

# Mechanical Properties of Highly Filled Elastomers.

## II. Relationship between Filler Characteristics, Thermal Expansion, and Bulk Moduli

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### Synopsis

Model substances were prepared of a polyurethane rubber filled with different amounts of various fractions of sodium chloride. Eight filler fractions were used of sizes in the range of 1-480  $\mu\text{m}$ . The amount of filler was varied between 0 and 50 vol.-%. An experimental method is described by which thermal expansion and bulk modulus of an isotropic material may be simultaneously determined as functions of temperature. The materials were investigated for thermal expansion and bulk modulus. All filled and unfilled samples show a glass-rubber transition, at which temperature the thermal expansion coefficient increases considerably and the bulk modulus decreases sharply. These temperatures do not depend on amount or size of filler. The values of the bulk moduli and the thermal expansion coefficients are independent of filler size, but depend considerably on the volume fraction of filler. These values may be predicted by means of a simple macroscopic theory (Fröhlich-Sack-Van der Poel,) describing the bulk modulus, the thermal expansion, and the density of the composite material in terms of the corresponding properties of the components and of their relative amounts.

### INTRODUCTION

Recently the mechanical properties of highly filled elastomers have aroused considerable interest in connection with the use of these materials as solid propellants in rocketry. Most composite propellants consist of elastomers highly filled with inorganic oxidizer. Mixing is effected in an uncrosslinked state where the polymer has still low molecular weight and the consistency of a viscous fluid. Then the mixture is cast or extruded into the desired shape and hardened by polymerization and crosslinking. The degrees of loading for those systems are very high and are, depending on composition, between 65 and 85 vol.-%.

For the proper understanding of the mechanical behavior of solid propellants, knowledge is essential on the relationship between composition and mechanical properties of these highly filled elastomers. The work described here was undertaken to investigate the influence of filler characteristics, such as size, shape, and content on the mechanical behavior of filled elastomers.

To avoid complications in the preparation and handling, this investigation was performed with chemically inert fillers. The compounds were prepared on a kilogram scale, and consisted of polyurethane rubber filled with various amounts of fractions of sodium chloride. The size of the fractions ranged from 1 to 480  $\mu\text{m}$ . The amounts incorporated were varied in the range of 0–50 vol.-%.

These substances were subjected to extensive mechanical investigations. Tensile properties and shear moduli of these substances in relation to filler characteristics have been published elsewhere.<sup>1</sup> The present paper deals with thermal expansion and with the behavior under hydrostatic pressure as related to filler characteristics.

## EXPERIMENTAL

### Technique for the Determination of Bulk Modulus and Thermal Expansion

An apparatus was developed for the determination of bulk modulus and thermal expansion. The principle of the method is as follows.

A specimen of rectangular cross section (3.5 mm.  $\times$  7.0 mm.) and 92 mm. in length is subjected to hydrostatic liquid pressure in a pressure vessel and its length measured at different temperatures and at different hydrostatic

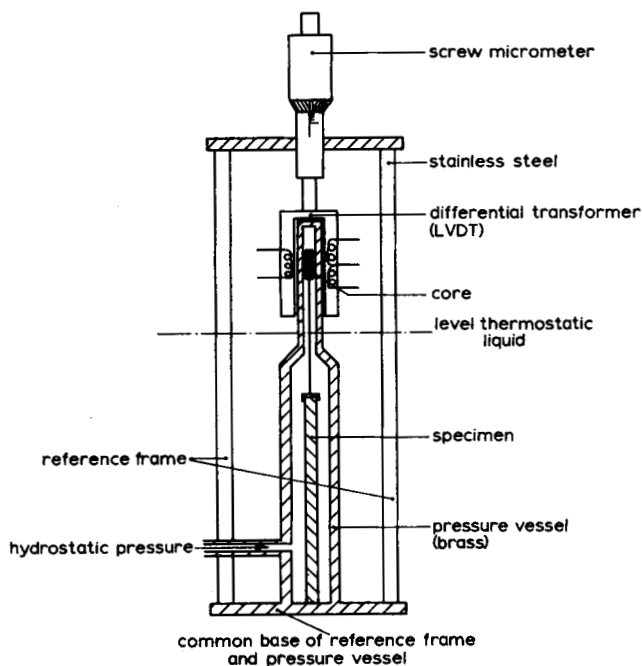


Fig. 1. Schematic drawing of pressure vessel and reference frame of the apparatus for the determination of bulk modulus and thermal expansion.

pressures. Assuming the material under investigation to be isotropic, this yields thermal expansion coefficient and bulk modulus as a function of temperature.

A scheme of the pressure vessel of the apparatus is shown in Figure 1. The specimen is standing freely in the pressure vessel. It carries at its upper end a pen with the core for the linear variable differential transformer (LVDT) device. The pressure vessel is a brass cylinder which is shaped at its upper end to include the core and to fit loosely into the coils of the differential transformer. A reference frame of stainless steel is fixed to the pressure vessel. This reference frame carries the coils of the LVDT device at its upper end by means of a screw micrometer. With this arrangement, the dimensions of the pressure vessel do not influence the measurement of the length of the specimen, and no correction is needed for the inflation of the pressure vessel during pressurization. However, when measuring the change in length of the specimen at atmospheric pressure due to thermal expansion, a correction has to be applied for the thermal expansion of the reference frame. This correction was determined experimentally by calibrating the apparatus by a measurement of the thermal expansion of a tungsten specimen with well-known small thermal expansion coefficient.

The choice of the pressurization liquid gave rise to some problems. A liquid should be chosen which causes as little swelling of the specimen as possible and at the same time remains fluid within the range of temperatures of measurement. The most appropriate liquid found so far, and used throughout this investigation, was a silicone oil (Midland silicone MS 200; freezing point  $-70^{\circ}\text{C}.$ ). This choice limited the lower end of the temperature range of measurement to  $-70^{\circ}\text{C}.$

Liquid pressure of a constant prescribed value is exerted by loading the liquid by means of a piston and a constant weight. This yields constant pressure also during the periods of change of temperature in the test chamber. The pressure is measured accurately to within 0.5% by a Bourdon manometer which is at room temperature.

The pressure vessel is immersed into a thermostatic bath which is filled with methanol. Its temperature is regulated by alternative operation of an electric heating coil and a cooling spiral through which liquid nitrogen is pumped. The temperature of the bath is controlled by means of a platinum resistance thermometer, which is compared with an electrically driven resistance in a Wheatstone bridge. The signal of the bridge, after amplification, is used to operate on-off controls of either the electric heating coil or the centrifugal pump for liquid nitrogen transport.

By means of this regulating system, it is possible either to keep the thermostatic bath at a constant mean temperature, or to heat or to cool it at a constant rate between 0.1 and  $0.5^{\circ}\text{C}./\text{min}.$  When regulating at constant temperature, the temperature of the bath fluctuates due to the on-off control with a frequency of about 0.3 cycle/sec. and an amplitude of  $0.1^{\circ}\text{C}.$  It is estimated that in this way constant temperature in the test chamber may be achieved within  $0.02^{\circ}\text{C}.$

Before describing the measurement procedure, it is useful to discuss the creep behavior under constant pressure at different temperatures. Results of measurements on an unfilled rubber (Vulkollan 18/40) are shown in Figure 2. The procedure in this case was the following. The specimen was brought to the temperature indicated by linear cooling or heating at a rate of  $0.5^\circ\text{C./min.}$ , it was kept at this temperature for 10 min., its length was read, and a hydrostatic pressure of  $150\text{ kg./cm.}^2$  was applied suddenly. The length of the specimen was then read as a function of the time elapsed after pressurization. During the whole procedure, the temperature of the thermostat was kept constant as indicated. A time-dependent bulk modulus  $K$  was calculated from the data; this is shown in Figure 2.

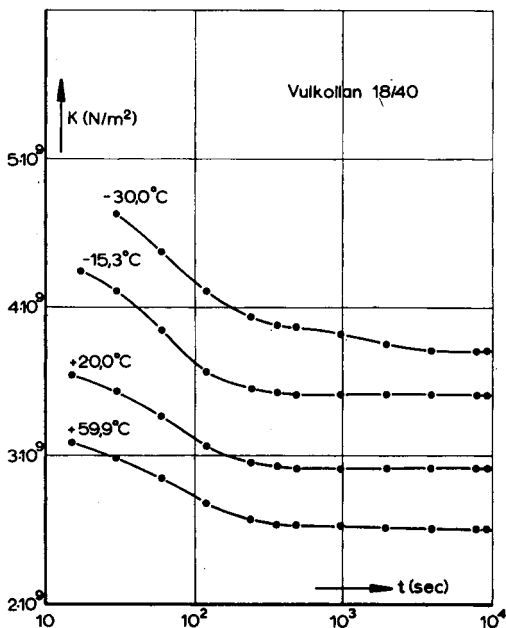


Fig. 2. Bulk modulus at various temperatures in compression creep experiments as function of time for Vulkollan 18/40 under constant pressure of  $150\text{ kg./cm.}^2$ .

A transition in the bulk modulus is seen to occur at all temperatures in the same time range, i.e., between 10 sec. and about 4 min. At longer times, the bulk modulus seems to be rather independent of time, though it still depends considerably on temperature. The short-time transition may be identified with the transition from adiabatic to isothermal conditions. Directly after pressurization, a temperature rise of about  $0.5^\circ\text{C.}$  occurs in the specimen, and a temperature rise of about  $2.5^\circ\text{C.}$  occurs in the silicone oil. This gives rise to thermal expansion of the specimen which counteracts the effect of hydrostatic pressure. This results into high values of the adiabatic bulk modulus directly after pressurization. In the course of some minutes, specimen and silicone oil attain the temperature of the bath

due to heat conduction. Then an isothermal value of the bulk modulus is observed.

The procedure for measuring thermal expansion and bulk modulus was carefully standardized to avoid difficulties in connection with adiabatic temperature rise, and with thermal volume relaxation.

The specimen was brought to a temperature of 60°C. at a heating rate of 1°C./min. at atmospheric pressure. At 60°C. it was conditioned 5 min., its length was measured, it was pressurized with 150 kg./cm.<sup>2</sup>, and its length was measured again 4 min. after pressurization. Then the pressure was released, and the specimen was cooled down to 40°C. at a constant cooling rate of 0.5°C./min. At 40°C., the procedure was repeated; and so on. In this manner, thermal expansion and bulk modulus were determined for each sample on one specimen in one run without interruptions at temperatures of 60, 40, 20, 0, -20, -35, -40, -45, -48, -51, -55, -58, -60, -65, and -70°C.

The following remark should be made concerning linearity of the bulk modulus. In the temperature range between -40 and +60°C., the materials investigated show rubberlike behavior in this type of measurement. In this temperature range, the bulk modulus is expected to be independent of the value of the hydrostatic pressure, as long as the latter does not become too high. This could indeed be confirmed by incidental checks of linearity, comparing volume changes at pressures of 50, 100, and 150 kg./cm.<sup>2</sup>.

In the transition region from glasslike to rubberlike behavior, which in our case extends from -40 to -65°C., one should not expect linearity of the volume change with pressure, as has been shown recently by Heydemann.<sup>2</sup>

The accuracy of the measurement of the bulk modulus is estimated to be within 2% in the temperature range between +60 and -40°C. At lower temperatures the measurement seems to be less accurate, but certainly better than within 8%.

Experimental methods similar to that described above, have been published by Heydemann<sup>2</sup> and Surland.<sup>3</sup>

### Materials

All samples of urethane rubbers were based on a linear (polypropylene ether) glycol of a molecular weight of about 2000. The molecules of the polyether were lengthened with toluene diisocyanate and crosslinked by means of trimethylol propane in the presence of a catalyst, at a temperature of about 80°C. Full details on the preparation and characteristics of unfilled and filled rubbers have been given previously.<sup>1</sup>

Milled sodium chloride, classified into eight different fractions, was used as filler material throughout. The six larger fractions were obtained by sieving; description and treatment of these fractions were given earlier.<sup>1</sup> The smallest two fractions were obtained by air separation. They were prepared by milling of the sodium chloride in a pin mill (160 L, Alpine,

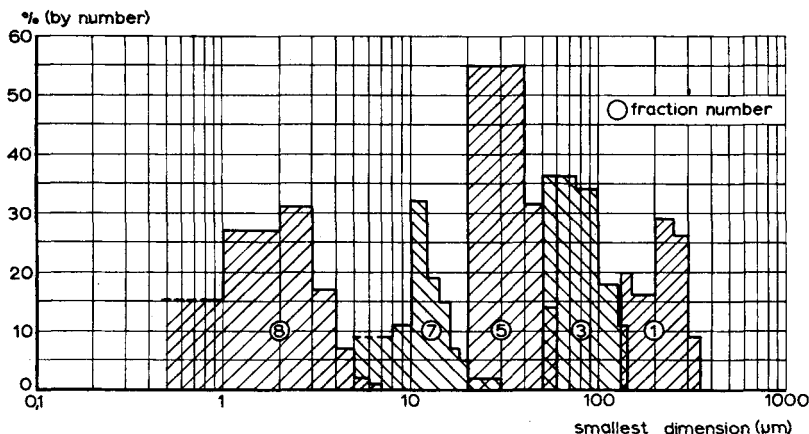


Fig. 3. Distribution functions (not normalized) of the smallest dimension of the particle size of fractions 1, 3, 5, 7, and 8 of sodium chloride filler.

Augsburg) followed by air separation (Walther separator). The particle size distribution of all fractions was determined by counting 1000 particles under the microscope. For five fractions, the particle size distribution is given in Figure 3. Note, however, that the distribution functions shown are not converted to unit area.

Micrographs of the six larger fractions were given earlier.<sup>1</sup> Microscopic investigation of fractions 7 and 8 was performed, but no clear photographs were obtained. There was, however, a strong indication of agglomeration in these smallest two fractions.

A summary of the materials investigated is given in Table I. All samples prepared had about the same composition of the pure rubber (except for the amount of catalyst). They were filled with different amounts of the single fractions of sodium chloride. All samples were obtained completely homogeneous and free of voids. In all cases it was possible to machine specimens for the determination of bulk moduli and thermal expansion. Samples and specimens were always kept in desiccators above  $P_2O_5$  at least for 14 days prior to measurements.

All samples were subjected to a number of routine control measurements: the density at 20°C. as a control of filler content, the swelling in two solvents as a control of the degree of crosslinking of the rubber matrix, and the Shore A hardness. Results of these tests are given in Table I.

As pointed out previously, the density measurement constitutes an accurate method for control of composition and homogeneity. Experimental values of the density in general agreed well with theoretical values for the density as calculated by means of the formula:

$$d^{20} = d_r^{20} + (d_f^{20} - d_r^{20}) c \quad (1)$$

where  $d^{20}$  = density of filled rubber at 20°C.;  $d_r^{20}$  = density of unfilled rubber at 20°C. =  $1.072 \pm 0.001$  g./cm.<sup>3</sup>;  $d_f^{20}$  = density of sodium chloride

TABLE I  
 Composition and Properties of NaCl-Filled Polyurethane Rubbers

Sample no.	NaCl filler			Density $d_{20}^0$ , g./cm. <sup>3</sup>	Shore A hardness	Swelling, % volume increase	
	Amount, vol.-%	Fraction number	Particle size $\mu\text{m}$			Chl.	Tri.
29	0	—	—	1.0738	50	390	307
41	0	—	—	1.0721	54	370	280
110	0	—	—	1.0716	46	410	312
52	31	1	300-480	1.4243	75	387	300
47	41.3			1.5274	84 <sup>1</sup> / <sub>2</sub>	394	295
44	51.5			1.6365	88 <sup>1</sup> / <sub>2</sub>	376	287
55	21	2	210-300	1.3041	64 <sup>1</sup> / <sub>2</sub>	396	310
53	31			1.4235	73 <sup>1</sup> / <sub>2</sub>	395	300
49	42			1.5332	82	380	288
65	10.4	4	90-105	1.1856	55 <sup>1</sup> / <sub>2</sub>	407	308
64	20.7			1.3002	64	404	306
62	31.1			1.4158	75	388	294
60	41.4			1.5269	82	408	299
66	41.2	5	50-60	1.5257	82	416	300
77	10.4	6	33-40	1.1857	56 <sup>1</sup> / <sub>2</sub>	395	300
76	20.7			1.2985	64	408	301
71	31.2			1.4163	76	408	306
70	40.7			1.5217	83 <sup>1</sup> / <sub>2</sub>	410	298
93	19.8	7	8-20	1.2866	69	432	322
92	30			1.3934	77	429	318
90	9.8	8	1-5	1.1770	64 <sup>1</sup> / <sub>2</sub>	427	314
91	19.9			1.2894	72	415	310

at 20°C. =  $2.169 \pm 0.001$  g./cm.<sup>3</sup>;  $c$  = volume fraction of filler, as calculated from the weight ratios of the components used for preparation.\*

The correlation between density at 20°C. and filler concentration is shown in Figure 4. For most of the samples, the deviations from this correlation correspond to deviations in filler content smaller than 0.2 vol.-%. Only in a few cases do the deviations amount to about 1% by volume of filler content. In these cases, filler content was investigated by a third, independent method: part of the sample was used to perform chemical analysis by determination of the chlorine content, which again leads to a value for the filler fraction.

Values obtained for the filler content of the samples by three different methods, viz., weight of ingredients, density of the samples, and chemical analysis of the samples, were compared. From this comparison it followed, that, generally, filler content is well defined and known to 0.2 vol.-%. In a few cases, differences in samples with higher filler contents may amount to 0.5 vol.-% and, in one single case, even to more than 1 vol.-%. In the second column of Table I we have cited the values of filler content which

\* For the calculation of  $c$ , use is made of the values of the density of the pure components at 20°C.

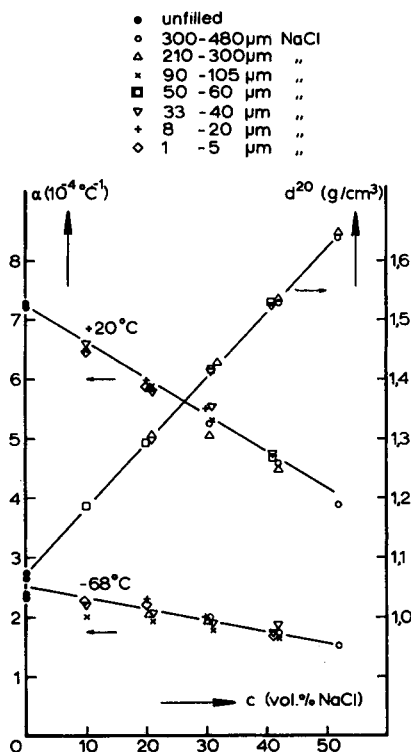


Fig. 4. Density at 20°C., volume expansivity at 20°C., and volume expansivity at -68°C. as functions of filler content for all samples of polyurethane rubbers investigated. The drawn lines correspond with the theoretical values due to eqs. (1) for density, (6) for thermal expansivity at 20°C., and (7) for thermal expansivity at -68°C. In the latter case, the theoretical line shows a small positive curvature.

were assumed to be the most probable. These values were used as nominal values everywhere in the following discussion of physical properties and filler content.

## RELATIONSHIP BETWEEN THERMAL EXPANSION AND FILLER CHARACTERISTICS

### Thermal Expansion Data of Filled Rubbers

Thermal expansion data of a commercial unfilled rubber with a chemical composition different from those listed in Table I, are given in Figure 5. The plot of specific volume  $v$  versus temperature  $T$  shows two regions in which it may be approximated by straight lines. These intersect at a well defined temperature, known as the glass transition temperature  $T_g$ . Apart from its well-known dependence on cooling speed, the glass transition temperature seems to be sharply located in temperature scale by this definition; it may be determined with an accuracy within 1°C.



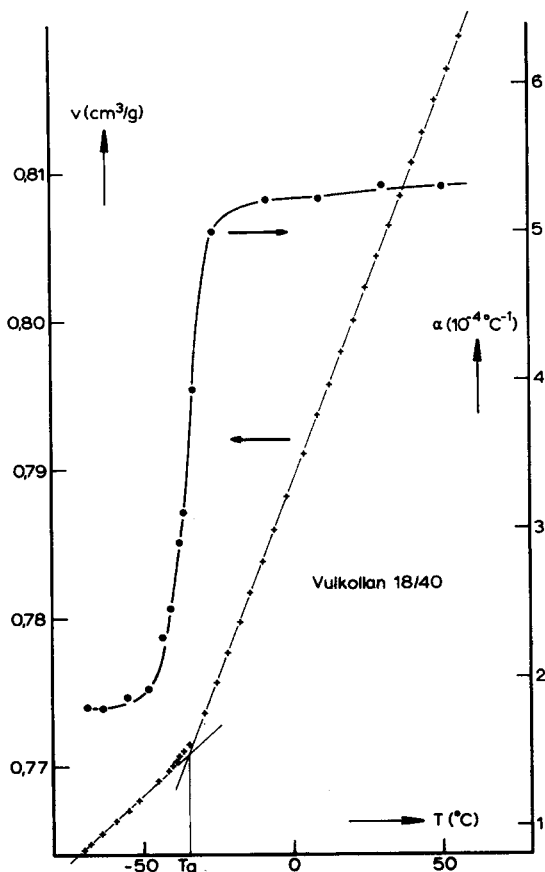


Fig. 5. Specific volume  $v$  and volume expansivity  $\alpha$  as functions of temperature for Vulkollan 18/40.

A different way to define the glass transition, which resembles much more the transition phenomena observed for other physical properties, is to consider the temperature dependence of the volume expansivity. The volume expansivity  $\alpha$  is defined by

$$\alpha = (1/v) dv/dT \quad (2)$$

The volume expansivity, also plotted in Figure 5, shows a broad transition increasing from  $1.8 \times 10^{-4} \text{C}^{-1}$  in the glassy region to  $5.2 \times 10^{-4} \text{C}^{-1}$  in the rubbery region within a temperature interval of  $30^\circ\text{C}$ . The use of the volume expansivity to characterize the glass transition was recently emphasized by Heydemann.<sup>2</sup>

Vulkollan 18/40 was chosen for the illustration of the  $v$ - $T$  and  $\alpha$ - $T$  curves, as the transition region is located well within the accessible temperature scale in this case. For the type of rubbers listed in Table I, the transition temperature is about  $16^\circ\text{C}$ . lower; consequently, for these

△	3600/55	21 vol.-% NaCl	210 - 300 $\mu$ m
*	3600/64	20,7	90 - 105
▽	3600/76	20,7	33 - 40
+	3600/93	19,6	8 - 20
◇	3600/91	19,5	1 - 5

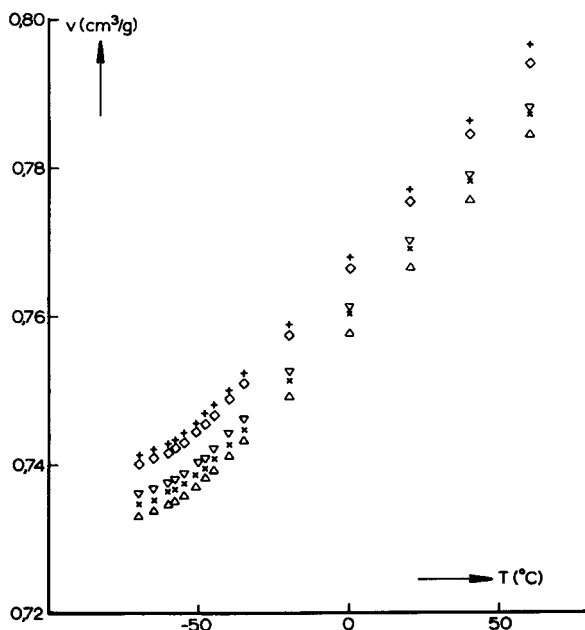


Fig. 6. Specific volume  $v$  as a function of temperature for polyurethane rubbers filled with 20 vol.-% of different filler fractions.

rubbers the lower constant level of  $\alpha$  in the glassy region is just no longer accessible to the experimental method (which was limited to temperatures above  $-70^{\circ}\text{C}$ ).

Thermal expansion data were determined for all samples listed in Table I. Specific volumes and densities were calculated as functions of temperature, using the results of the measurement of thermal expansion combined with the results of the measurement of the density at  $20^{\circ}\text{C}$ . Specific volume versus temperature curves are plotted in Figures 6 and 7 for samples which contained, respectively, about 20 and 40 vol.-% of filler. Specific volume versus temperature curves for the other materials resembled very much the pictures of Figures 6 and 7. They are not shown here. Specific volume versus temperature data and volume expansivity versus temperature data were found to be independent of filler size, and to be uniquely determined by the filler content. All data could be described with sufficient accuracy by relations (5) and (6) given below.

Differences in specific volume occurring in Figures 6 and 7 correspond to minor differences in the exact degree of filling of the samples, which is indicated in the respective figures.

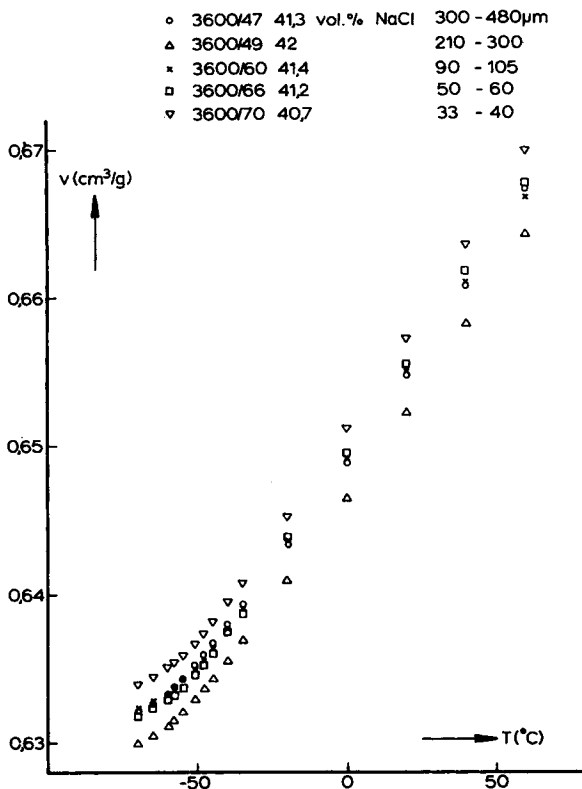


Fig. 7. Specific volume  $v$  as a function of temperature for polyurethane rubbers filled with 40 vol.-% of different filler fractions.

### Glass Transition Temperature in Relation to Filler Characteristics

Glass transition temperatures were determined from the data of Figures 6 and 7 in the following manner. The points for the specific volumes at  $0^{\circ}\text{C}$ . and at  $40^{\circ}\text{C}$ . were connected by a straight line. From the inclination of that line, the volume expansivity at  $20^{\circ}\text{C}$ . was determined and plotted in Figure 4. Further, the points for the specific volumes at  $-70^{\circ}\text{C}$ . and at  $-65^{\circ}\text{C}$ . were connected by a straight line. From the inclination of that line, the volume expansivity at  $-68^{\circ}\text{C}$ . was determined and plotted in Figure 4. Both straight lines were intersected, and from the intersection  $T_g$  was read.

In Table II, glass transition temperatures for all materials are arranged according to filler structure. Neither the degree of filler nor the size of filler has a significant effect on the glass transition temperature. Such effects, if present, would not exceed a shift of  $3^{\circ}\text{C}$ . for the whole range investigated. This is in accordance with the independence of the softening temperature of the transition of the shear moduli at 1 cycle/sec. of the filler characteristics, as published earlier.<sup>1</sup> Furthermore, it will be

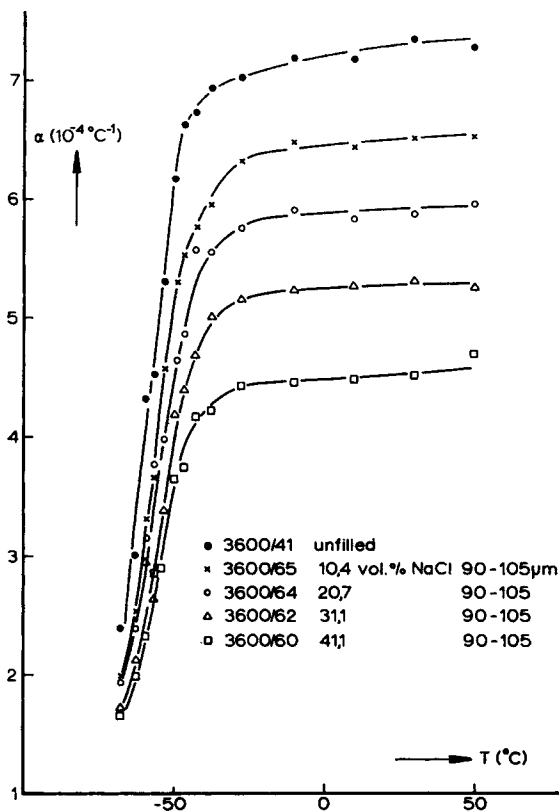


Fig. 8. Volume expansivity  $\alpha$  as a function of temperature for polyurethane rubbers filled with different amounts of fraction 4 (90-105  $\mu\text{m}$ ).

shown below that also the transition in bulk modulus is independent of filler characteristics.

In Figure 8 the volume expansivities are shown as functions of temper-

TABLE II  
Glass Transition Temperatures  $T_g$  in Relation to Filler Structure at a Cooling Rate of about 0.3°C./min.

		$T_g$ , °C.					
Filler content, vol. %	Fraction 1 (300-480 $\mu\text{m}$ )	Fraction 2 (210-300 $\mu\text{m}$ )	Fraction 4 (90-105 $\mu\text{m}$ )	Fraction 5 (50-60 $\mu\text{m}$ )	Fraction 6 (33-40 $\mu\text{m}$ )	Fraction 7 (8-20 $\mu\text{m}$ )	Fraction 8 (1-5 $\mu\text{m}$ )
10			-52.0		-51.6		-51.9
20		-50.2	-52.1		-51.1	-52.6	-52.2
30	-53.5	-51.0	-51.8		-52.2	-52.4	
40	-54.0	-52.0	-50.9	-51.8	-50.7		
50	-53.8						
Unfilled rubber				-51			

ature for a series of rubbers filled with increasing amounts of fraction 4 (90–105  $\mu\text{m}$ ). The levels of expansivity in the rubbery state depend considerably on the filler content. Furthermore, there seems to be a slight shift of the transition of the expansivity to higher temperatures with increasing filler content. That is not necessarily in disagreement with the observation of the independence of the glass transition temperature of filler content. The glass transition temperature will correspond with the midpoint of the transition range in expansivity, which is also influenced by the levels of  $\alpha$  in the glassy and rubbery range. No systematic change in the position of this midpoint is observed with filler content. A similar situation has been met already for the position of the softening temperatures in shear moduli transitions.<sup>1</sup>

### Thermal Expansion in Relation to Filler Characteristics

Finally, the relationship between density, thermal expansion, and composition is considered in more detail. It was mentioned already that the density of the samples measured at 20°C. showed a good correlation with the content of sodium chloride. This correlation was written:

$$d^{20} = d_r^{20} + (d_f^{20} - d_r^{20})c_{20} \quad (1)$$

We have now added a subscript 20 to the symbol  $c$  to indicate that the volume concentration of filler is a quantity changing with temperature.

Some care should be taken in defining filler content by volume. The filler content by weight,  $w$ , is a straightforward quantity, independent of temperature and directly determined from either the weight of the components during preparation or from chemical analysis of the composite material. Unfortunately,  $w$  is less appropriate for formulating the theoretical approaches to the mechanics of composite materials. From the filler content by weight,  $w$ , a filler content by volume,  $c$ , may be defined by means of the equations:

$$c = \frac{w/d_f}{w/d_f + (1 - w)/d_r} \quad (3)$$

$$1 - c = \frac{(1 - w)/d_r}{w/d_f + (1 - w)/d_r} \quad (4)$$

where  $d_f$  and  $d_r$  are densities of pure filler material and pure rubber at the temperature of consideration. Under this definition,  $c$ , though only slightly, depends on temperature, as the ratio  $d_f/d_r$  will depend on temperature. It should be realized that  $c$  is not a measure of the volume fraction of filler present as such in the composite material;  $c$  is rather the fractional volume taken by the filler in a mixture of the components at temperature  $T$ , prior to preparation of the composite material.

Assuming that thermal expansion of both components is unhampered in the composite material, and takes place in the same way as in a pure

mixture of the components, we would expect eq. (1) to be valid for all temperatures:

$$d = d_r + (d_f - d_r)c \quad (5)$$

Here  $d$ ,  $d_r$ , and  $d_f$  are the densities of the composite material, the rubber, and the filler at temperature  $T$ , and  $c$  is the volume content of filler as defined by eq. (3). In this case, the thermal expansion coefficient  $\alpha$  of the composite material could be calculated from the expansion coefficients of the components by the equation:

$$\alpha = \alpha_r + (\alpha_f - \alpha_r)c \quad (6)$$

In real cases, the thermal expansion of the one component will be hampered by the presence of the other component in the filled material, and the thermal expansion coefficient of the composite material should be smaller than the right-hand side of eq. (6). Simultaneously, the additivity of volumes expressed through an equation of type of eq. (5) should not be expected in general, but at one single temperature,  $T_0$ , at the utmost. This may be the temperature at which the composite material was prepared, if the process of preparation itself does not involve a volume contraction.

A theory of the thermal expansion of composite materials was formulated by Kerner.<sup>4,5</sup> Kerner used a model which had been considered earlier by Fröhlich and Sack<sup>6</sup> and by Van der Poel<sup>7</sup> for the calculation of mechanical properties of composite materials.

The problem is to predict the volume expansion coefficient  $\alpha$  of a composite solid, which consists of hard particles of shear modulus  $G_1$ , bulk modulus  $K_1$ , Poisson's ratio  $\mu_1$ , and volume expansion coefficient  $\alpha_1$ , dispersed in a soft binder of shear modulus  $G_2$ , bulk modulus  $K_2$ , Poisson's ratio  $\mu_2$ , and volume expansion coefficient  $\alpha_2$ . The volume concentration of the particles is  $c$ ; the shape and size of the particles do not enter the theory explicitly. All calculations are performed within the scope of Hookean thermoelastic theory for isotropic materials with coefficients of thermal expansion that are independent of temperature.

The composite solid is represented by a sphere whose inside has been replaced by the microscopic structure of the material: a composite sphere is considered which consists of three concentric spheres. The inner elastic sphere with material properties  $G_1$ ,  $K_1$ ,  $\mu_1$ , and  $\alpha_1$  of radius  $c^{1/3}$ , is surrounded by and fixed to a spherical shell of outer radius 1 and material properties  $G_2$ ,  $K_2$ ,  $\mu_2$ ,  $\alpha_2$ ; the latter is surrounded by and fixed to a shell of the homogeneous material of, still unknown, material properties  $G$ ,  $K$ ,  $\alpha$ , and outer radius  $R$ .

The thermal expansion of the composite sphere is calculated, and compared with the thermal expansion of a homogeneous sphere of material properties  $G$ ,  $K$ ,  $\alpha$ , and of radius  $R$ . Assuming the thermal expansion of both spheres to be identical, the following equation for  $\alpha$  results:

$$\alpha = \alpha_1 c + \alpha_2 (1 - c) - (\alpha_2 - \alpha_1) c (1 - c) \times \frac{(1/K_2) - (1/K_1)}{[(1 - c)/K_1] + (c/K_2) + (3/4G_2)} \quad (7)$$

The third term on the right-hand side of eq. (7) gives the deviation from the simple formula (6), and is a measure for the thermal stresses occurring in composite systems during temperature changes. This term is seen to be unequal to zero only if both expansion coefficients and both bulk compressibilities are different. Its order of magnitude is further seen to be proportional to  $G_2/K_2$  in all cases where this ratio is small.

Therefore, in the entire rubberlike region of the binder, the third term in eq. (7) will not contribute more than a few per cent to the volume expansivity of the composite solid. If the latter is prepared in the rubberlike region of the binder, the simple formula, eq. (6), and therefore also eq. (5), is expected to hold with very good approximation, and no considerable thermal stresses are built up, as long as the rubberlike region is not left. This is the reason why eqs. (1) and (5) are found to be valid, notwithstanding the fact that the materials are prepared at elevated temperatures and that the preparation involves contraction during the polymerization process.

Thermal expansion coefficients at 20°C. are plotted in Figure 4 and compared with the linear relation (6) with

$$\alpha_r = 7.23 \times 10^{-4} \text{°C.}^{-1}$$

$$\alpha_f = 1.13 \times 10^{-4} \text{°C.}^{-1}$$

No significant deviations from linearity are found in the  $\alpha$ - $c$  relation. In the same figure, the expansion coefficients in the glassy region are shown as function of filler content. It should be borne in mind, however, that the accuracy of the  $\alpha$  values in the glassy region is much less than that of the  $\alpha$  values in the rubbery region.

## RELATIONSHIP BETWEEN BULK MODULI AND FILLER CHARACTERISTICS

### Bulk Moduli versus Temperature for Unfilled Polyurethane Rubbers

The course of bulk moduli versus temperature is shown in Figures 9 and 10 for, respectively, Vulkollan 18/40 and three samples of unfilled polyurethane rubber based on linear polyether. Similarly to the behavior of the shear modulus<sup>1</sup> and the volume expansivity, the bulk modulus shows a softening region corresponding to the glass-rubber transition. The position of the glass-rubber transition in temperature is compared for both unfilled rubbers in Table III. From this table it is seen that the softening region in bulk modulus is about 15°C. lower than the softening region in shear modulus, which is in accordance with the frequency dependence of the glass-rubber transition. Further, the glass transition

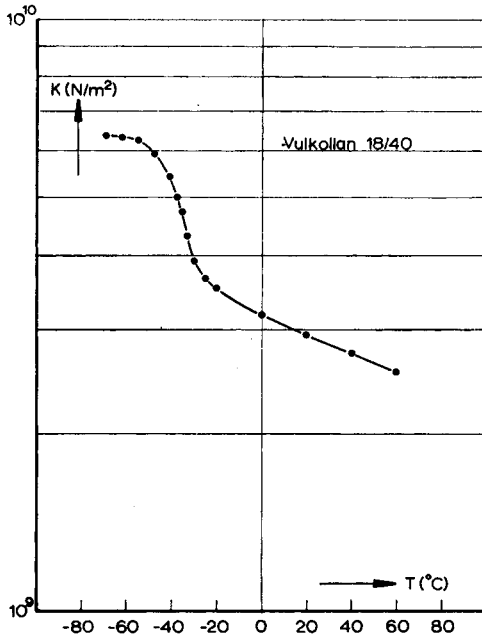


Fig. 9. Bulk modulus  $K$  as a function of temperature for Vulkollan 18/40 (measurement 4 min. after pressurization with 150 kg./cm.<sup>2</sup>).

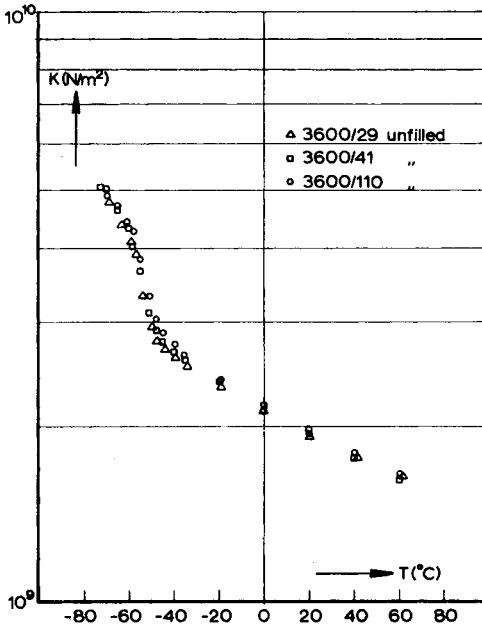


Fig. 10. Bulk modulus  $K$  as a function of temperature for three samples of unfilled polyurethane rubber prepared on different dates.



temperature is about 12°C. lower than the softening region in shear modulus.

TABLE III

Position of the Glass-Rubber Transition in Various Techniques for Different Rubbers

Material	Midpoint of softening region in shear, 1 cycle/sec., °C.	Midpoint of softening region in bulk modulus (4 min.), °C.	Glass transition temperature $T_g$ (cooling rate 0.3°C./min.), C.
Vulkollan 18/40	-26	-35.6	-35.5
Unfilled polyurethane rubbers based on linear polyether			
3600/29	-40	-56.5	-53.0
3600/41	-40	-55.3	-50.9
3600/110	-38	-53.8	-51.6

The transition in bulk modulus for an unfilled rubber is connected with a decrease to about half of its value in the glassy state, while the transition in shear modulus was found to be connected with a decrease to about 1/1000 of its value in the glassy state. The breadth of the transition is about the same, namely, 30°C., in both cases. The transition in bulk modulus is also less pronounced than the transition in shear modulus for another reason. While shear moduli show approximately temperature-independent levels in the glassy and rubbery state, the bulk moduli continue to decrease with temperature in the rubbery region also. This is clearly seen in Figure 9, where the transition is situated well within the accessible temperature range. It is not quite clear from this figure whether the bulk modulus will bend to a constant level in the glassy region or not.

No significant differences are found in the course of bulk modulus versus temperature for the three samples of the same composition prepared at different dates, as illustrated by Figure 10.

### Bulk Moduli versus Temperature for Filled Polyurethane Rubbers

Bulk moduli as a function of temperature have been determined for all samples cited in Table I. As an example, Figure 11 illustrates the influence of filler content on the course of the bulk modulus for samples containing different amounts of filler of the same fraction. Bulk moduli of samples containing different amounts of other filler fractions yield pictures which are very similar to that of Figure 11; these are not given here.

All filled and unfilled samples show a softening region where the bulk modulus drops to about one-half of its value in the glassy state. The position of the softening region does not depend on the content or size of filler.

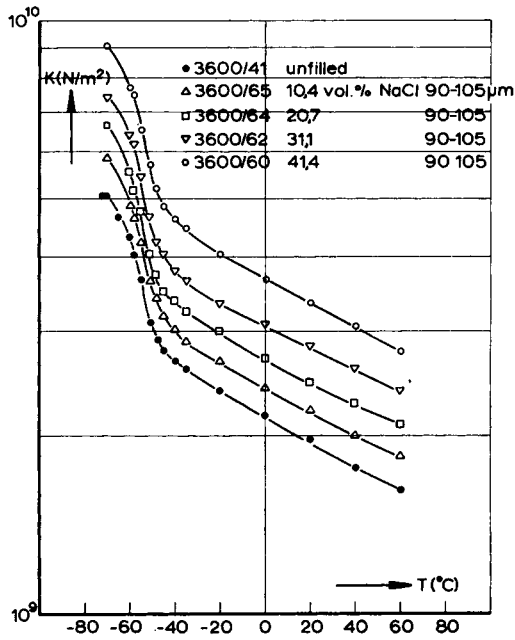


Fig. 11. Bulk modulus  $K$  vs. temperature for polyurethane rubber filled with different amounts of fraction 4 (90-105  $\mu\text{m}$ ).

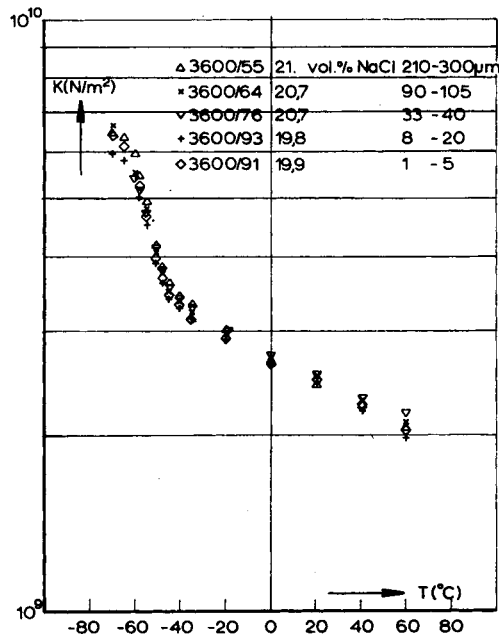


Fig. 12. Bulk modulus  $K$  vs. temperature for polyurethane rubber filled with 20 vol.-% of different fractions.

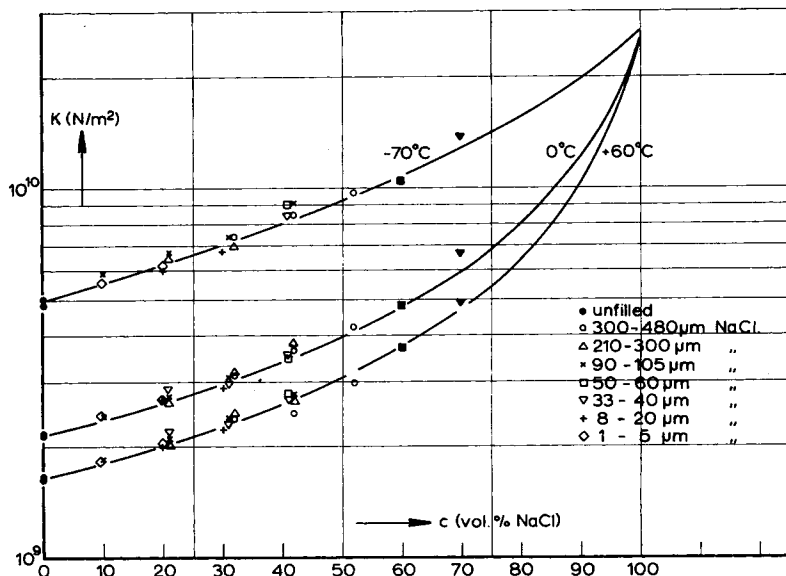


Fig. 13. Bulk moduli at  $-70$ ,  $0$ , and  $60^{\circ}\text{C}$ . as functions of filler concentration for various sodium chloride fractions. The line drawn through experimental points associated with the temperature of  $-70^{\circ}\text{C}$ . is the theoretical line due to eq. (9) with parameter values  $K_1/K_2 = 5.28$ ,  $\mu_2 = 0.36$ . The line drawn through experimental points associated with  $0^{\circ}\text{C}$ . is the theoretical line due to eq. (10) with parameter value  $K_1/K_2 = 11.9$ . The line drawn through the experimental points associated with the temperature of  $60^{\circ}\text{C}$ . is the theoretical line due to eq. (10) with parameter value  $K_1/K_2 = 15.2$ .

Absence of a significant influence of size on the course of bulk moduli is demonstrated in Figure 12. This figure shows bulk moduli versus temperature for samples containing about the same amount (20 vol.-%) of different filler fractions. Whenever smaller differences occur, these do not show up in significant trends as an influence of size.

Thus, the course of the bulk modulus versus temperature of the filled elastomer depends largely on the amount of filler only. Bulk moduli at all temperatures increase strongly with filler content.

TABLE IV  
Thermal and Elastic Constants of Sodium Chloride<sup>a</sup>

Temperature, $^{\circ}\text{C}$ .	Density $d$ , $\text{g./cm.}^3$	Volume expansivity $\alpha$ , $10^{-5}\text{C.}^{-1}$	Shear modulus $G$ $10^{10}\text{N./m.}^2$	Young's modulus $E$ , $10^{10}\text{N./m.}^2$	Bulk modulus $K$ , $10^{10}\text{N./m.}^2$	Poisson's ratio $\mu$
$-70$	2.184	10.14	1.30	4.92	2.64	0.189
$0$	2.168	11.13	1.28	4.54	2.55	0.204
$20$	2.163	11.34	1.28	4.43	2.53	0.208
$60$	2.152	11.97	1.26	4.25	2.49	0.215

<sup>a</sup> Values for the thermal constants of pure NaCl crystals according to Henglein,<sup>8</sup> values for the elastic constants of pure NaCl crystals according to Rose<sup>9</sup> and Durand.<sup>10</sup>  $G$ ,  $E$ , and  $\mu$  values given refer to the 0, [0, 1] direction of the crystal.

The values of bulk moduli at three temperatures are shown versus composition in Figure 13. The value at  $-70^{\circ}\text{C}$ . may be taken as representative for the glassy state and the value at  $0^{\circ}\text{C}$ . as representative for the rubbery state.\*

Moduli are plotted versus filler composition for various fractions and are seen to depend on the filler content only. The points indicated at 100% filler concentration in this graph are the values of the bulk modulus for pure sodium chloride crystals at the respective temperatures.

Values for the thermal and elastic constants of sodium chloride, as far as used in this report are given in Table IV.

### Discussion of Results; Theory of Bulk Moduli of Composite Materials

The results obtained for the bulk modulus-temperature curves for sodium chloride-filled urethane rubbers may well be described in terms of a simple macroscopic theory. This is the same theory which has been successfully used to describe the behavior of the same materials in shear<sup>1</sup> and in thermal expansion.

The composite solid is represented by the composite sphere already described above. The deformation of this composite sphere is calculated under hydrostatic pressure and is compared with the deformation of a homogeneous sphere of the unknown material. Assuming the volume changes of both spheres to be equal, one finds the following equation for the effective bulk modulus of the composite material:<sup>5,7</sup>

$$\frac{K}{K_2} = \frac{1 + 2 [(1 - 2\mu_2)/(1 + \mu_2)] [(K_2/K_1)(1 - c) + c]}{1 - c + c(K_2/K_1) + 2(K_2/K_1) [(1 - 2\mu_2)/(1 + \mu_2)]} \quad (9)$$

In many cases, the binder will be in the rubbery state, which means that  $\mu_2 = 1/2$ , or that  $G_2 \ll K_2$ ; in those cases eq. (9) may be written very simply:

$$1/K = (c/K_1) + [(1 - c)/K_2] \quad (10)$$

Bulk compliances then behave simply in an additive manner, the bulk compliance of the composite material being a linear function of the filler concentration.

In cases where the binder does not behave as a rubbery material, eq. (9) may be rewritten to estimate the deviations from additivity of both compliances. To this end,  $\mu_2$  is expressed by  $K_2$  and  $G_2$ , and eq. (9) is inverted; one thus obtains:

$$\frac{1}{K} = \frac{c}{K_1} + \frac{1 - c}{K_2} - \frac{c(1 - c) [(1/K_2) - (1/K_1)]^2}{(3/4G_2) + (c/K_2) + [(1 - c)/K_1]} \quad (11)$$

Comparison of this theory with experimental results found in this investigation is made in Figure 13. The solid line drawn through the ex-

\* Remember the restriction that no real glassy or rubbery levels exist for the bulk modulus. Therefore, the choice of a representative temperature is quite arbitrary.

perimental points belonging to moduli at 60°C., is the theoretical modulus concentration dependence according to eq. (9) with the parameter values  $K_1/K_2 = 15.2$ ,  $\mu_2 = 1/2$ ;<sup>\*</sup> the solid line drawn through the experimental points belonging to moduli at 0°C., is the theoretical modulus concentration dependence according to eq. (9) with the parameter values  $K_1/K_2 = 11.9$ ,  $\mu_2 = 1/2$ ;<sup>†</sup> the line drawn through the experimental points belonging to moduli at -70°C. is the theoretical modulus concentration dependence according to eq. (9) with the parameter values  $K_1/K_2 = 5.28$ ,  $\mu_2 = 0.36$ .<sup>‡</sup>

Within the accuracy of the measurement, excellent agreement is found between theory and experiment.

Concluding, it may be stated that the bulk modulus versus temperature curve of the filled elastomer may be well predicted through the Fröhlich-Sack-Van der Poel theory from the bulk modulus versus temperature curve of the unfilled rubber, the volume concentration, and the elastic properties of the filler particles. In some cases, information on Poisson's ratio of the binder may also be needed for this purpose.

No comparison with results from the literature on bulk moduli of filled rubbers can be performed here, as no such data are at present available to the authors.

Having information on the bulk modulus versus temperature behavior, and on the shear modulus versus temperature behavior of the same samples of filled rubbers, it should be possible to discuss the course of Poisson's ratio with temperature, which is a very important quantity for the knowledge of the stress distribution in case-bonded grains. This matter will be dealt with in a further publication.

### Grueneisen's Constant in Relation to Filler Characteristics

Another quantity, which is of extreme importance for the calculation of thermal stresses occurring in case-bonded grains, is the so-called Grueneisen constant  $\alpha K$ , which is the product of volume expansivity and bulk modulus. This was introduced by Grueneisen,<sup>11</sup> who proposed the equation

$$\alpha K/c_v = \gamma \quad (12)$$

<sup>\*</sup>  $K_1 = 2.49 \times 10^{10}$  N./m.<sup>2</sup> = bulk modulus of sodium chloride at +60°C.;  $K_2 = 1.64 \times 10^9$  N./m.<sup>2</sup> = bulk modulus of pure rubber at +60°C.;  $G_2 = 1.34 \times 10^8$  N./m.<sup>2</sup> = shear modulus of pure rubber at +60°C., extrapolated to the characteristic time (4 min.) of the bulk modulus.

<sup>†</sup>  $K_1 = 2.55 \times 10^{10}$  N./m.<sup>2</sup> = bulk modulus of sodium chloride at 0°C.;  $K_2 = 2.15 \times 10^9$  N./m.<sup>2</sup> = bulk modulus of pure rubber at 0°C.;  $G_2 = 1.32 \times 10^8$  N./m.<sup>2</sup> = shear modulus of pure rubber at 0°C., extrapolated to the characteristic time (4 min.) of the bulk modulus.

<sup>‡</sup>  $K_1 = 2.64 \times 10^{10}$  N./m.<sup>2</sup> = bulk modulus of sodium chloride at -70°C.;  $K_2 = 5.00 \times 10^9$  N./m.<sup>2</sup> = bulk modulus of pure rubber at -70°C.;  $G_2 = 1.47 \times 10^8$  N./m.<sup>2</sup> = shear modulus of pure rubber at -70°C., extrapolated to the characteristic time of 4 min., by a temperature shift of 11°C. from the results of measurement at 1 cycle/sec.<sup>2</sup> From that extrapolation,  $\mu_2 = (3K_2 - 2G_2)/(6K_2 + 2G_2)$  is estimated to be approximately equal to 0.36.

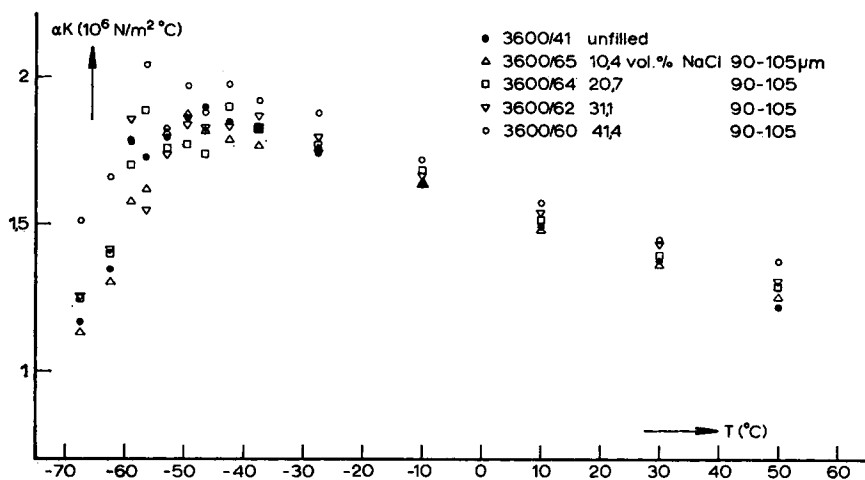


Fig. 14. Grueneisen's parameter,  $\alpha K$ , as a function of temperature for a series of polyurethane rubbers filled with different amounts of fraction 4 (90–105  $\mu\text{m}$ ).

where  $c_v$  is the specific heat at constant volume per unit volume, and where  $\gamma$  should be a temperature-independent numerical constant only slightly varying for different materials ( $1 < \gamma < 3$ ).

Freudenthal<sup>12</sup> discussed the importance of Grueneisen's constant in thermal stress problems, and argued that also the product  $\alpha K$  itself should be a weakly varying property.

$\alpha K$  gives directly the thermal pressures in a construction under three-dimensional restraint associated with a temperature change of 1°C.; together with Poisson's ratio,  $\alpha K$  determines also the magnitude of thermal stresses in more general cases.

From the independence of bulk moduli and of volume expansivities it follows immediately that also  $\alpha K$  is independent of the grain size of the filler material. Its temperature dependence and its dependence on filler content are illustrated in Figure 14, where  $\alpha K$  is plotted for a series of rubbers filled with increasing amounts of fraction 4 (90–105  $\mu\text{m}$ ).

It is seen that Grueneisen's constant passes through a definite maximum, which is situated in the glass-rubber transition region. On the other hand, the occurring variations with temperature in  $\alpha K$  are smaller than the variations found in both factors  $\alpha$  and  $K$ . Especially,  $\alpha$  and  $K$  both depend definitely on filler content, while the dependence of product  $\alpha K$  on filler content seems to be very weak.

This may be an important indication for thermal stress analysis in materials of a filler content that is not known exactly.

## CONCLUSIONS

(1) It has been possible to prepare filled urethane rubbers in which the filler content could be varied between 0 and 50 vol.-%, accurately to within 0.2% in most cases.

(2) Densities at 20°C. are proportional to filler content and independent of filler size.

(3) Thermal expansion curves and bulk moduli show glass-rubber transitions for all filled and unfilled materials investigated. The corresponding transition temperatures are independent of filler size and filler content. The glass transition temperature obtained from thermal contraction measurements is about 3°C. higher than the midpoint of the glass-rubber transition of bulk moduli with a characteristic time of 4 min. The latter are about 15°C. lower than the midpoints of the glass-rubber transition of shear moduli at 1 cycle/sec.

(4) Thermal expansion coefficients in the rubbery and in the glassy state are independent of filler size and linear functions of the filler content.

(5) Bulk moduli versus temperature curves of filled rubbers are independent of filler size and increase with filler content; they may be predicted from the bulk modulus versus temperature curve of the unfilled rubber, the elastic properties of the filler, and the filler content.

(6) A simple macroscopic theory (Fröhlich-Sack-Van der Poel) which was appropriate to describe results on shear moduli versus temperature curves of the same filled rubbers is sufficient to describe the behavior in thermal expansion and under hydrostatic pressure in complete agreement with experimental accuracy.

(7) Grueneisen's coefficients are independent of filler size and only weakly dependent on filler content. They vary between 1.1 and  $2.1 \times 10^6$  N./m.<sup>2</sup>/°C. and run through a maximum in the glass-rubber transition region.

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### References

1. Schwarzl, F. R., H. W. Bree, and C. J. Nederveen, *Proceedings 4th International Congress of Rheology, Providence*, 1963, in press.
2. Heydemann, P., and H. D. Guicking, *Kolloid-Z.*, **193**, 16 (1964).
3. Surland, C. C., *Exptl. Mech.*, **2**, 110 (1962).
4. Kerner, E. H., *Proc. Phys. Soc.*, **B69**, 802 (1956).
5. Kerner, E. H., *Proc. Phys. Soc.*, **B69**, 808 (1956).
6. Fröhlich, H., and R. Sack, *Proc. Roy. Soc. (London)*, **A185**, 415 (1946).
7. Van der Poel, C., *Rheol. Acta*, **1**, 198 (1958).
8. Henglein, A., *Z. Physik. Chem.*, **115**, 97 (1925).
9. Rose, F. E., *Phys. Rev.*, **49**, 50 (1936).
10. Durand, M. A., *Phys. Rev.*, **50**, 449 (1936).
11. Grueneisen, E., *Ann. Physik*, **26**, 393 (1908).
12. Freudenthal, A. M., *J. Appl. Phys.*, **31**, 434 (1960).

### Résumé

On a préparé des substances modèles au départ d'un caoutchouc de polyuréthane chargé de différentes quantités de plusieurs fractions de chlorure de sodium. On a employé huit fractions de charge possédant des dimensions situées entre 1 et 480  $\mu\text{m}$ . On a fait varier la quantité de charge entre 0 et 50 pour cent en volume. On décrit une méthode expérimentale au moyen de laquelle la dilatation thermique et le module global d'une substance isotropique peuvent être déterminés simultanément en fonction de la température. Les substances ont été étudiées du point de vue de la dilatation thermique et du module global. Tous les échantillons chargés et non-chargés présentent une transition vitreuse-caoutchouteuse, température à laquelle le coefficient de dilatation thermique augmente considérablement et le module global diminue brusquement. Ces températures ne dépendent pas de la quantité ni de la dimension de la charge. Les valeurs des modules globaux et des coefficients de dilatation thermique sont indépendantes de la dimension de la charge, mais dépendent fortement de la fraction en volume de la charge. Ces valeurs peuvent être prévues au moyen d'une théorie macroscopique simple (Fröhlich-Sack-Van-der Poel), qui décrit le module global, la dilatation thermique et la densité des matériaux du mélange en fonction des propriétés correspondantes des composants et de leurs quantités relatives.

### Zusammenfassung

Modellsubstanzen wurden aus einem mit verschiedenen Mengen verschiedener Natriumchloridfraktionen gefüllten Polyurethankautschuk dargestellt. Acht Füllstofffraktionen mit Grössen zwischen 1 und 480  $\mu\text{m}$  wurden verwendet. Die Menge des Füllstoffs wurde zwischen 0 und 50 Volumsprozent variiert. Die experimentelle Methode zur gleichzeitigen Bestimmung der thermischen Ausdehnung und des Kompressionsmoduls eines isotropen Materials in Abhängigkeit von der Temperatur wird beschrieben. Die Stoffe wurden in Bezug auf thermische Ausdehnung und Kompressionsmodul untersucht. Alle gefüllten und ungefüllten Proben zeigen eine Glas-Kautschukumwandlung, bei welcher Temperatur der thermische Ausdehnungskoeffizient beträchtlich ansteigt und der Kompressionsmodul scharf absinkt. Diese Temperatur hängt weder von der Menge noch von der Grösse des Füllstoffs ab. Die Werte des Kompressionsmoduls und des thermischen Expansionskoeffizienten sind von der Füllstoffgrösse unabhängig, zeigen jedoch eine beträchtliche Abhängigkeit von Volumbruch des Füllstoffs. Die Werte kann durch eine einfache makroskopische Theorie (Fröhlich-Sack-Van der Poel) erklärt werden, in welcher der Kompressionsmodul, die thermische Ausdehnung und die Dichte des zusammengesetzten Materials durch die entsprechenden Eigenschaften der Komponenten und ihre relative Menge ausgedrückt wird.

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