Particulate-Filled Glassy Polymers

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Synopsis

Glass beads, NaCl crystals, or other imperfections act as stress concentrators in glassy polymers causing early crazing upon stressing. Stress–strain curves of glassy thermoplastic polymers filled with uncoupled glass beads or NaCl crystals exhibit a knee, or a slope-discontinuity point. The characteristics of the slope change, related to crazing, are studied in the present work. Foams were produced from the polymer/salt samples by soaking them in water resulting in complete leaching of the salt. This preparation procedure gives open-cell foams and there are strong indications that these polymeric foams have a highly cracked structure formed during the extraction step.

INTRODUCTION

The stress–strain curves of glassy thermoplastic polymers filled with uncoupled glass beads exhibit a knee, or a slope-discontinuity point, which is absent on the curves of the glassy unfilled polymers.[1,2] It has been shown that crazing is involved in the change of the slope.[2–4] The critical strain and stress characteristic to crazing in the unfilled polymer can be calculated from the slope-discontinuity data $D(\epsilon_D, \sigma_D)$ by using a simple quantitative model.[2,5,6] The stress at the discontinuity σ_D is independent of the bead concentration ϕ for volume fractions up to about 0.35. σ_D varies with the specific polymer tested and it decreases linearly with increasing temperature.

Glass beads, holes,[7] rubber or steel balls,[8,9] etc., act as stress concentrators and a nonuniform stress field is obtained in a stressed sample. Imperfections in general will concentrate the stress and result in enhanced crazing. Sodium chloride crystals can thus be used as stress concentrators by incorporating them into glassy polymers. Foams can be produced from the polymer/salt samples by soaking in water and leaching out the salt.

The purpose of the present work is to study glassy polymer/NaCl composites and compare them with glassy polymer/glass bead composites particularly in regard to their slope-discontinuity behavior. Additionally, it is desired to obtain some preliminary data on glassy polymeric foams produced by salt extraction.

EXPERIMENTAL

NaCl (ground 105–210 μm) and glass bead (Ballotini CP02, decoupled, 4–44 μm) filled composites were prepared with polymethyl methacrylate (PMMA, Diakon MH-253, ICI), polysulfone (PSF, Bakelite P-1700, Union Carbide), polystyrene (PS, Lustrex HF-55, Monsanto), and styrene-acrylonitrile copolymer (SAN, Kostil, Montecatini, Edison). The procedure for preparing compression molded specimens is described elsewhere.[3] Salt content was determined by ashing small pieces. The salt dispersion was very uniform represented by standard deviations of about ±0.5% by volume.

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Tensile specimens containing NaCl were soaked in water for periods of several months. All samples were initially soaked in water at 50°C during three months. The water temperature was then gradually incrased to 80°C for additional three months. The PSF samples were soaked in boiling water during the three months following the three months extraction in water at 50°C. These treatments resulted in essentially salt-free samples.

Tensile tests were performed using an Instron universal tester at a crosshead speed of 0.2 cm/min.

RESULTS AND DISCUSSION

Composite materials consisting of NaCl crystals embedded in a rubbery polyurethane matrix were studied by Schwarzl et al.[10] Nielsen and Lee[11] studied the dynamic mechanical properties of polystyrene filled with ground rocksalt and polystyrene foams produced by extracting the salt with water. Polyurethane foams were prepared by Smith[12] by salt extraction and Thomas[13] described this method as suitable for preparation of open-cell flexible materials. The fabrication of open-cell polyethylene foams by NaCl extraction with water was described by Fossey and Smith.[14] A preliminary quantitative insight into the leaching process was made by Narkis and Narkis.[15]

Sodium chloride has a modulus about 10 times that of glassy polymers while the modulus of glass beads is about 25 times greater. Surprisingly low modulus values were found for PMMA/NaCl composites, as shown in Table I. Nielsen[11] has reported a similar conclusion particularly for the high salt concentration range, attributing this result to the presence of air cavities in his samples as evidenced by electron microscopy studies. Figure 1 shows a fractured surface of PMMA/NaCl composite. The salt particle consists of many irregular rectangular small crystals packed very inefficiently. Such particles introduce numerous cavities into the structure resulting in a composite having a pseudofoam structure. The critical cavities are those existing between the particle contour and the surrounding matrix. This description, based on Figure 1, and the very poor adhesion between contact surfaces of the salt and the polymer explains the too low values of the modulus of PMMA/NaCl composites.

Stress–strain curves of PMMA/NaCl composites are exhibited in Figure 2 showing the presence of the knee (slope discontinuity). The modulus is shown

TABLE I
Comparison of PMMA/Glass Bead Composites with PMMA/NaCl Composites at Various Filler Concentrations

PMMA/glass beads (4–44 μm)				PMMA/NaCl (105–210 μm)			
ϕ	E (Kg/cm^2)	ϵ_D (%)	σ_D[a] (Kg/cm^2)	ϕ	E (Kg/cm^2)	ϵ_D (%)	σ_D[b] (Kg/cm^2)
0.0	31,800	—	—	0.0	31,800	—	—
0.103	36,200	0.61	219	0.055	32,000	0.35	110
0.184	46,900	0.54	250	0.114	32,600	0.30	97
0.222	52,300	0.44	231	0.223	36,800	0.28	107
0.262	53,600	0.44	239	0.331	40,900	0.23	97
				0.443	47,500	0.23	108

[a] $(\sigma_D)_{av} = 235$.
[b] $(\sigma_D)_{av} = 104$.

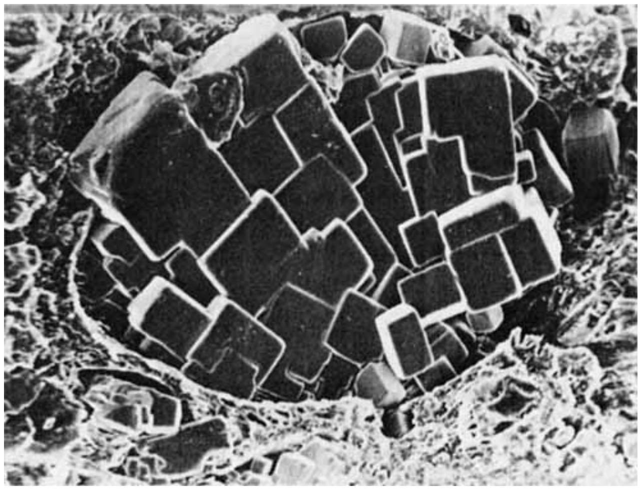

Fig. 1. Fractured surface of PMMA/NaCl composite, 500×.

to increase with salt content while the stress at break decreases in agreement with previous results obtained on glass bead filled glassy polymers.[1,3] The slope-discontinuity characteristics read from Figure 2 are summarized in Table I and compared with glass bead filled PMMA. It is important to note that σ_D of the PMMA/NaCl composites is roughly constant (independent of ϕ, in agreement with numerous previous results on glass bead filled thermoplastics) however its

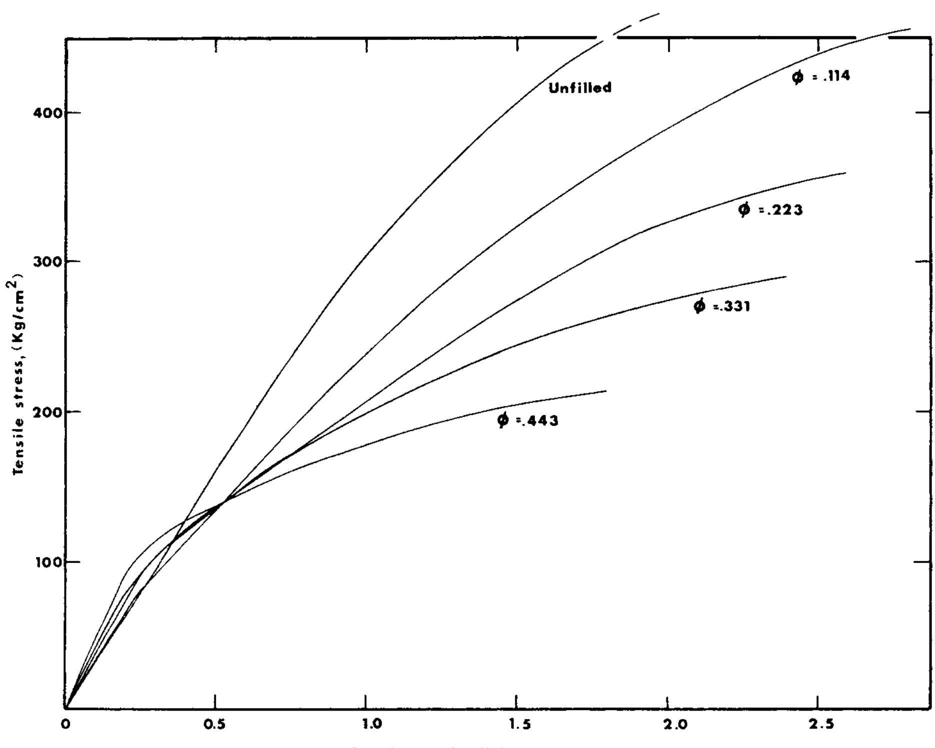

Fig. 2. Stress–strain curves of PMMA/NaCl composites.

average value is appreciably lower than that of the PMMA/glass bead composites (104 compared to 235 Kg/cm^2). One can assume[2,6] that factors causing enhanced stress concentrations will yield lower σ_D values. In the present case (PMMA/NaCl vs PMMA/glass bead composites) the salt crystal has a lower modulus, it has sharp edges and corners and its combination with PMMA gives unexpected low modulus values (probably due to introduction of air cavities). All these factors act in the same direction, namely, causing higher stress concentrations in the samples and resulting in the low σ_D value of 104 Kg/cm^2. The slope-discontinuity data of glass bead filled composites can be processed[2] to give critical strain values for initiation of crazing in the polymer. Such a procedure is lacking for nonspherical rigid inclusions such as the NaCl particles.

Having confirmed the nondependency of σ_D on ϕ for PMMA/NaCl composites (a well-known experimental fact for many glassy polymer/glass bead composites) several other polymers were tested as shown in Table II. This table compares data of NaCl with glass bead composites for four polymers at about the same filler volume content. Table II shows that σ_D of the four NaCl filled polymers is significantly lower than σ_D values of the same polymers filled with glass beads. It is also interesting to note that these four polymers filled with NaCl differ only slightly in their σ_D values (85–109 Kg/cm^2) while they differ appreciably when filled with glass beads (107–268 Kg/cm^2). The table also shows higher moduli ratios E_c/E_p (composite to polymer) for the glass bead composites in comparison with the corresponding NaCl composites.

Salt-filled and void-filled samples were produced in the present work as described earlier. On addition of rigid particles into the polymer the modulus increases while addition of voids results in an opposite effect. This behavior is exhibited in Figure 3 together with theoretical predictions according to the Kerner equation.[16] The experimental modulus values of the PMMA foams are too low in comparison with the theoretical line. It is important to emphasize that the system being examined is essentially an open-cell foam containing nonspherical voids while the theoretical model assumes a spherical closed-cell structure. Nielsen[11] has also found lower modulus values for his polystyrene foams prepared by NaCl extraction. Nielsen suggests that these low modulus values might be the result of cracks formed in the polymer due to high osmotic pressures probably developed during the water extraction step. Although direct evidence for the presence of cracks in the void containing polymer has not been

TABLE II

Comparison of NaCl with Glass Bead Composites at About the Same Volume Content of Filler

	Polymer/NaCl (105–210 μm)					Polymer/glass beads (4–44 μm)				
Polymer	ϕ	E (Kg/cm^2)	ϵ_D (%)	σ_D (Kg/cm^2)	E_c/E_p	ϕ	E (Kg/cm^2)	ϵ_D (%)	σ_D (Kg/cm^2)	E_c/E_p
PMMA	0.0	31,800	···	···	1.0	0.0	31,800	···	···	1.0
PMMA	0.223	36,800	0.27	107	1.16	0.222	52,300	0.44	231	1.64
PSF	0.0	24,500	···	···	1.0	0.0	24,500	···	···	1.0
PSF	0.207	32,800	0.32	105	1.34	0.203	40,000	0.67	268	1.63
PS	0.0	27,000	···	···	1.0	0.0	24,700[a]	···	···	1.0
PS	0.214	40,100	0.22	85	1.49	0.21	37,500	0.29	107	1.52
SAN	0.0	33,900	···	···	1.0	0.0	32,900[b]	···	···	1.0
SAN	0.221	44,000	0.25	109	1.30	0.21	46,100	0.37	167	1.40

[a] Data on polystyrene/glass bead composites taken from reference 3.

[b] Data on SAN/glass bead composites taken from reference 1.

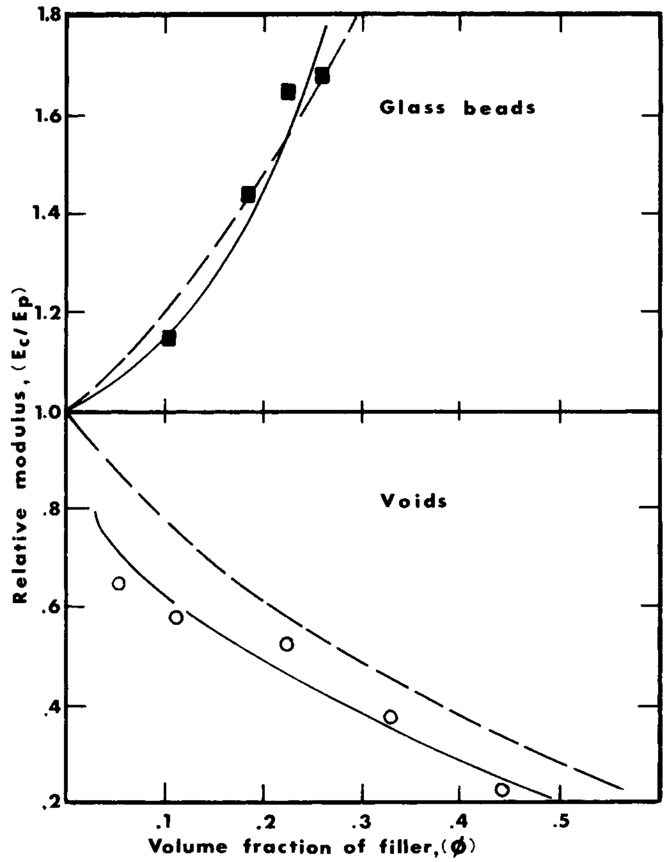

Fig. 3. Dependence of relative modulus on volume fraction of filler for PMMA/glass bead and PMMA/void composites. - - -, Kerner equation (ref. 16).

found it is well established[12–14] that open-cell structures are obtained by leaching out NaCl from polymers with water.

On addition of rigid particles to glassy polymers their tensile yield stress is well known to decrease. This decrease can be reduced by using appropriate coupling agents. Nicolais and Narkis[1] studied glass bead filled glassy polymers and proposed an equation relating yield stress to volume content of the spherical rigid filler. This equation has since been confirmed for many systems consisting of clean (nontreated) glass beads. Experimental stress at break data for PMMA composites are shown in Figure 4. It is interesting to note from the figure that PMMA filled with glass beads or NaCl has similar stress at break values. The data presented in Figure 4 for the PMMA foams is of great importance. It is seen clearly that PMMA foam containing 5% voids only has a stress at break of 155 compared to 600 Kg/cm^2 for the virgin polymer. This dramatic reduction in strength caused by "adding" 5% voids into the structure can be explained only on the basis of a cracked structure. Such a cracked structure is formed during the long extraction step by large internal forces developed by the high osmotic pressures. Figure 4 also shows similar strength values for the 5% to 45% voids in the PMMA foams, pointing out that the structure is severely cracked already in the 5% sample, thus, adding more voids is practically insignificant.

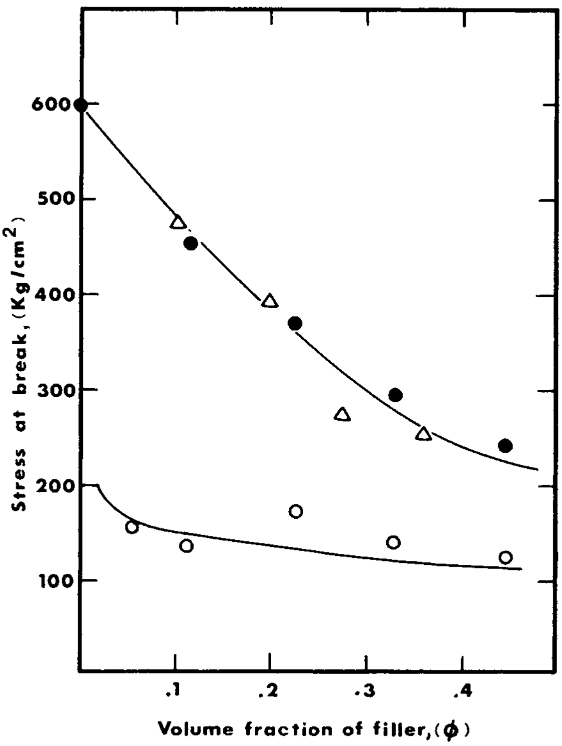

Fig. 4. Stress at break vs volume fraction of filler: ●, PMMA/NaCl; △, PMMA/glass beads; ○, PMMA/voids.

Some additional information is gained from the data summarized in Table III. Four polymeric foams obtained by salt extraction with water and having about the same void content are compared. The experimental moduli values are always lower than the corresponding theoretical prediction (Kerner equation) with the exception of polystyrene (reason unknown). The experimental moduli ratios of PMMA, PSF, and SAN are in very good agreement among themselves and are about 10% lower than the theoretical predictions.

TABLE III
Modulus Data on Four Polymeric Foams Produced by Salt Extraction

Polymer	ϕ voids	E (Kg/cm^2)	E_c/E_p expt.	E_c/E_p Kerner
PMMA	0.0	31,800	1.0	1.0
PMMA	0.223	16,700	0.53	0.59
PSF	0.0	24,500	1.0	1.0
PSF	0.207	13,400	0.55	0.62
PS	0.0	27,000	1.0	1.0
PS	0.214	18,600	0.69	0.61
SAN	0.0	33,900	1.0	1.0
SAN	0.221	17,900	0.53	0.60

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