Some Mechanical Properties of Particulate-Filled Thermosetting and Thermoplastic Polymers

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Synopsis

A semiempirical, single-parameter equation describes the modulus of particulate systems

$$\frac{E_c}{E_p} = \frac{1}{K(1 - \phi^{1/3})}.$$

This equation has been found applicable for thermoplastic/glass bead systems, and it is further verified for particulate thermosetting systems (epoxy and polyester matrices). The temperature effect on the modulus of epoxy/glass bead composites is also analyzed. Crazing characteristics calculated from tensile data of thermoplastic/glass bead composites are summarized and compared with literature results on the corresponding unfilled polymers. The effect of coupling agents and preliminary results on rigid foams are also presented.

INTRODUCTION

Glassy polymers, thermosetting and thermoplastic, containing glass beads were studied by several authors. Glassy polymers, at room temperature, have a modulus in the range of 2.5×10^{10} to 3×10^{10} dynes/cm^2 while the modulus of glass beads is about 70×10^{10} dynes/cm^2 giving a moduli ratio of about 25. This ratio increases with temperature. The stiffer glass beads reinforce the modulus of the polymer, an effect which is often compared with predictions of the well-known Kerner equation.[1]

Glassy thermoplastic polymers containing uncoupled glass beads (the "no adhesion" case) were studied by Nicolais, Narkis, and Lavengood.[2,3] These authors found that the stress–strain curves of the particulate systems exhibit a knee, or a slope-discontinuity point, which is absent on the curves of glassy unfilled polymers. The point at which the slope discontinuity occurs (ϵ_D, σ_D) has the following characteristics:

σ_D does not depend on the bead concentration at least up to 30–35 per cent by volume.

σ_D is temperature dependent, decreasing linearly with temperature.

σ_D depends on the specific polymer being tested: so far values in the range of 1000 to 3500 psi at room temperature have been found.

ϵ_D is related to σ_D via the composite modulus E_c,

$$\sigma_D = E_c \epsilon_D. \tag{1}$$

The strain in the polymer ϵ_p is related to the composite strain ϵ_c by an equation which was formulated by Smith[4]:

$$\epsilon_c = \epsilon_p \, (1 - \phi^{1/3}) \tag{2}$$

and specifically for the discontinuity point

$$\epsilon_D = \epsilon'_p \, (1 - \phi^{1/3}) \tag{2a}$$

where ϵ'_p is the strain in the polymer at the discontinuity conditions. ϵ'_p values were calculated from experimental ϵ_D–ϕ data and found to be practically independent of the bead volume fraction.[5]

The slope change on the stress–strain curves is accompanied by stress whitening over the entire gage length of the sample.[5,6] This phenomenon and several other reasons, which will not be repeated here, have led to the conjecture of crazing being involved in the change of the slope.[3] That crazing plays an important role in causing the slope discontinuity has gained a significant support by finding a good agreement between calculated ϵ'_p values and literature data on critical strains.[7] These critical strains for the onset of crazing were measured directly on unfilled polymers by several researchers.

Equation (2a) can be expressed as follows by employing the corresponding Hooke laws:

$$\frac{\sigma_D}{E_c} = \frac{\sigma'_p}{E_p} \, (1 - \phi^{1/3}) \tag{3}$$

or

$$\frac{E_c}{E_p} = \frac{1}{(\sigma'_p/\sigma_D) \, (1 - \phi^{1/3})} \tag{3a}$$

where E_p is the polymer modulus and $\sigma'_p = E_p \epsilon'_p$; σ_D and σ'_p are both independent of ϕ, and therefore $\sigma'_p/\sigma_D = K$, where K is a constant (not a function of ϕ). Thus,

$$\frac{E_c}{E_p} = \frac{1}{K(1 - \phi^{1/3})}. \tag{4}$$

Glass beads, holes,[8] rubber or steel balls,[9,10] etc., act as stress concentrators, and a nonuniform stress field is obtained in a stressed sample. Maximum stress concentrations due to the presence of inclusions in a continuous matrix were calculated by Goodier.[11] Goodier's elastic analysis predicts the following numerical values for maximum stress concentration: for a rigid spherical inclusion, about 2; for a rigid cylindrical inclusion, about 1.5; and for a circular hole, about 3. Whether K represents a stress concentration factor which may be compared with Goodier's prediction is uncertain, but it is noteworthy that K values in the range of 1.5 to 1.65 were found[5] (Goodier's prediction, about 2). These K values were shown to be independent of ϕ and were calculated by using E_c–ϕ data at room temperature and eq. (4).

Equation (4) is a one-parameter equation which, in principle, can predict E_c/E_p ratios as function of ϕ for a given value of K. At filler concentrations of $\phi = 0.037$ and $\phi = 0.061$ and for $K = 1.5$ and $K = 1.65$, respectively, eq. (4) gives $E_c = E_p$, i.e., at lower corresponding concentrations, $E_c < E_p$, which is not valid. Experience has shown that eq. (4) works well in the range of $\phi =$

0.1 to 0.5 (this is the practical range of interest) where $K < 1.65$, and it is not applicable in the lower concentration range. No effort has been made to modify the equation in order to include the $\phi < 0.1$ range. Equation (4) is restricted to rigid spherical inclusions, while the Kerner equation is applicable to rigid, soft, or gas spherical inclusions.

In the present paper, new data on thermoplastic/glass bead systems are shown for vinyl chloride–propylene copolymer AIRCO 470 (VCP), poly-(methyl methacrylate) (PMMA), cellulose acetate butyrate (CAB), and high-impact polystyrene (HIPS). Sample preparation procedures and testing conditions were described previously.[3,5] Literature $E_c–\phi$ data on particulate thermosetting systems are compared with eq. (4). Preliminary results on rigid thermoplastic foams are also presented.

RESULTS AND DISCUSSION

Rubber-toughened glassy thermoplastics are unique in their high-impact resistance; examples are high-impact polystyrenes, ABS polymers, etc. The modulus of glassy polymers decreases on the addition of soft rubbery balls, whereas rigid glass beads result in higher moduli. Henry[12] has recently studied crazing characteristics of rubber-modified styrene–acrylonitrile (SAN) copolymer samples in ethanol. In his experiments, the rubber content was changed from 0% to 50%, and it is interesting to compare Henry's conclusions to those obtained for glass bead containing polymers:

The macroscopic critical strain increases with the rubber content (rigid glass beads result in an opposite effect).

The microscopic critical strain was calculated and found to be nearly constant over the range of rubber content studied (ϵ'_p was similarly found to be independent of ϕ for glass beads containing systems).

Henry concludes that the macroscopic critical stress "increases with rubber content, although only slightly". A closer inspection of his results shows that critical stresses of 983, 930, 1039 and 1099 psi were found for 0, 10, 23 and 50% rubber content respectively. Practically the critical stress can be regarded as constant over the very wide range of rubber content (this is similar to the non-dependency of σ_D on ϕ for polymer/glass bead systems).

σ_D is not a function of ϕ in the range of $\phi_1 < \phi < \phi_2$ where ϕ_1 will be about
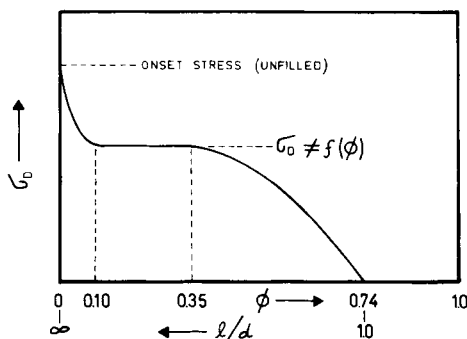

Fig. 1. The variation of σ_D with ϕ (or l/d), schematic representation.
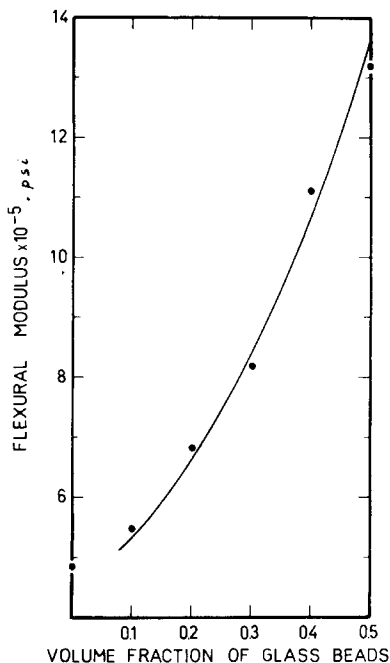
Fig. 2. Mallick and Broutman's data for epoxy/glass bead systems.[13] Line corresponds to eq. (4) with $K = 1.7$.

3–7% and $\phi_2 \simeq 0.35$. The zero-to-ϕ_1 range is assumed to exhibit a transition zone where the onset stress decreases from its maximum value for the un-filled polymer to its plateau. The transition zone idea is presently a theoretical expectation as no experimental work has been done in this low context of glass beads. The higher glass bead concentrations ($\phi_2 > 0.35$) represent a case where a single bead is no longer isolated from the effect of its neighbors. Lower external stresses are required in order to build local stresses (or strains) high enough to initiate crazing due to the interaction of stress fields around neighbor beads. σ_D therefore decreases at high concentrations of beads in agreement with results of Matsuo et al.[9] These authors used samples containing two balls and studied various onset criteria as a function of l/d, where l is the center spacing between two balls and d is the ball diameter. A critical value of $l/d = 1.45$ was found for the two rubber balls (onset stress plateau for $l/d > 1.45$) which corresponds to about $\phi = 0.18$. A schematic ex-pected curve is shown in Figure 1 which represents the variation of σ_D with ϕ.

Mallick and Broutman[13] have recently reported E_c–ϕ results in flexure on epoxy/glass bead systems. Their experimental data agree very well with eq. (4) for $K = 1.7$, as shown in Figure 2. Sahu and Broutman[14] reported pre-viously on other epoxy/glass bead composites and their E_c–ϕ data (not shown here) are best described by eq. (4) with $K = 1.65$. In the same publication,[14] results for polyester/glass bead systems are presented. These results are shown in Figure 3 to be in good agreement with eq. (4) for $K = 1.6$. It is gen-erally accepted that the surface state of glass beads, whether clean or treated, has no practical effect on the modulus which is a low-strain property. The "treated" modulus, however, is often found to be slightly higher than the
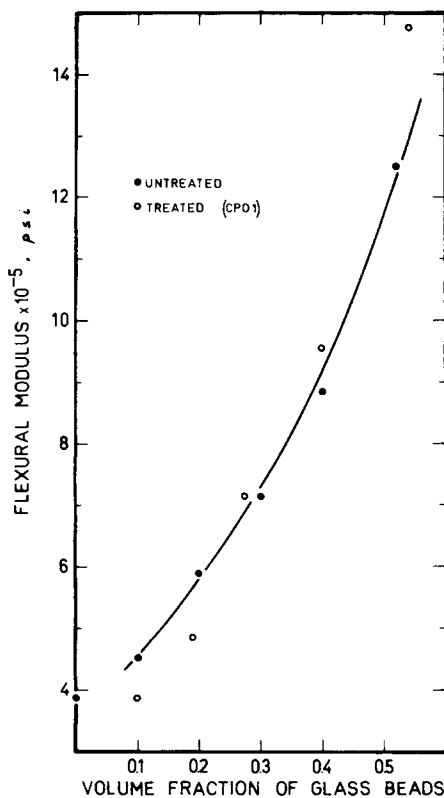
Fig. 3. Sahu and Broutman's data for polyester/glass bead systems.[14] Line corresponds to eq. (4) with $K = 1.6$.

"untreated" one (up to 5%), and this difference may increase further in the range of higher bead volume fractions (0.4 and more).

Jenness and Kline[15] have thoroughly studied the dynamic mechanical properties of epoxy composites containing glass microspheres, atomized aluminum, powdered silica, and other fillers. Aluminum and silica particles have about the same modulus as glass beads and are described as quasispherical in that they are neither flakes nor fibers. Experimental dynamic moduli ratios E'_c/E'_p (composite to polymer) are plotted versus ϕ for silica and aluminum in Figure 4. Assuming a similar behavior for silica and aluminum, the best line through all data points with eq. (4) is obtained for $K = 1.4$. Jenness and Kline have shown that Kerner's equation deviates strongly from their silica and aluminum results for $E_f/E_p = 20$ and even if E_f/E_p is equal to infinity (E_f and E_p are the moduli of filler and polymer, respectively).

The temperature effect on the modulus of particulate systems and on K was investigated by using Jenness and Kline's[15] $E'_c/E'_p-\phi$ data on epoxy/glass bead systems from $-173°C$ to $72°C$ (a range of $245°C$). By fitting eq. (4) to the data K values from 1.8 to 1.5 were found for $-173°$ to $72°C$, respectively. Wambach[16] also studied similar systems in the temperature range of $25°$ to $150°C$ (a range of $125°C$). His data and lines corresponding to eq. (4) are shown in Figure 5. Here again, K decreases from 1.6 to 1.45 when the temperature increases from $25°$ to $150°C$. The modulus of glass and other
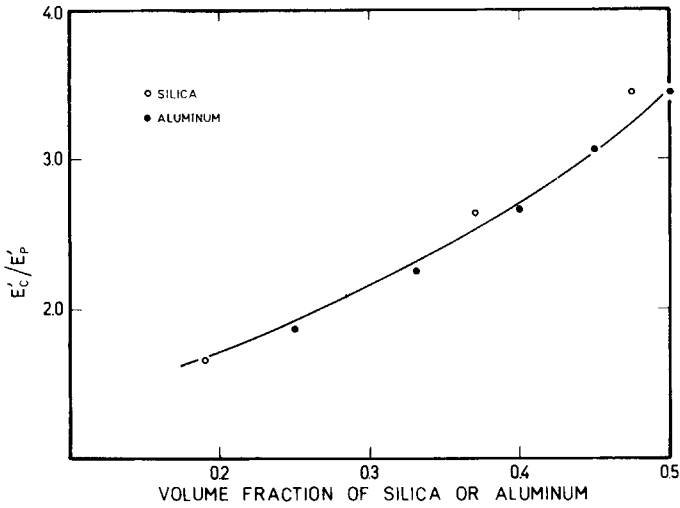
Fig. 4. Jenness and Kline's dynamic data for epoxy/silica and epoxy/aluminum systems.[15] Line corresponds to eq. (4) with $K = 1.4$.

inorganic rigid fillers is less affected by temperature than the modulus of polymers. The ratio E_f/E_p, therefore, increases with increasing temperature. The temperature effect is undoubtedly much more complicated, and it is not the E_f/E_p ratio that determines alone the ability to concentrate the stress.
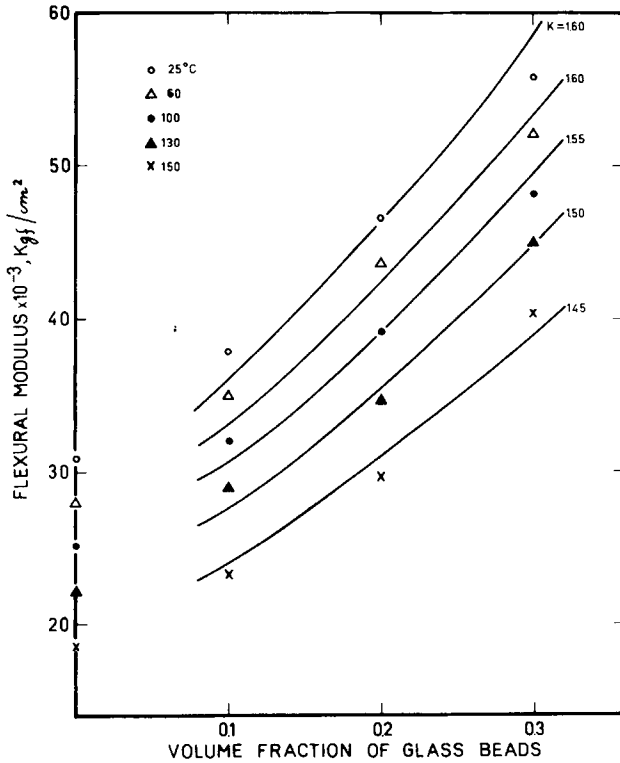

Fig. 5. Wambach's data for epoxy/glass bead systems at various temperatures.[16] Lines are drawn according to eq. (4).

TABLE I
Tensile Properties of Thermoplastic Polymers Containing Decoupled Glass Beads
(Ballotini CPO2)[a]

ϕ	E, kg/cm^2	σ_D, kg/cm^2	ϵ_D, %	ϵ'_p eq. (2a), %	K eq. (4)
Vinyl Chloride–Propylene Copolymer (VCP)					
0	25800	—	—	—	—
0.1	33000	155	0.47	0.88	1.46
0.2	44300	145	0.33	0.79	1.41
0.3	52600	149	0.28	0.86	1.48
0.4	67700	149	0.22	0.84	1.45
Poly(methyl Methacrylate) (PMMA)					
0	33500	—	—	—	—
0.1	39200	166	0.43	0.79	1.60
0.2	45900	158	0.35	0.83	1.76
0.3	59200	158	0.27	0.81	1.71
Cellulose Acetate Butyrate (CAB)					
0	13000	—	—	—	—
0.1	16300	98	0.60	1.12	1.49
0.2	21600	98	0.46	1.09	1.46
0.3	28300	97	0.36	1.03	1.40
High-Impact Polystyrene (HIPS)					
0	20000	—	—	—	—
0.1	22900	91	0.40	0.75	1.63
0.2	29900	85	0.29	0.69	1.61
0.3	39000	82	0.21	0.63	1.55

[a] $T = 24°C$; $\epsilon = 3.3 \times 10^{-2}$ min^{-1}.

The polymer has a thermal expansion coefficient which is greater than that of the filler particles. The polymer will therefore shrink around the particles as the system cools down and tensile forces will be developed. In addition, the poisson ratio, especially that of the polymer, will change with temperature. The applicability of eq. (4) shows that selection of a proper value of K will practically account for most of the changes taking place.

The general applicability of eq. (4) to describe the modulus of particulate systems containing rigid spherical fillers ($\phi = 0.1$ to 0.5) in thermoplastic or thermosetting matrices has been confirmed. More literature on E_c–ϕ data which is not discussed here can be found elsewhere.[6,17,18]

The slope discontinuity data (ϵ_D, σ_D) and E_p (E_c is a dependent variable, $E_c = \sigma_D/\epsilon_D$) can be employed to calculate the critical strain ϵ'_p from eq. (2a), K from eq. (4), and σ'_p since $\sigma'_p = K\sigma_D$. A summary of slope-discontinuity results as a function of ϕ for VCP, PMMA, CAB, and HIPS is given in Table I. The nondependence of σ_D on ϕ and similarly the nondependence of calculated ϵ'_p and K values on ϕ are in agreement with previous results for other polymers.[2,3,5] Table II summarizes results for the polymers studied in this work together with other polymers reported previously.[5] A comparison between ϵ'_p (calculated critical strain) and ϵ_p (direct determination of critical strain in the unfilled polymer) has been made, and good agreement for PVC, PS and PPO was pointed out. A summary of ϵ_p values is given in Kambour's excellent review on crazing in thermoplastics.[7] Kambour claims that the

TABLE II
Summary of Average Tensile Results

Polymer	σ_D, psi	$E_p \times 10^{-5}$, psi	ϵ'_p eq. (2a), %	ϵ_p litera- ture,[e] %	K eq. (4)	$\sigma'_p = K\sigma_D$, psi
PVC	1880	4.70	0.63	0.75[19]	1.53	2900
PS	1540	3.53	0.72	0.75[20]	1.65	2540
SAN[a]	2390	4.70	0.81	0.49[7]	1.59	3800
ABS	1750	2.40	1.10	—	1.50	2620
PPO[b]	3300	2.95	1.67	1.50[21]	1.56	5150
VCP	2200	3.80	0.84	—	1.45	3190
PMMA	2360	4.90	0.81	0.8; 1.3[7]	1.69	3990
CAB	1430	1.92	1.08	—	1.45	2070
HIPS	1260	2.94	0.69	—	1.60	2020
PC[c]	—	3.40[7]	—	1.8[7]	—	—
PSF[d]	—	3.60[7]	—	2.5[24]	—	—

[a] Styrene–acrylonitrile copolymer (SAN).
[b] Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO).
[c] Polycarbonate (PC).
[d] Polysulfone (PSF).
[e] Direct experimental literature data of critical strains for onset of crazing in unfilled polymers.

critical strain for polystyrene in air was originally set by Maxwell and Rahm[20] at 0.75% and that the value obtained by Ziegler and Brown,[22] 0.35%, is the currently accepted one. A value of about 1% can be seen in Figure 7 of Matsuo et al.[9] The author has recently calculated ϵ'_p values of 0.58% (new unpublished data). The lower ϵ'_p values found (compared to 0.72% , see Table II) are due to a higher modulus (around 4.4×10^5 compared to 3.53×10^5 psi, see Table II) while σ_D was still close to 1540 psi. A critical strain of 0.49% is reported by Kambour[7] for SAN copolymer, but this result cannot be compared with $\epsilon'_p = 0.81\%$ (Table II) since it is not known whether the two copolymers are similar. Kambour gives two values of the onset strain for crazing in PMMA: 0.8% (a private communication of W. F. Bartoe to Kambour 1969, and also Menges and Schmidt[23]); and 1.3% (R. P. Kambour, unpublished observations). Needless to say, the calculated strain of 0.81% (Table II) agrees very well with the results of Bartoe, and Menges and Schmidt. Table II also contains literature results for the critical strain of polycarbonate and polysulfone. Attempts to mold polycarbonate/glass bead samples have not been successful while polysulfone/bead samples can be prepared with no special difficulty. Results on polysulfone will be published at a later date; preliminary experiments have shown that polysulfone has ϵ'_p and σ'_p values higher than those reported for the first nine polymers in Table II, at least in qualitative agreement with Kambour.[24]

It has been emphasized that the slope-discontinuity method is valid for the "no adhesion" case, i.e., clean beads with no coupling agents, are used. Coupling agents are often used in practice for better stress transfer to the rigid inclusions and for greater resistance to environmental conditions. Low-strain properties of particulate systems, such as the modulus, are only slightly affected by the presence of coupling agents while higher yield strength and lower fracture toughness are a result of improved adhesion.[18] σ_D, being a low-strain property, was reported to increase when coupling agents are

TABLE III
Comparison of Rigid Foams with Glass Bead Composites

ϕ	System	$E_c \times 10^{-5}$, psi	ϵ_D, %	σ_D, psi
0	PS	4.50	. . .	. . .
0.172	PS/beads	6.66	0.23	1540
0.172	PS/air	3.04 (3.10)*	0.44	1420
0	PVC	4.50	. . .	. . .
0.217	PVC/beads	7.38	0.25	1880
0.217	PVC/air	2.12 (2.82)[a]	0.87	1850

[a]Predicted values according to Kerner.

used.[3,5] An appropriate criterion for coupling efficiency based on this phenomenon has not been worked out yet. In coupled systems, the knee on the stress–strain curve is more difficult to locate, and sometimes the knee does not show up at all (see Table 1 in ref. 3). A comparison of σ_D values for coupled and corresponding decoupled systems has given the following results: ABS, 2330 and 1750 psi (ratio = 1.33); PVC, 2960 and 1870 psi (ratio = 1.58); PMMA, 2790 and 2350 psi (ratio = 1.19); and CAB, 1430 and 1430 psi, respectively (ratio = 1.0). It is clearly seen that σ_D (coupled)/σ_D (decoupled) varies significantly, and that apparently a better coupling efficiency was achieved in the PVC systems. The latter system was further studied to check whether the incorporation of additives will change σ_D. A processing aid, Acryloid K-120N (Rohm and Haas), has been found to affect only slightly the general mechanical properties of PVC. This additive, however, reduced σ_D of the coupled system in respect to its concentration. Recalling that σ_D of the decoupled system was 1870 psi, σ_D for the coupled PVC system was 2960 (ratio = 1.58), 2660 (ratio = 1.42), and 2230 psi (ratio = 1.19) for 0, 5% and 10% of the processing aid, respectively.

The function of glass beads has been suggested to be that of stress concentrators. Imperfections in general, rigid and soft inclusions or holes, will concentrate the stress and result in enhanced crazing. In the case of glass bead composites, the appearance of the knee had to be discussed in terms of crazing, dewetting, or both.[3] If the glass beads are replaced by holes and a knee is still found, dewetting is obviously ruled out and the idea of crazing initiation at the slope-discontinuity point is further supported. Two preliminary experiments were carried out with PS/NaCl and PVC/NaCl samples. The samples which contained 30% NaCl by weight (17.2% and 21.7% by volume for the PS and PVC, respectively) were soaked in water for long periods of time until the salt was leached out completely. After drying, the samples, which were actually rigid foams, were tested in tension and a knee was found on the stress–strain curves. The results are summarized in Table III and compared with glass bead composites containing the same volume fraction of beads. σ_D is shown to be similar for the air and glass bead composites. A direct comparison, however, is undesirable since the salt particles were not spherical and the foams produced are essentially open cell foams.[25] The mechanical response of open or closed cell foams is undoubtedly different. For comparison, calculated moduli according to the Kerner equation are also shown. In view of the promising results, these systems will be further studied in the future.

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