

Polyvinylcarbazole Foams. II. Properties

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Synopsis

The uniformity, heat and solvent resistance, and thermal conductivity of foamed polyvinylcarbazole have been examined. Compressive and tensile properties, dielectric constant, and loss factor have been determined between ambient temperature and the softening range. Some features of the properties are attributed to the degree of orientation of the polymer molecules, which is thought to be the greater, the lower the density of the foam. The good high temperature stability is attributed to sterically impeded reversibility of the polymerization of vinylcarbazole.

INTRODUCTION

Foamed polyvinylcarbazole panels and other shapes in the density range 0.05–0.2 g./cc. have been molded from polymer granules prepared by the aqueous dispersion polymerization of vinylcarbazole.¹ Various chemical and physical properties of these foams have been studied both at ambient and at elevated temperature on panels of foamed polyvinylcarbazole or on samples cut from these. These panels, which are beige or buff in color, consist of a skin of high density and a core of much lower density. The polymer in the skin is continuous, and the thickness of the skin appears to be greatest at the point of fusion between granules.

The interior structure of granule-based panels is a network of strands and pores.¹ The strands are not completely random, but tend to be directed perpendicular to the main plane. Uniformity is generally better the lower the density. The bead-based panels¹ were molded at a density only of 0.1 g./cc. with a view to improve uniformity.

Polyvinylcarbazole has a softening range known to be remarkably high for a vinyl polymer, the Martens number of the bulk polymer having been quoted as 150°C.,² its Vicat softening point as 190°C.,³ its heat distortion temperature as 100–150°C.,³ its flow temperature as 270°C.,³ and the highest continuous temperature to which it may be exposed as 120°C.²

The high softening range would be of little advantage unless the polymer were of adequate thermal stability. This has therefore been examined on the foam. Other properties have been determined in most cases over a range of temperatures up to the softening point of the foam. The dielectric

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TABLE I
Homogeneity of Density of Granule-Based and Bead-Based Foamed Polyvinylcarbazole Panels

Panel type	Panel No.	Panel nominal density, g./cc.	Samples tested		Average, g./cc.	Density of sample ^s			
			Un-stoved	Stoved		Std. deviation		Max. deviation	
						g./cc.	%	g./cc.	%
Granule-based panels ^a	109	0.073	3	3	0.055	0.0037	6.7	0.006	10.9
	165	0.103	3	4	0.101	0.0305	30.1	0.045	44.6
	185	0.179	3	3	0.203	0.056	27.6	0.102	50.2
Bead-based panels ^b	329	0.102		20	0.100	0.0084	8.4	0.014	14
	328	0.103		20	0.099	0.0072	7.2	0.016	16

^a Nominal size of granule-based panels: 12 × 12 × 1 in.

^b Nominal size of bead-based panels: 6 × 6 × 1 in.

constant and the loss factor ($\tan \delta$) at radar frequencies have been determined over a temperature range also on foam which had been subjected to various heat treatments.

The foamed polyvinylcarbazole of all the densities proved remarkably easy to machine. It was easily milled, hand sawn, and drilled, and could even be sanded to the precise finish required for the determination of the compressive properties. Sheets of only 2 mm. thickness were mechanically stable. The foam could be ground to a powder without cooling.

MATERIALS

Bead-based and granule-based polyvinylcarbazole foam¹ dried to constant weight at 80°C. was used, unless stated otherwise.

Aircraft fluids used were: gasoline fuel, 100/130 grade; kerosene fuel, Shell Turbine Fuel 650; mineral oil, piston engine lubricating oil, Aero-shell oil 100; turbine engine oil, Aeroshell turbine oil No. 3; cleaning fluid, Aeroshell fluid No. 14; deicing fluid, Aeroshell compound No. 7; ester-type lubricating oil, Aeroshell oil 750; hydraulic oil, Aeroshell fluid No. 4 (Shell Mex and B.P. Ltd.).

RESULTS

Uniformity

This has been examined on granule-base (12 × 12 × 1 in.) and bead-based (6 × 6 × 1 in.) panels (Table I). The granule-based panels were cut into two slabs. The smaller, being a quarter of the whole panel, was cut into 20 pieces, while the larger was subjected to heat treatment (Table II) before being cut into 50 pieces. The weight loss during the heat treat-

TABLE IIA
Weight Loss on Heat-Stoving up to 170°C. of Granule-Based
Foamed Polyvinylcarbazole Panels^a

Original bulk density, g./cc.	Original weight, g.	Weight after stoving, g.	Over all weight loss, %	Weight loss, %		
				After 45 hr. at 150°C.	After addtl. 66 hr. at 150°C.	After addtl. 97 hr. at 170°C.
0.065-0.071	125.5	120.5	4.0	2.4	0.8	0.9
	128.0	122.5	4.3	2.7	0.8	0.8
	118.0	114.5	3.0	1.7	0.4	0.9
0.094-0.104	177.5	169.0	4.8	2.3	1.1	1.1
	176.0	166.5	5.4	2.6	1.1	1.7
	187.5	177.5	5.3	2.4	1.1	1.6
0.175-0.182	326.5	307.0	6.0	2.6	1.3	1.7
	316.5	298.0	5.7	2.4	1.2	1.8
	312.5	294.5	5.6	2.2	1.2	2.0

^a All panels previously dried to constant weight at 80°C.

TABLE IIB
Weight Loss on Heat-Stoving up to 170°C. of Bead-Based
Foamed Polyvinylcarbazole Panels*

Original bulk density, g./cc.	Original weight, g.	Weight after stoving, g.	Over all, weight loss, %	Weight loss, %		
				After 24 hr. at 130°C.	After addtl. 24 hr. at 150°C.	After addtl. 30 hr. at 170°C.
0.100-0.107	60.0	58.5	2.2	1.67	0.83	—
	60.5	59.5	1.7	0.83	0.87	—
	60.5	58.0	4.1	2.48	0.81	0.81
	59.0	57.0	3.4	1.70	1.70	—
	63.0	60.5	4.0	2.38	0.81	0.81
	61.0	59.0	3.3	1.64	0.83	0.83

* All panels previously dried to constant weight of 80°C.

ment was relatively small at 3-6%, and results were obtained both on unstoved and stoved samples. The bead-based panels were stoved whole and cut into 20 pieces, and the densities of all these were determined.

Heat Stability

The foamed panels of polyvinylcarbazole were normally oven-dried to constant weight at 80°C. The effect of further heating in an oven to temperatures up to 170°C. upon granule-based (12 × 12 × 1 in.) and bead-based (6 × 6 × 1 in.) panels was examined, the temperature being increased by stages as shown. The bead-based panels were stoved whole, but a quarter section was cut from the granule-based panels which was left unstoved, while the larger portion was stoved whole. The samples to test uniformity (Table I) were cut from these panels. After this treatment the panels had darkened somewhat, but apart from this, little distortion or other deterioration was noted.

The effect of a still higher temperature applied under reduced pressure (2-3 mm. Hg) upon granule-based panels was found to be small (Table III). Samples were cut and heated at 160°C. at this pressure until there was no further loss of weight. On raising the temperature to 220-230°C. there was a further small, but declining, loss in weight. The volatiles were condensed. They included dioxane, impure tetramethylsuccinodinitrile, m.p. 145-60°C., and carbazole, m.p. 244-247°C. While being heated at 220-230°C. the foam contracted and became somewhat distorted.

When granule-based foam, which had been heated under reduced pressure (2-3 mm. Hg) at 160°C. (41 hr.) and at 200-220°C. (2 hr.), was heated also at 250-260°C. (20 hr.), and at 320-330°C. (6 hr.) there was little further loss of weight (1.03%), while a mixture of carbazole and polyvinylcarbazole (assumed to be formed by the thermal polymerization of depolymerized polyvinylcarbazole) was isolated from just beyond the hot zone.

The Vicat softening point of foamed polyvinylcarbazole granules (relative viscosity 2.69) was found to be 200°C., compared with 173.5°C. for bulk polyvinylcarbazole of higher molecular weight (relative viscosity 4.62).

TABLE III
Weight Losses on Heat-Stoving up to 230°C. of Granule-Based
Foamed Polyvinylcarbazole^a

	Sample 1	Sample 2
Initial Sample Weight, g.	28.8195	31.6784
Weight losses after heating, %		
160°C., 19 hr.	4.5	4.8
160°C., 85 hr.	4.35	4.75
Additional weight losses, %		
85 hr., 160°C.		
Additional 5 hr., 220-230°C.	0.32	0.49
Additional 21 hr., 220-230°C.	0.51	0.51

^a Samples were cut from a 12 × 12 × 1 in. panel of bulk density 0.067 g./cc.

TABLE IV
Dimensional Stability and Weight Loss of Granule-Based
Foamed Polyvinylcarbazole

Density, g./cc.	Temp., °C.	Time, hr.	Distortion, %	Weight loss, %
0.05-0.07	180	4	<1	2.5
		24	<1	2.2
	180	240	<1	2.9
		190	3	—
	200	1	<1	2.3
		2	<1	2.5
		4	<1	3.1
		1	>3	3.1
0.10-0.12	180	4	<1	2.6
		24	<1	3.2
	180	240	1	3.3
		190	3	—
	200	1	>3	2.7
		2	>3	3.2
		3	>3	3.4
		1	<1	3.1
0.16-0.18	160	24	<1	3.0
		288	<1	3.6
	170	24	1	4.06
		288	1	4.5
	180	24	5	4.8
		1	>5	3.2
	190	2	>5	3.8

TABLE V
Selected Compressive Properties and Densities of Granule-Based
Foamed Polyvinylcarbazole

Code no.	Temp., °C.	Density, g./cc.	Max. compressive modulus, psi	Load, psi
At 20°C.				
93/4	—	0.201	8128	190
93/2	—	0.201	7770	173.5
110/4	—	0.137	4004	99.1
104/2	—	0.095	3587	74.6
105/3	—	0.098	2635	67.5
105/2	—	0.108	3537	83.1
133/6	—	0.060	712	14.1
133/4	—	0.065	1162	11.5
133/1	—	0.055	841	13.7
At 60°C.				
110/8	60-70	0.151	4214	99.1
110/5	58	0.150	5360	111.4
106/1	61	0.173	4678	125.6
104/9	—	0.106	3411	68.9
104/7	—	0.095	2908	81.4
108/5	—	0.119	3302	64.7
133/5	—	0.053	685	18.9
129/7	—	0.054	626	17.0
115/8	—	0.059	811	18.4

(continued)

The dimensional stability was examined on 1 in. cubes cut from granule-based foam panels ($6 \times 6 \times 1$ in.), which had been dried to constant weight at 80°C., distortion being shown as per cent change in the dimension in which the greatest change was observed (Table IV). The temperature was limited by the softening range of the material, which was the higher the lower the density of the foam.

Compressive Data

These were determined on granule-based foam of each of the three density ranges at temperatures between 20°C. and a maximum temperature which depended on the density of the foam. A Denison testing machine, Type T42V, sited in an air-conditioned room held at 20°C. was adapted by fitting it with electrically heated approximately 5 in. square plates controlled by a Variac transformer. For determinations at the higher temperatures a copper-constantan thermocouple was inserted centrally through one of the sides of the sample, which was surrounded with glass wool insulant. Compressive data only were obtained in the dimension perpendicular to the plane of the panels.

The 1-in. sides of $6 \times 6 \times 1$ in. panels were sanded to remove the outer

TABLE V (continued)

Code no.	Temp., °C.	Density, g./cc.	Max. compressive modulus, psi	Load, psi
At 100°C.				
107/8	98-100	0.160	3965	68.2
107/3	100-102	0.168	3350	70
107/1	100-102	0.149	3397	83.6
108/2	100-102	0.111	2414	51.4
111/3	100/101	0.090	2414	21.0
129/9	110	0.060	772	15.5
115/6	106	0.057	613	8.9
116/2	102	0.053	437	11.0
At 140°C.				
110/3	142	0.146	2286	44.1
110/9	140-143	0.152	2623	50.1
93/1	137-142	0.203	4040	71.5
104/1	137-140	0.097	2319	48.7
111/4	136-140	0.126	2246	64.0
108/3	138-142	0.109	1581	14.7
115/4	144-145	0.058	669	9.9
116/6	142-140	0.052	374	9.2
115/2	138-144	0.059	843	10.2
At 160°C.				
106/2	158-160	0.179	3046	6.64
107/6	156-158	0.168	2204	8.4
106/6	158	0.172	1895	2.71
111/2	156-158	0.104	960	25.6
104/4	157-160	0.103	1206	39.2
104/5	158-162	0.114	1551	20.0
At 180°C.				
129/3	190	0.059	413	6.65
115/3	176-174	0.058	481	13.6
116/7	179-182	0.044	200	7.6

surface, and the panels were then sawed into nine approximately $2 \times 2 \times 1$ in. samples, from which test samples were selected by a random procedure. The selected samples were sanded on the 1-in. thick surfaces until square, and their main surfaces were sanded by hand until parallel to within 0.001 in. They were then measured and weighed. Strain was measured by two strain gauges sited at the movable lower anvil surface near opposite corners of the sample. For measurements at 60-140°C. samples were preheated in an oven for about 16 hr.; for the higher temperatures preheating periods were 30-60 min.

In calculating the results the original area and thickness of the sample were used throughout. The sample thickness decreased generally by less

than 5% before the material began to flow, and measurements were often taken to a decrease in thickness of 10%, while at the same time the area increased probably by a smaller amount, although no data were obtained, deformation being irregular under the largest loads.

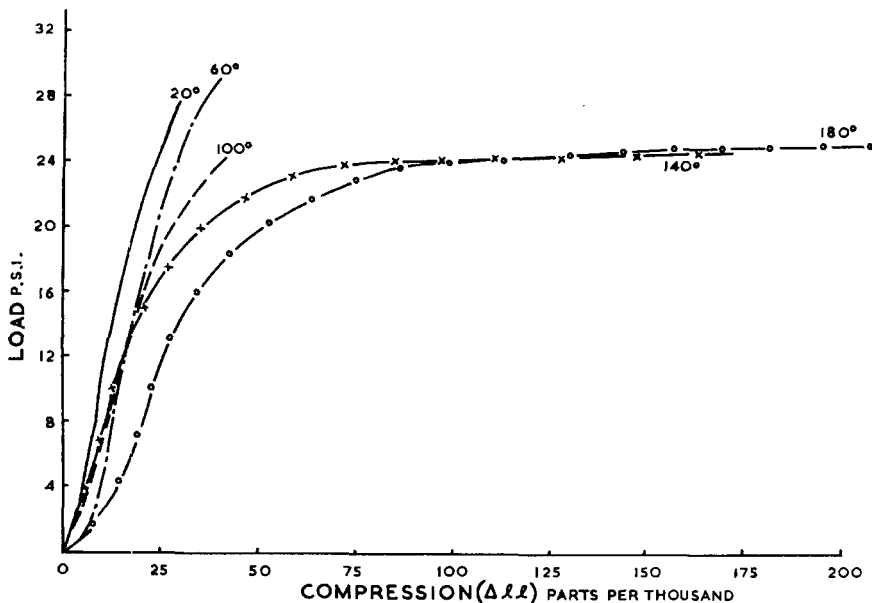


Fig. 1. Compressive strength of polyvinylcarbazole foam, density 0.05-0.07 g./cc.

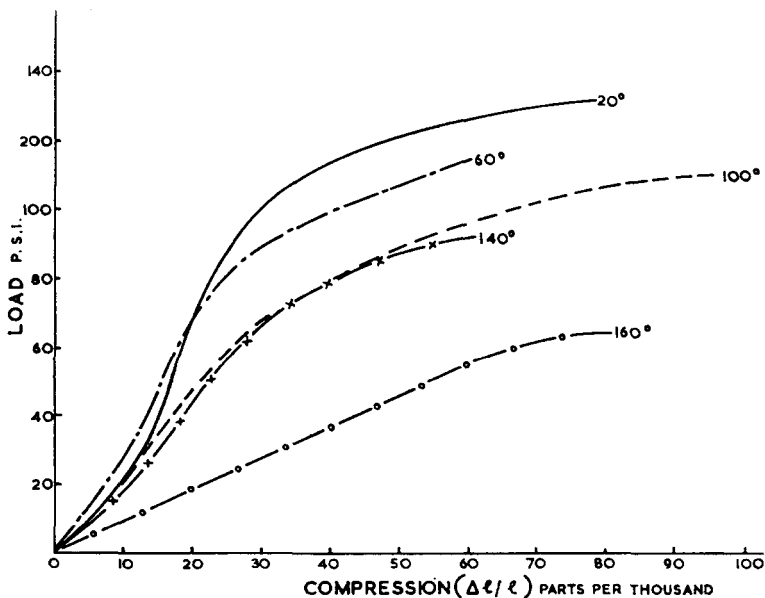


Fig. 2. Compressive strength of polyvinylcarbazole foam, density 0.10-0.12 g./cc.

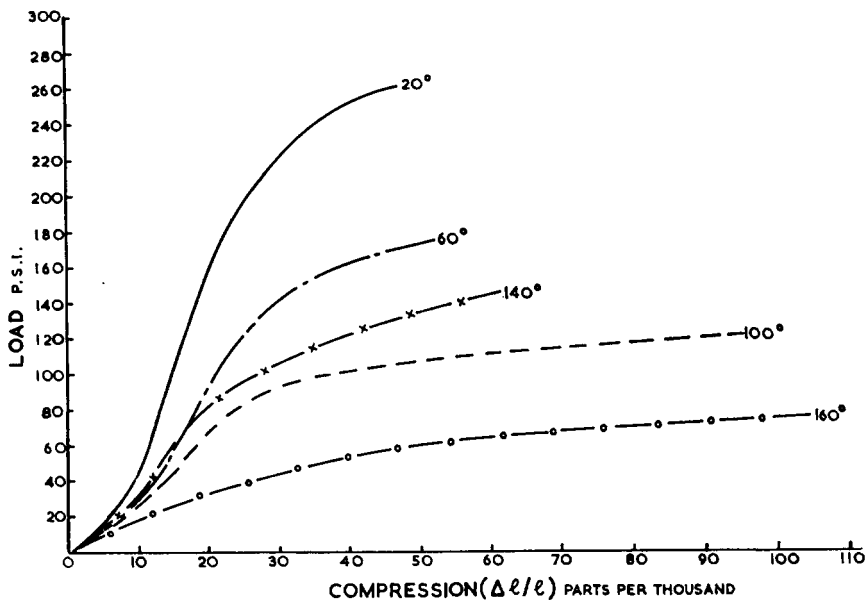


Fig. 3. Compressive strength of polyvinylcarbazole foam, density 0.16–0.18 g./cc.

On the lightest foam, measurements could be made up to 180°C. but samples in the two higher density ranges deformed too much at this temperature without a load being applied, so that the maximum temperature for these samples was limited to 160°C. At all densities there was a notable change of pattern at the highest temperature, the results indicating that the plasticity of the material began to increase appreciably.

Variation in the results from samples of nominally the same density were large, owing mainly to the variation in density.

Selected results are shown in Table V and in Figures 1–3.

TABLE VI
Incidence of Different Types of Failure of Granule-Based
Foamed Polyvinylcarbazole under Tension

Nominal sample density, g./cc.	Type of failure ^a	No.	%
0.06	B	25	100
0.1	A	3	12
	B	9	36
	C and D	13	52
	A	1	4
0.18	B	5	20
	C	3	12
	B and D	1	4
	B and E	1	4
	C and D	14	56

^a See text.

TABLE VII
Ultimate Tensile Strength of Granule-Based Foamed Polyvinylcarbazole

Material density, g./cc.	Test temperature, °C.	Specimen number	Tensile strength, psi	Type of failure*
0.06	Ambient	1	22.0	B
		2	18.8	B
		3	29.3	B
		4	17.8	B
		5	19.2	B
		Mean	21.4	
0.06	50	1	25.4	B
		2	20.2	B
		3	15.3	B
		4	26.7	B
		5	45.0	B
		Mean	26.5	
0.06	100	1	23.3	B
		2	31.2	B
		3	19.0	B
		4	21.3	B
		5	42.2	B
		Mean	27.4	
0.06	150	1	25.5	B
		2	35.6	B
		3	27.1	B
		4	24.7	B
		5	16.7	B
		Mean	25.9	
0.06	180	1	15.8	B
		2	10.5	B
		3	20.2	B
		4	19.7	B
		5	37.2	B

(continued)

Tensile Data

The determinations were made on samples ($2 \times 2 \times 1$ in.) cut from $6 \times 6 \times 1$ in. granule-based panels. Determinations were made only through the thickness of the samples, which was of particular practical interest and which at 1 in. did not allow the use of waisted specimen. The samples were bonded individually between the ground end surfaces of 1 in. diameter steel cylinders with an adhesive compounded from Shell Epikote 828 100 parts, crushed fused quartz 50 parts, and Epikote DDM 27 parts, applied cold to the degreased bonding surfaces.

During bonding the steel cylinders were held coaxially with the sample and were lightly pressed against it, while a curing temperature of 60°C .

TABLE VII (continued)

Material density, g./cc.	Test temperature, °C.	Specimen number	Tensile strength, psi	Type of failure ^a
0.11	Ambient	Mean	20.7	
		1	0	A
		2	74.2	B
		3	16.6	C,D
		4	48.6	B
0.11	50	5	68.4	B
		Mean	41.6	
		1	19.6	C,D
		2	39.4	C,D
		3	32.2	B
0.11	100	4	52.5	B
		5	47.7	B
		Mean	38.3	
		1	96.0	B
		2	27.0	C,D
0.11	150	3	38.2	C,D
		4	78.1	B
		5	24.0	C,D
		Mean	52.7	
		1	48.4	B
0.11	180	2	0	A
		3	0	A
		4	54.5	C,D
		5	76.5	C,D
		Mean	35.9	
0.11	180	1	35.6	C,D
		2	36.9	C,D
		3	19.5	C,D
		4	37.6	C,D
		5	35.0	C,D

(continued)

was applied. The bonded specimens were shaped roughly with a knife, and the cylindrical surfaces (diameter 1 in.) were then ground with coarse and finally with fine sandpaper.

The tensile determinations were made in a Hounsfield type W tensometer, fitted for the higher temperatures with a Wild-Barfield furnace, thermostated to maintain the set temperature within limits of less than $\pm 2^\circ\text{C}$., the sample being preheated in the rig for 60 min. The tensometer was operated at a crosshead speed of 0.25 in./min.

Widely scattered results were obtained (Tables VI-IX), and several types of failure were distinguished: (A) failure at small or zero load, due

TABLE VII (continued)

Material density, g./cc.	Test temperature, °C.	Specimen number	Tensile strength, psi	Type of failure ^a
0.18	Ambient	Mean	32.9	
		1	78.8	B
		2	127.1	C,D
		3	92.5	B
		4	107.5	B
		5	121.8	B
0.18	50	Mean	105.5	
		1	38.6	C,D
		2	60.1	C,D
		3	69.5	C
		4	71.6	C
		5	45.9	C,D
0.18	100	Mean	57.1	
		1	47.0	C,D
		2	55.2	C
		3	39.1	C,D
		4	52.9	C,D
		5	54.7	C,D
0.18	150	Mean	49.8	
		1	0	A
		2	56.9	C,D
		3	37.0	C,D
		4	54.7	C,D
		5	38.0	C,D
0.18	180	Mean	37.3	
		1	53.0	B,D
		2	70.2	B,E
		3	69.5	B
		4	56.6	C,D
		5	70.0	C,D
		Mean	63.9	

^a See text.

to complete failure of cohesion; (B) failure within body of specimen, near metal interface; (C) failure within body of specimen, not near metal interface; (D) failure partially due to area of little cohesion between beads; (E) small area of adhesion failure (metal/material).

On the whole, the tensile strength is proportional to the density of the foam, and there is remarkably little loss of strength with increasing temperature.

TABLE VIII
Tensile Properties of Granule-Based Foamed Polyvinylcarbazole:
Elongation at 10 psi and at Failure

Ma- terial den- sity, g./cc.	Temp., °C.	Elongation, %									
		At 10 psi					At failure				
0.06	20	0.44	0.43	0.3	0.5	0.51	0.9	0.72	0.95	0.82	0.98
	50	0.95	1.3	1.7	2.8	0.4	2.3	2.6	2.7	4.6	1.7
	100	1.05	0.95	1.7	1.2	0.7	2.4	2.8	3.1	2.8	2.8
	150	1.3	1.2	1.9	1.3	2.35	3.3	4.1	4.0	2.9	2.5
	180	3.5	(7.2)	3.4	2.4	1.0	5.4	(5.6)	6.8	4.2	3.2
0.11	20	0.1	0.46	0.15	0.2		0.9	0.75	0.7	1.35	
	50	0.95	0.45	0.7	0.2	0.3	1.5	1.7	1.9	1.1	1.45
	100	0.15	1.35	0.35	0.2	1.0	1.35	3.4	1.35	1.7	2.3
	150	0.4	0.5	0.2			1.8	2.8	1.2		
0.18	180	0.5	0.3	2.3	0.7	1.1	1.65	2.05	4.4	2.35	3.6
	20	0.15	0.05	0.1	0.06	0.05	1.25	0.55	0.85	0.6	0.65
	50	0.2	0.12	0.2	0.1	0.1	0.8	0.9	1.3	0.8	0.5
	100	0.4	0.25	0.55	0.35	0.2	2.0	1.4	2.0	1.8	1.1
	150	0.3	0.6	0.2	0.5		1.5	2.3	0.9	1.6	
180	0.6	0.4	0.25	0.25	0.2	3.0	2.5	1.6	1.4	1.2	

Thermal Conductivity

This was determined on granule-based foamed panels ($6 \times 6 \times 1$ in.). A heavy block of aluminum was surrounded by the insulation and the cooling curves were obtained starting from temperatures of 100–200°C. Results are shown in Table X.

Dielectric Constant and Loss Factor at Radar Frequencies

The dielectric constant was measured at ambient temperature on whole panels (approximately $12 \times 12 \times 1$ in.) using measurement of the insertion phase difference, defined as the phase change effected when a sheet of dielectric material is introduced into the path of an electromagnetic wave in free space. It was measured at 9375 Mcycle/sec. by using a wave guide bridge. The introduction of a panel of the dielectric material between the horns of the assembly produces a phase delay resulting in unbalance, and the adjustment which has to be made to the phase changer and alternator to restore balance is a measure of the phase difference introduced by the sample.

The main surfaces of the granule-based panels which had been dried to constant weight at 80°C. differed, in that one was flat and the other somewhat convex. Their densities were estimated from their weight and volume, using their mean thickness to find the latter. One of the panels (12/67) was used afterwards also in wave guide measurements of dielectric constant and loss factor.

TABLE IX
Tensile Properties of Granule-Based Foamed Polyvinylcarbazole: Loads to Effect 0.5% Elongation and Failure

Material density, g./cc.	Temp., °C.	Load, psi									
		At 0.5% elongation					At failure				
0.06	20	11.75	11.25	17.5	10.0	9.5	21.5	16.25	26.25	16.5	18.0
	50	5	3.75	2.75	1.75	12.5	25.5	20.0	14.5	25.5	44
	100	5	5.2	3.0	4.25	7.5	22.5	29.25	18.0	18.0	39.5
	150	3.75	4.0	3.5	4.0	2.0	22.0	31.0	25.5	22.0	14.0
	180	1.25	0.75	1.5	2.0	5.0	15.0	7.75	19.0	16.25	30.75
0.11	20	42	10.5	35	25	17	74	15.5	48.5	68.5	48
	50	5	12.5	7.5	24.5	5	16	39	28.5	51	22
	100	35	4	14	23	5	90	25	38	76	22
	150	11.5	10	26	7.25	4.75	41.5	54.5	61	33.25	32.5
	180	10	8.5	2.25	89	95	35.5	33.5	18.5	92.5	107
0.18	20	32	112	53	26.5	42	78	120	69.5	122	46
	50	22.5	35	26	48	26.5	36.5	60	34	45.5	54.5
	100	12	20	9	14.5	26.5	47	51.5	46	33	65
	150	17.5	8.0	27.5	10	27.5	50.5	37	46	59	65
	180	8.0	12.5	19	20.5	27.5	49.5	66.0	59	51.5	65

TABLE X
Thermal Conductivity of Granule-Based Foamed Polyvinylcarbazole

Code no. of panel	Density, g./cc.	Mean tempera- ture, °C.	Thermal conductivity	
			kcal. cm. ⁻² sec. ⁻¹ C. ⁻¹ cm.	British Units
319-21/6/8	0.053	83	0.000082	0.24
325-38/6/25	0.11	84	0.000077	0.22
325-38/6/23	0.18	92	0.000075	0.22

Measurements of the dielectric constant by Insertion phase difference were made by using parallel polarization and an angle of incidence of 30° (Table XI).

TABLE XI
Dielectric Constants ϵ of Unstoved, Granule-Based Foamed
Polyvinylcarbazole Panels by Measurement of their Insertion Phase Difference

Panel no.	Density, g./cc.	Thickness, in.		Dielectric constant ϵ	
		Mean	Variation	Mean	Variation
79	0.061	1.142	+0.033 -0.027	1.078	+0.002 -0.002
89	0.094	1.079	+0.016 -0.019	1.115	+0.003 -0.003
87	0.093	1.108	+0.032 -0.028	1.130	+0.007 -0.007
12/43	0.130	1.196	+0.039 -0.031	1.163	+0.007 -0.007
12/51	0.135	1.205	+0.045 -0.040	1.165	+0.008 -0.008
12/42	0.130	1.192	+0.038 -0.032	1.191	+0.006 -0.007
12/38	0.148	1.147	+0.033 -0.032	1.175	+0.007 -0.006
12/67	0.135	1.222	+0.058 -0.057	1.186	+0.010 -0.010

Most measurements of dielectric constant and $\tan \delta$ were carried out in a circular wave guide of 0.9 in. diameter at 9375 Mcycle/sec. by using the shortened line method of von Hippel. The method has the advantage of allowing the use of smaller (usually 0.9 in. diameter, 2 in. long) samples, so that the relationship between density and dielectric constant could be studied more easily, and with the use of panels 2 in. thick, samples could be cut in any direction relative to the panel plane. By externally heating the wave guide the measurements could be obtained up to the softening range of the material. Measurements were made on samples from the panels which having been dried to constant weight at 80°C. were then cut, one quarter being used directly for the measurements shown (Table XII),

while three quarters were stoved (Tables I and II) before being cut into samples for measurement (Tables XIII, XIV). Several measurements were made on samples cut from an unstoved panel, which had been used for insertion phase difference measurements (Tables XI and XV).

The samples used for the measurements shown in Tables XII, XV, and XIV were all cut with the main dimension in the plane of the panel. Granule-based foamed panels ($6 \times 6 \times 2$ in.) were stoved by heating at 180°C . for 32 hr. Samples ($2 \times 1\frac{1}{4} \times 1\frac{1}{4}$ in.) were cut with the main dimension perpendicular to the plane of the panels.

TABLE XII
Dielectric Constant ϵ and $\tan \delta$ of Samples Cut from Unstoved
Granule-Based Foamed Polyvinylcarbazole Panels

Density, g./cc.	Temp., $^\circ\text{C}$.	Dielectric constant ϵ	$\tan \delta$ $\times 10^4$	Time before repeat measure- ment, hr.	Dimensional changes
0.060	20	1.071	4		No distortion; average length change, -0.5% ; total weight loss, 3.6% .
	180	1.070	7		
	180	1.070	6	0.5	
	180	1.070	6	0.5	
	191	1.070	6		
	192	1.070	6	1	
	201	1.070	6		
	200	1.070	6	0.5	
	200	1.070	5	0.5	
0.134	21	1.169	10		Definite swelling; average length change, $+7.0\%$; total weight loss, 2.9% .
	180	1.153	15		
	179	1.153	14	0.5	
	179	1.152	14	0.5	
0.179	20	1.220	16		Definite swelling; average length change, $+9.8\%$; total weight loss, 2.6% .
	179	1.192	25	2	

Similar measurements were made also on samples cut in the plane of panels from stoved (Tables I and II) bead-based foamed polyvinylcarbazole (Table XVI).

A linear relationship between dielectric constant and the density of the foamed polyvinylcarbazole is to be expected, and Figures 4 and 5 show that, subject to appreciable scatter, this applies both to the stoved and unstoved material.

The homogeneity of the dielectric constant of both granule- and bead-based foamed polyvinylcarbazole panels has been measured on the samples cut to determine their homogeneity of density (Table I). Stoving had little effect upon the dielectric constant and the results for both stoved and unstoved specimen have been combined (Table XVII).

TABLE XIII
Dielectric Constant ϵ and $\tan \delta$ of Samples Cut from Stoved
Granule-Based Foamed Polyvinylcarbazole

Density, g./cc.	Temp., °C.	Dielectric constant ϵ	$\tan \delta$ $\times 10^4$	Time before repeat measure- ment, hr.	Weight loss, %		Dimensional changes
					Incre- ment	Total	
0.59	21	1.073	4				No distortion; average length change, nil.
	177	1.074	7				
	177	1.074	7	0.5			
	177	1.074	7	0.5		0.2	
0.087	21	1.111	7				No distortion; average length change, -0.9%.
	183	1.110	8				
	182	1.110	8	1.0			
	191	1.110	8				
	191	1.110	8	0.5			
	192	1.110	8	0.5			
	204	1.110	8				
	204	1.110	8	1.0		0.6	
0.133	19	1.173	9				Slight distortion; average length change, +0.30%; max. diameter change, -4.4%.
	180	1.175	15				
	180	1.175	15	1.0			
	191	1.175	16				
	191	1.175	15	1.0			
	200	1.175	16				
	200	1.175	16	1.0			
	211	1.176	17				
211	1.177	19	1.0		0.4		
0.245	20	1.319	21				Considerable dis- tortion at 216°C.; average length change, +2.1%; max. diameter change, -19.4%
	179	1.321	35	2	0.13	0.13	
	188	1.319	35	2.25	0.33	0.46	
	198	1.322	35	2.25	0.10	0.56	
	205	1.316	34	2	0.13	0.69	
	216	1.347	35	2	0.17	0.86	

TABLE XIV
Dielectric Constant ϵ and $\tan \delta$ of Samples Cut Through the Thickness
of Stoved Granule-Based Foamed Polyvinylcarbazole Panels^a

Density, g./cc.	Temperature, °C.	Dielectric constant ϵ	$\tan \delta \times 10^4$
0.081	20	1.102	7
	180	1.098	11
0.089	20	1.115	8
	180	1.116	11
0.092	20	1.123	8
	180	1.122	12

^a There was no distortion of any sample at 180°C.

TABLE XV
Dielectric Constant ϵ and $\tan \delta$ Samples Cut from Unstoved Granule-Based
Foamed Polyvinylcarbazole Panel 12/67 (see Table XI)

Density, g./cc.	Temperature, °C.	Dielectric constant ϵ	$\tan \delta \times 10^4$
0.079	20	1.101	9
	180	1.100	18
0.096	20	1.149	9
	180	1.141	15
0.099	20	1.114	10
	180	1.110	16
0.100	20	1.107	12
	180	1.103	19
0.131	20	1.198	11
	180	1.190	18

TABLE XVI
Dielectric Constant ϵ and $\tan \delta$ of Samples Cut from Stoved,
Bead-Based Foamed Polyvinylcarbazole Panels

Density, g./cc.	Temp., °C.	Dielec- tric con- stant ϵ	$\tan \delta$ $\times 10^4$	Time before repeat measure- ment, hr.	Weight loss, %		Dimensional changes	
					Incre- ment	Total		
0.074	19	1.093	7				Distorted; average length change, -4.2%; max. diameter change, -18%.	
	190	1.093	10					
	200	1.093	10					
	199	1.094	10	1.0				
	209	1.094	10					
	209	1.094	10	1.0				
	218	1.095	12					
	218	1.098	12	2.75				
0.082	20	1.104	6				Distorted; average length change, -1.6%; max. diameter change, -14.8%.	
	190	1.104	10					
	190	1.104	10	1.0				
	199	1.104	9					
	199	1.103	9	1.0				
	209	1.107	9					
	209	1.107	9	1.0				
	219	1.108	10					
0.083	20	1.097	9				Distorted; average length change, -1.3%; max. diameter change, -12.4%.	
	177	1.097	13	1.75	0.40	0.40		
	185	1.102	15	1.75	0.54	0.94		
	195	1.100	14	1.25	0.02	0.96		
	206	1.100	14	1.75	0.41	1.37		
	216	1.106	13	1.75	0.11	1.48		

TABLE XVII
 Homogeneity of Dielectric Constant ϵ and of $\tan \delta$ of Granule- and Bead-Based Foamed Polyvinylcarbazole Panels

Panel type	Panel no.	Samples tested			Dielectric constant ϵ				$\tan \delta \times 10^4$	
		Un-stoved	Stoved	Average	Standard	Deviation, %	Max.	Deviation, %	Un-stoved	Stoved
Granule-based panels (12 × 12 × 1 in.)	109	3	3	1.072	0.0028	3.9	0.006	8.4	4-5	2-4
	165	3	4	1.128	0.040	31.3	0.069	54.0	5-10	3-9
	185	3	3	1.243	0.057	23.5	0.079	32.5	12-16	9-21
Bead-based panels (6 × 6 × 1 in.)	328	—	4	1.106	—	—	0.009	8.2	—	5-6
	329	—	4	1.117	—	—	0.015	12.8	—	5-9

The bead-based panels are seen to be more homogeneous as regards dielectric constant and $\tan \delta$ than the granule-based panels.

Conditions of high humidity were found to have no discernible effect upon the dielectric constant and $\tan \delta$ of granule-based foamed polyvinylcarbazole (Table XVIII). Samples cut from an unstoved granule-based panel were kept in a desiccator for several days. After determination of the dielectric constant and $\tan \delta$ (at 9375 Mcycle/sec.) at ambient tem-

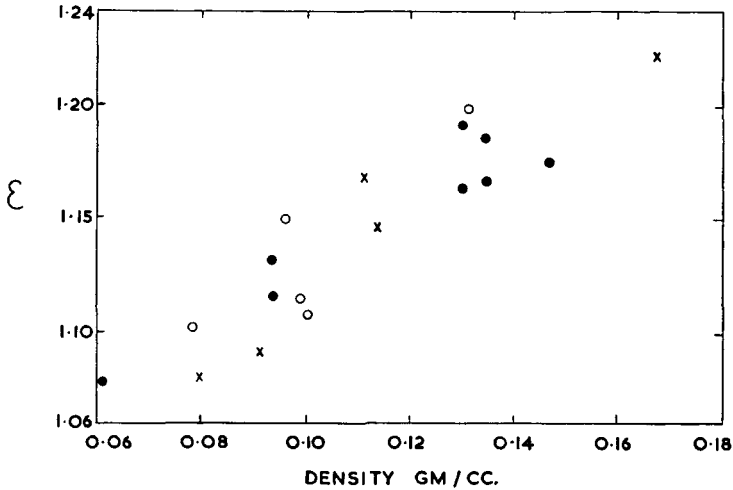


Fig. 4. Dielectric constants of samples cut from granule-based foamed polyvinylcarbazole panel: (●) from insertion phase difference; (○) unstoved specimens, waveguide method; (×) stoved specimens, waveguide method.

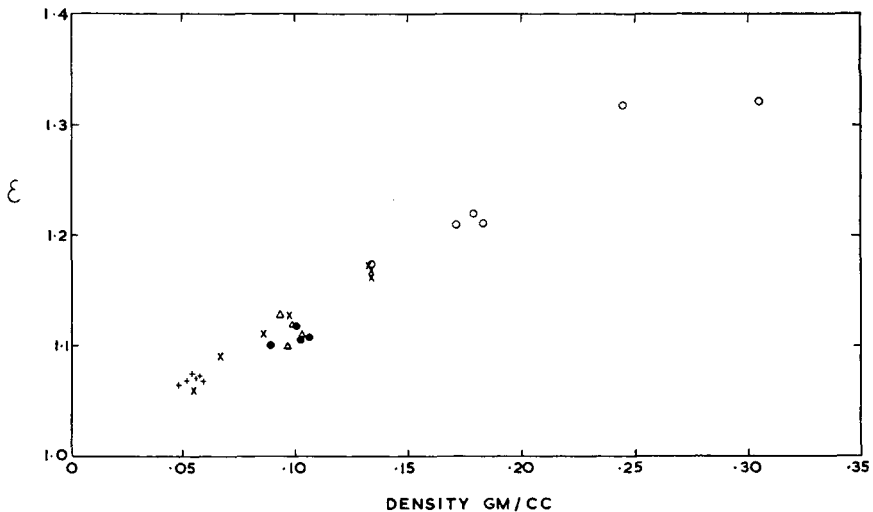


Fig. 5. Dielectric constants of samples cut from foamed polyvinylcarbazole panels: (+) panel 109; (×) panel 165; (○) panel 185; (●) panel 328; (Δ) panel 329.

TABLE XVIII
Effect of High Humidity at Ambient Temperature Upon the Dielectric Constant ϵ
and $\tan \delta$ of Samples Cut from Granule-Based Foamed Polyvinylcarbazole Panels

Density, g./cc.	Period in humid atmosphere, days	Dielectric constant ϵ	$\tan \delta \times 10^4$
0.069	0	1.081	10
	7	1.084	10
	14	1.087	9
	21	1.087	10
	28	1.087	11
	35	1.096	10
	42	1.084	19
	49	1.085	9
	56	1.085	9
	0.070	0	1.089
7		1.087	9
14		1.091	9
21		1.090	11
28		1.090	11
35		1.091	11
42		1.089	12
49		1.093	12
56		1.092	11
0.083		0	1.103
	7	1.103	12
	14	1.102	12
	21	1.104	28
	28	1.104	14
	35	1.103	12
	42	1.102	12
	49	1.103	12
	56	1.103	12

perature, the samples were exposed at ambient temperature to an atmosphere saturated with water vapor, the dielectric constant and $\tan \delta$ being redetermined at weekly intervals. No significant effect could be observed.

Effect of Aircraft Fluids and of Other Liquids

Granule-based foamed polyvinylcarbazole panels ($6 \times 6 \times 1$ in.) were dried to constant weight at 80°C . and were cut into $2 \times 2 \times 1$ in. samples which were immersed under the fluids in sealed vessels at ambient temperature or under an open condenser at 120°C . The weights of the blocks were determined before and after immersion (Table XIX), and the distances between the center points of the samples were measured by a micrometer screw gauge to an accuracy of 0.005 (Table XX).

The effects of some other liquids during 65 hr. at ambient temperature upon 1.5 cm. cubes of granule-based foamed polyvinylcarbazole are summarized in Table XXI.

TABLE XIX.
Weight Increases of $2 \times 2 \times 1$ in. Samples of Granule-Based Unstoved Foamed Polyvinylcarbazole Upon Immersion under Various Aircraft Fluids

Aircraft fluid	Im- mersion time, hr.	Weight increase, %			
		Immersion at ambient temp.			Immersion at 120°C., density 0.16-0.18 g./cc.
		Density 0.05-0.07 g./cc.	Density 0.10-0.12 g./cc.	Density 0.16-0.18 g./cc.	
Gasoline fuel, 100-130 grade	4 ¹ / ₂	—	0.1	0.1	—
	24	25	3	0.3	5.0
	144	93.8	—	—	—
	384	—	25.5	9.9	—
Kerosene fuel, Shell turbine fuel 650	4 ¹ / ₂	—	6	1.5	—
	24	30	11	3.7	15
	144	77.2	—	—	—
	384	—	21.3	14.7	—
Mineral oil, piston en- gine lubricating oil, Aeroshell oil 100	24	70	10	4.2	17
	144	119	—	—	—
	384	—	25.5	16.4	—
Turbine engine oil, Aero- shell turbine oil No. 3	24	52	9.4	5.5	14
	144	73.5	20.6	11.5	—
Cleaning fluid, Aero- shell fluid 14, (b.p. 95°C.)	24	52	7.1	2.5	11 ^a
	144	86	—	—	—
	384	—	22.8	11.9	—
Deicing fluid, Aeroshell compound 7	24	55	8.1	3.2	24.2
	144	79.6	—	—	—
	384	—	18.4	9.6	—
Ester-type lubricating oil, Aeroshell turbine oil 750	24	77	11.2	4.6	46.5
	144	102.9	—	—	—
	360	—	—	16.1	—
	384	—	24.4	—	—
Hydraulic oil, Aero- shell fluid 4	24	51	7.8	3.6	13.7
	144	80.2	—	—	—
	384	—	19.8	14.4	—
Water	24	14.7	0.2	0.2	28.4 ^b
	144	56.2	—	—	—
	360	—	12.0	6.0	—

^a Immersion at 95°C.

^b Immersion at 100°C.

Some effects of contact with several boiling organic liquids were examined on samples ($3 \times 1.5 \times 1.5$ cm.), cut from granule-based foamed polyvinylcarbazole panels (density 0.1 g./cc.), which were immersed under 100 ml. of the boiling liquids for 3 hr. and were then dried at 80°C. for 3 hr. (Table XXII).

Inflammability

When ignited the foam sustains combustion in air with a very smoky flame.

TABLE XX
Dimensional Changes of $2 \times 2 \times 1$ in. Samples of Granule-Based Unstoved Foamed Polyvinylcarbazole Upon Immersion Under Various Aircraft Fluids

Fluid	Dimensional changes ^a			
	Density 0.05-0.07 g./cc., ambient temp.	Density 0.10-0.12 g./cc., ambient temp.	Density 0.16-0.18 g./cc., ambient temp.	Density 0.16-0.18 g./cc., 120°C.
Gasoline fuel	+X _a	0	0	0
Kerosene fuel, Shell turbine fuel 650	+X _a	0	-X _c	0
Mineral oil, piston engine lubricating oil, Aeroshell oil 100	-X _b		-X _b	-X _b
Turbine engine oil, Aeroshell turbine oil No. 3	0	0	0	0
Cleaning fluid, Aeroshell fluid 14 (b.p. 95°C.)	-X _{a,b,c}	0	0	0 ^b
Deicing fluid, Aeroshell compound 7	-X _b	0	0	-X _{b,c}
Ester-type lubricating oil, Aeroshell turbine oil 750	-X _b	0	+X _a	-X _{a,b}
Hydraulic oil, Aeroshell fluid 4	0	0	0	+X _a
Water	0	0	0	-X _{b,c}

^a 0 denotes a dimensional change of less than 0.05%; X denotes a dimensional change greater than 0.05%; the subscripts denote dimension, a being perpendicular to the plane of the sample, and b and c normal to it; + indicates expansion and - contraction.

^b Immersion at 95°C.

TABLE XXI
Effects of Selected Liquids on Granule-Based Unstoved Foamed Polyvinylcarbazole During 65 hr. at Ambient Temperature

Liquid	Effect
Dilute hydrochloric acid	None
Dilute sulfuric acid	None
Dilute nitric acid	Yellow coloration
n-Hexane	None after 16 hr.
Diethyl ether	Softened, a little polymer dissolved
Ethyl acetate	None
Methylene dichloride	Completely soluble in a few minutes
Chloroform	Completely soluble in a few minutes
Carbon tetrachloride	Almost no effect
Dimethylformamide	Completely soluble in a few minutes
Cyclohexane	None
Benzene	Completely soluble during 1 hr.
Toluene	Softened, some swelling, about 50% soluble
Xylene	Softened without swelling, slightly soluble
Dioxane	Slowly soluble
Tetrahydrofuran	Slowly and incompletely soluble
Pyridine	Soluble

TABLE XXII
Effects of Boiling Organic Liquids on Granule-Based Unstoved
Foamed Polyvinylcarbazole

Liquid	Effect	Polyvinylcarbazole, g.	
		Before	After
<i>n</i> -Hexane	None	0.959	0.957
Petroleum ether (80-100)	None	1.071	1.095
Cyclohexane	None	1.095	1.085
Carbon tetrachloride	Shrinkage and distortion	1.042	1.083

DISCUSSION

The uniformity of polyvinylcarbazole panels molded from the smaller beads¹ is clearly superior to that of panels molded from the larger granules. Superficial examination indicates that the pore size of the structure is similar for those derived both from beads and granules provided they are molded to the same density. After cutting the surface skin from panels, there is little difference between the surface roughness of bead- and of granule-based panels. This is in keeping with the view expressed on the mode by which beads and granules are formed during the aqueous dispersion polymerization of vinylcarbazole.¹

The uniformity within granule-based panels is greater the lower their density.

The softening behavior of polyvinylcarbazole deserves further study. The present results indicate that the Vicat softening point of foamed polyvinylcarbazole is higher than that of bulk polymer of even higher molecular weight; the lower the density of the foamed polymer, the higher the maximum temperature at which the foam retains some compressive strength. Polymerization to foamed granules and molding of the latter is thought to result in increased molecular orientation, which is held responsible for the higher softening temperature.

Thermal stability appears to be an outstanding property of this polymer, especially when residual volatiles have been removed by gradually increasing the temperature to which the foam is exposed. Above 220°C. carbazole is slowly formed, and product which can be ascribed to depolymerization is formed very slowly, even at 320-330°C. Thermal depolymerization of vinyl polymers becomes appreciable at atmospheric pressure, in an atmosphere essentially free of monomer, well below the ceiling temperature for the polymerization.⁴ In the case of styrene, for which the ceiling temperature is about 300°C., depolymerization is appreciable already at 200°C. The concept of a ceiling temperature requires not only a thermodynamic equilibrium between polymerization and depolymerization, but mechanistically reaction paths by which both reactions can proceed. In polyvinylcarbazole, the large carbazole groups are (even at the ends of the polymer molecule) owing to steric hindrance unable to rotate freely

around the bond linking them to the polyethylene chain. It is suggested that such rotation may be required for depolymerization to occur, and that when rotation is restricted severely, depolymerization is also impeded, so that the conditions for a ceiling temperature do not apply. The thermal depolymerization occurs in the present case slowly and at an exceptionally high temperature, and since the simultaneous formation of carbazole under these conditions must proceed by an irreversible decomposition, the polymerization of vinylcarbazole is not regarded as being fully reversible. The relationship between the structure of polyvinylcarbazole and the nature of its thermal decomposition lie clearly at the heart of its exceptional thermal stability, and further study which should include determination of its heat of polymerization and of the constants of the Arrhenius equation, might show how further improvement might be obtained.

The compressive and especially the tensile properties of foamed polyvinylcarbazole can no doubt be markedly improved further by improved impregnation and molding techniques.¹ The small effect of the temperature upon the tensile properties is remarkable. The effect of stoving upon these properties demands further attention.

Polyvinylcarbazole is seen to be remarkably hydrophobic, as shown particularly by the persistence of its excellent dielectric properties at radar frequency even under conditions of high humidity. The solubility of polyvinylcarbazole in organic liquids is often very specific; thus benzene is a good solvent, whereas toluene and xylene only produce swelling. Its solubility in benzene depends on the conditions under which it has been polymerized.¹ There is some analogy to the specificity with which solvent impregnation improves the molding behavior of the foamed polymer granules.¹

Lack of sensitivity to humidity and temperature is probably the outstanding feature of the excellent dielectric properties of this material.

The thermal conductivities of the foamed panels are those to be expected from a good air-containing insulant.

The electrical data and some of the data regarding the uniformity and heat stability were obtained by Mr. G. M. Brydon, Caswell Research Laboratories of Plessey Co. (U.K.) Ltd., and the tensile data were by Mr. J. A. Mead, Yarsley Testing Laboratories Ltd. The thermal conductivity measurements were made by Mr. Bishop, Royal Aircraft Establishment, Farnborough, Hants.

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Résumé

L'uniformité, la résistance à la chaleur et aux solvants, et la conductivité thermique de mousses de polyvinyl carbazol ont été examinées. Les propriétés de compression et de tension, la constante diélectrique et le facteur de pertes ont été déterminés entre la température ambiante et la température de ramollissement. Certaines données concernant ces propriétés ont été attribuées au degré d'orientation des molécules polymériques qu'on admet être la plus élevée à densité de la mousse la plus faible. La stabilité thermique bonne de ces polymères est due à l'empêchement stérique de la réversibilité de la polymérisation du vinyl-carbazol.

Zusammenfassung

Die Einheitlichkeit, Wärme- und Lösungsmittelbeständigkeit sowie die Wärmeleitfähigkeit von geschäumtem Polyvinylcarbazol wurde untersucht. Kompressions- und Zugeigenschaften, Dielektrizitätskonstante und Verlustfaktor wurden zwischen Raumtemperatur und dem Erweichungsbereich bestimmt. Zum Teil wird das Verhalten der Eigenschaften auf den Orientierungsgrad der Polymermoleküle zurückgeführt, von welchem angenommen wird, dass er um so grösser ist, je niedriger die Dichte des Schaumes ist. Die gute Hochtemperaturstabilität wird der sterisch gehinderten Reversibilität der Polymerisation von Vinylcarbazol zugeschrieben.

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