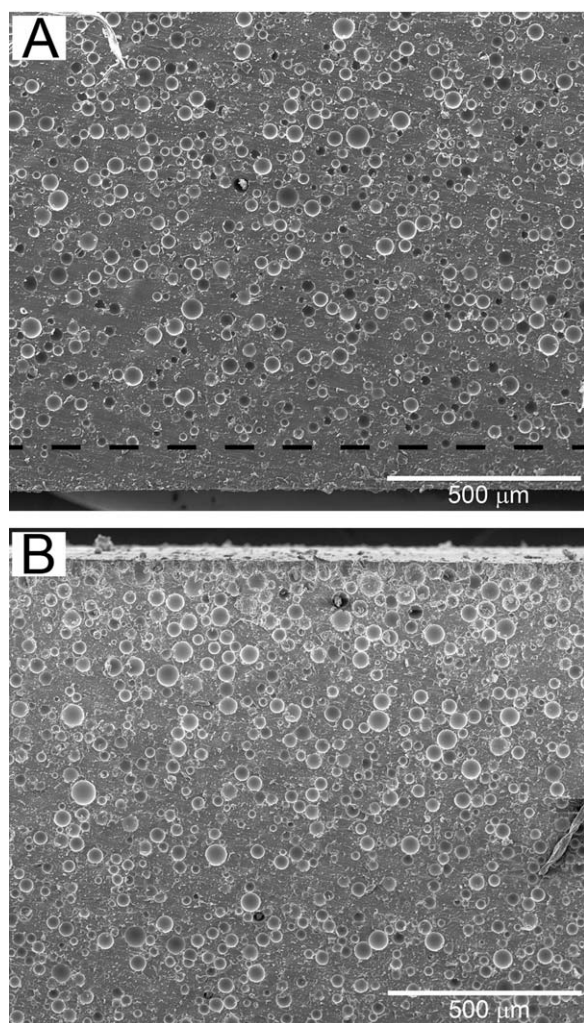
Figure 2. Scanning electron micrograph of experiment 6. The bottom margin (A) shows the 119 μm NBB (below the black dotted line). The top margin (B) shows microspheres extending to the surface.

70%. This indicates that the phenomenon, shown in Figure 2(A), would be difficult to manipulate at the current factor levels. At least two of these factors, (resin composition and bead loading), however, would be retained in follow-up experiments, as they are statistically significant in other responses. Resin composition (X1) has a positive effect of 151, indicating that the high factor level is associated with larger bead-free lower margin, as it allows a longer time before the curing polymer network restricts the buoyant migration of the beads. This result indicates that the rate of cure might be used to control final foam morphology. This property could be further studied to identify conditions to either limit migration, or possibly to manipulate it if the development goal involves a functional gradient.[28] The effect for bead loading (X4, −111), with the opposite sign from the resin composition's effect, implies that increasing bead loading to 35 vol-% reduces the NBB. While it is possible that the two experiments having no measurable NBB (experiments 3 & 4) can be attributed to the sampling location, it is notable that they also have the more highly accelerated cure, and the higher volume loading of the higher density

beads, all of which would be expected to limit the beads' mobility away from the bottom surface. For a discussion of the dummy factor in this interpretation, see the assessment of independent variables later in this section.

Bead loading (X4) governs foam density, and is the only statistically significant effect (Table V). The negative Plackett-Burman effect (−0.0431, Table IV) indicates that higher volume loading reduces foam density. Although the relative standard deviation of the responses is quite small (6.05%, Table III), the t-statistic exceeding the 80% significance level (−3.48, Table V) supports the conclusion that the factor is active, and furthermore suggests that density could be finely tuned through material selection. Interestingly, the bead density itself (X3) does not have a significant effect over the factor ranges tested. It is possible that greater contrast in this factor would be necessary to observe a significant effect. Also note that the wall thickness of the beads is known to be a relevant factor in foam properties,[29,30] but is not controlled in this study.

Similarly, bead loading (X4) has the largest effect on hardness (2.34, Table IV). The strong positive effect indicates that more beads produce a harder material. Three other variables have significance levels exceeding 70%: the negative effects for resin composition (X1, −1.31) and mixer pressure (X7, −1.26) imply that softer materials result from formulations containing more cure accelerator mixed under a higher pressure. The positive effect for bead distribution (X2, 0.788) indicates that harder materials result when the beads are of a single grade, not a mixture of the two. It is notable, however, that the two grades of microspheres differ less in their diameters than in their densities, and therefore may not reflect the ways in which a less overlapping bimodal size distribution might either mix or segregate in the finished foam.

Results for CTE and T_g are interesting cases (Representative dilatometry and DSC data appear in Figure 3). For each response all factors except one have t-statistics well above the 90% significance level, yet the limited change in responses (Table III) indicate that they are not practical response variables. The relative standard deviation of each response is notably small (11.0% for CTE and 0.46% for T_g). Such results illustrate the importance of viewing statistical values with a critical eye. Each response has one effect that stands out as the largest, in particular CTE. The bead loading (X4) has a negative effect, indicating lower thermal expansion, or greater dimensional stability, as a result of changing from the low factor level to the high factor level. In the case of T_g, however, the mixer pressure (X7) has the largest t-statistic (27.0, Table V). This implies, without an obvious physical justification, that increased T_g results from a resin containing less accelerator and from mixing at 20 kPa instead of 78 kPa. For both responses, the effects of the dummy factor are near zero (the ideal case), which validates the Plackett-Burman approach. While it is possible that all, or nearly all, factors could have very high significance for a given response, it is also a numerical consequence of small dummy effects, and indicates that other properties may be explored within the current factor range without large impacts on CTE and T_g.
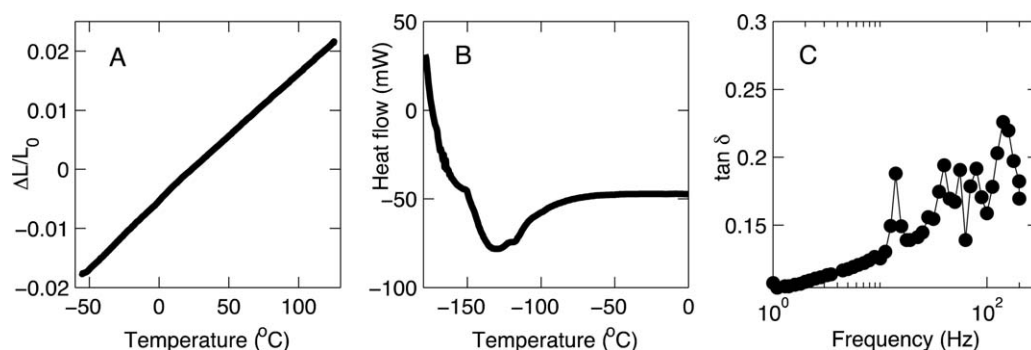
Figure 3. Representative data for experiment 6. (A) CTE (where $\Delta L/L_0$ represents change in length over initial length), (B) DSC and (C) DMA.

While no effects on tan δ exceed the 70% significance level (Representative DMA data is shown in Figure 3), the only effects greater than that of the dummy are resin composition (X1) and mixing rate (X6). No main effects relate to the bead properties, although bead loading (X4) has an effect equal to the dummy effect. As observed with other responses, experimental results are quite similar to one another (0.140 ± 0.033) indicating that tan δ is not a controllable response with the current experimental levels. High-damping polymers, however, are typically desirable for applications requiring the absorption of shock, vibration, or sound. These results suggest that other properties may be manipulated to a degree without significant changes in lower-frequency damping, but that an assessment higher-frequency damping would require additional experiments.

Assessment of Independent Variables

The most influential independent variables overall are the resin composition and the bead loading. That is, one variable each related to reaction kinetics and mechanical reinforcement, respectively, are the major factors across several properties. The bead distribution and bead density are lesser factors, possibly due to the current experimental levels. The mixing rate and the mixer pressure may be significant factors in some responses, although this significance may arise in part from small effects for the corresponding dummy factors. Notably, the mixer pressure has a larger-magnitude effects than the dummy for all responses except tan δ, and the mixing rate effects exceed the dummy for CTE, T_g and tan δ. This result emphasizes the importance of effective and uniform processing parameters. The approach to mixer settings in any further experiments would be to select those which are known to be effective, as there is no reason to optimize or retain a source of possibly insidious variability. Figure 4 illustrates a foam specimen (experiment 2), with air bubbles remaining after mixing at the slower rotation and the higher pressure.

The dummy factor effects are relatively small for physical, thermal and mechanical properties, yet noticeably larger for rheological properties and foam homogeneity (the NBB). Dummy effects substantially different from zero may indicate a lack of experimental or measurement precision, or the presence of effects which cannot be assessed with the Plackett-Burman. It is important to point out that while the Plackett-Burman can distinguish main effects from one another, main effects are also confounded with higher-order effects such as interactions. This is a necessary consequence of the orthogonal array's structure,[25] and a limitation which must be accepted in order to benefit from its screening capability.

To further explore the possibility of unaccounted polymer-bead interactions, two samples of Sylgard® 184 (91/9) with no beads were run as references. Rheology data is shown in Figure 5. Reference sample 1 was mixed at the low levels of mixing rate (X6) and mixer pressure (X7) whereas reference sample 2 was mixed at the high levels of mixing rate and mixer pressure. They show similar viscosities of 11.0 Pa*s and 13.7 Pa*s respectively, which are lower than more than half of the results of the Plackett-Burman experiments. This is consistent with the absence of beads, since the presence of beads introduces drag forces from fluid flowing around spheres.[31] These reference experiments also have similar gel points of 101.4 min and 94.8 min, closely resembling the four Plackett-Burman experiments having the low levels of resin composition. To the extent that the two reference samples may differ from one another, it is noteworthy that reference sample 2 has the more aggressive mixing parameters and that these lead to higher viscosity and shorter gel time.
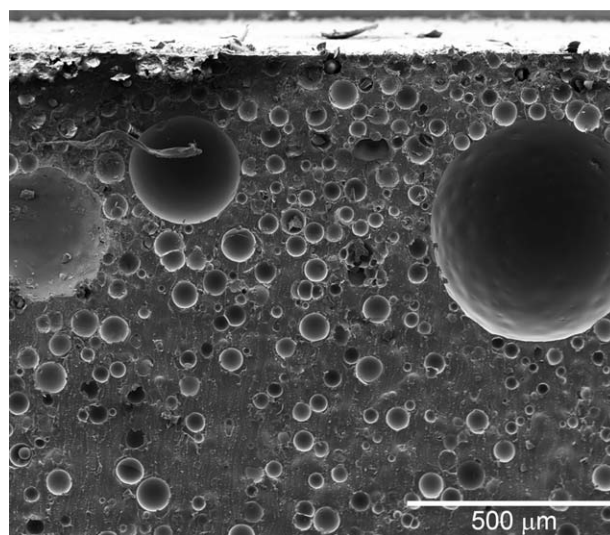

Figure 4. Scanning electron micrograph of experiment 2. Image shows air bubbles at the top margin.
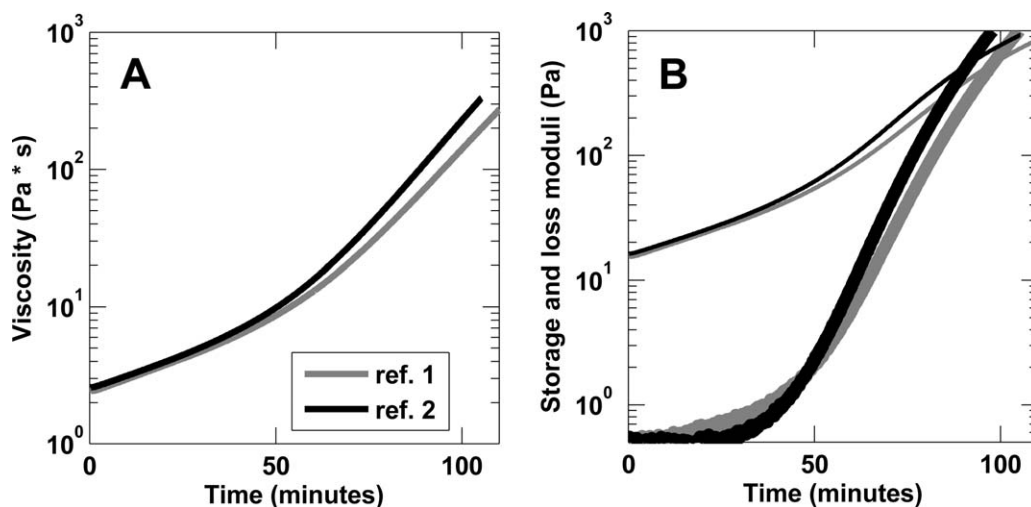
Figure 5. Rheology of two unfilled Sylgard® 184 reference samples. Samples were mixed at the low level of resin composition (X1). Viscosity profiles (A). Modulus profiles (B) for gel point determination: Reference sample 1 shown as G′ (thick gray line) and G″ (thin gray line), Reference sample 2 shown as G′ (thick black line) and G″ (thin black line).

CONCLUSIONS

This eight-experiment orthogonal design provides a statistical basis for focusing syntactic foam development. The most readily controlled properties are the foam density and the gel point, primarily through the bead loading and resin composition. These two variables may also contribute to a lower foam margin free of microspheres. Greater contrast in bead densities, loadings and size distributions may be required to further understand this property. The mixing parameters, particularly the mixer pressure responsible for degassing, may introduce variability across numerous properties and should subsequently be controlled at levels known to be effective. Foam hardness, thermal expansion, and glass transition temperature are complex phenomena in which many factors are active from the perspective of the coefficient calculations. The low relative standard deviations of the CTE and T_g results, however, indicate that the responses do not change meaningfully. The very low glass transition temperature, due to a narrow range of observed values, is likewise not a practical response variable. Damping behavior does not depend on any bead-related variables. The magnitudes of dummy variable effects validate the Plackett-Burman methodology. They are frequently close to zero, and in other cases they are consistent with confounding effects, such as possible interactions. In eight experimental runs, therefore, we identify candidate factors for tuning material properties, highlight processing variables requiring control, eliminate some responses from future consideration, and are able to frame new questions regarding the foam. Compared to other possible statistical approaches such run economy can be recommended to reduce the time required for new foam development.

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