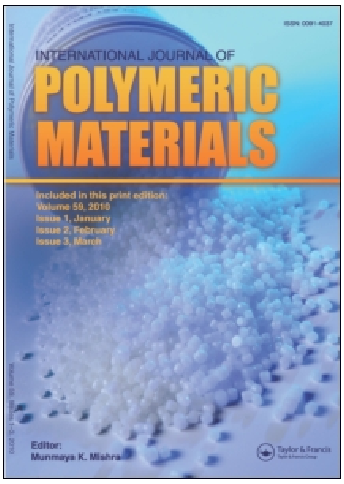

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Effect of Crosslinking Density and Dilution during Polymerization on the Stress-Strain and Viscoelastic Behaviour of (2-Hydroxyethyl Methacrylate) Networks in Dry and Swollen States filled with SiO_2

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Linear viscoelastic and stress-strain behaviour of poly(2-hydroxyethyl methacrylate) PHEMA networks filled with SiO_2 and prepared by crosslinking copolymerization has been investigated. The main attention was devoted to the effect of the volume concentration of the filler within the range $v_f = 0 - 0.194$, concentration of the crosslinking agent (ethylene dimethacrylate) within the concentration range $c = 0.13 - 7.84\%$, and water present during polymerization with the volume fraction of water ranging from 0.0 to 0.75. It was established that an increasing concentration of the filler had as its consequence a rapid increase in the modulus in the rubberlike region; this effect is more pronounced than in the case of natural rubber filled with active fillers. The effect of the filler decreases with swelling, which is in accordance with the assumption that the polymer-water interactions are stronger than the polymer-filler interactions. The presence of water during polymerization also leads to a decrease in the effect of SiO_2 in both dry and swollen systems. With increasing concentration of the filler, the retardation spectra are shifted toward longer times, and their slopes in the main transition region become smaller; this effect, however, is not pronounced on the whole. Whereas the concentration of the crosslinking agent affects the viscoelastic behaviour most, the water content during polymerization has no effect at all.

INTRODUCTION

The presence of the filler affects the mechanical behaviour of the polymers both in the main transition region and above all in the rubberlike state (cf. Ref. 1). The changes of properties of polymers due to filler are explained in terms of physical or chemical interactions of polymer molecules with the filler particles. In this respect, particles of carbon black having a large specific surface and a composition similar to that of a hydrocarbon chain are the most effective. Of the other fillers, SiO_2 exhibits the same activity in spite of its hydrophilic character; its particles have a specific area comparable with that of the carbon black particles.

Poly(2-hydroxyethyl methacrylate) networks (further PHEMA networks), if measured in a swollen state or at higher temperatures, have properties similar to those of natural or synthetic rubber at room temperature; in the dry state, however, the glass transition temperature, T_g of PHEMA, is higher by more than 150°.[2] The viscoelastic and equilibrium behaviour of this polymer prepared under various conditions, has been studied earlier in this laboratory (cf. Refs. 2–5) and elsewhere (cf. Refs. 6, 7). It was established that in the main transition region the effect of the hydroxyl groups of the side chains manifested itself in the shifting of the viscoelastic functions toward longer times.[2] On the contrary, the degree of crosslinking and network defects, sensitive to the preparation conditions, represent the main factors which influence the properties of the PHEMA network in the rubberlike state.[3-7]

It has been the aim of the present work to explain the effect of the concentration of the SiO_2 particles (Ultrasil VN-3, Degussa, W. Germany) upon the viscoelastic and stress-strain behaviour of the PHEMA networks, prepared by crosslinking copolymerization at various concentrations of water and the crosslinking agent. SiO_2 was selected intentionally with respect to the hydrophilic character of the particles.

EXPERIMENTAL PART

Preparation of samples. Samples were prepared by the crosslinking copolymerization of 2-hydroxyethyl methacrylate with a low content of ethylene dimethacrylate as the crosslinking agent and in the presence of water. A mixture of the monomers and water was mixed mechanically with a corresponding amount of the filler in a mortar. An initiator (isopropyl percarbonate, $c_i = 10^{-2}$mol/l) was added, and the mixture was polymerized between two polytetrafluorethylene (Teflon) plates at 55°C for approximately 4 hours. From plates having approximate dimensions 150 × 100 × 1 mm, specimens were cut out to be used in the measurements of the mechanical characteristics. All samples were extracted with distilled water at 100°C for 8 hours and then dried in the vacuum of an oil pump for approximately 14 days. For measurements in the swollen state, some of the samples were swollen with water to equilibrium. To investigate the effect of concentrations of the filler, crosslinking agent, and diluent during polymerization, three sets of polymers were prepared; their composition is given in Table I. Similar series of polymers without filler were also prepared for reasons of comparison.

TABLE I

Viscoelastic and equilibrium parameters of dry poly(2-hydroxyethyl methacrylate) samples containing Ultrasil VN-3

Sample	v_f	c %	v_o	T_S °C	G_o kp cm^{-2}	G_o^0 kp cm^{-2}	T_S^0
Effect of concentration of the filler							
1	0	0.13	0.60	137	2.6	2.6	137
2	0.033	0.13	0.60	137	—	2.6	137
3	0.065	0.13	0.60	138	4.0	2.6	137
4	0.093	0.13	0.60	138	7.0	2.6	137
5	0.119	0.13	0.60	140	10.5	2.6	137
6	0.130	0.13	0.60	140	—	2.6	137
7	0.170	0.13	0.60	142	31.0	2.6	137
8	0.194	0.13	0.60	144	58.0	2.6	137
Effect of concentration of the crosslinking agent							
9	0.119	0.13	0.60	140	10.5	2.6	137
10	0.119	0.22	0.60	139	—	—	137
11	0.119	0.46	0.60	137	10.5	2.5	136
12	0.119	1.00	0.60	136	17.0	3.5	140
13	0.119	1.95	0.60	140	15.5	4.5	144
14	0.119	3.86	0.60	152	27.5	7.8	148
15	0.119	7.84	0.60	165	48.0	11.1	161
Effect of concentration of water during polymerization							
16	0.093	0.13	1.00	138	23.6	4.1	137
17	0.093	0.13	0.80	140	12.0	3.6	141
18	0.093	0.13	0.60	138	7.0	2.6	139
19	0.093	0.13	0.40	137	5.0	2.5	137
20	0.093	0.13	0.25	—	—	—	—

Viscoelastic measurements. Viscoelastic measurements in creep were made on dry samples by means of a uni-directional elongation in nitrogen atmosphere and within the temperature range 80–200°C, using a procedure described earlier.[2] The creep compliance in elongation in the linear deformation region, $D(t)$, was measured within the time interval from 3 to 300 seconds and then conventionally expressed in terms of shear compliance, using a simplified relationship $J(t) = D(t)/3$. With the aid of the method of reduced variables,[8] superimposed curves were constructed for the individual samples by plotting the values of $J_p(t) = J(t)T\rho/T_o\rho_o$ against t/a_T for a reference temperature $T_o = 115°\text{C}$ (Figure 1); T is the temperature of measurement, ρ and ρ_o are system densities at temperatures T and T_o, respectively; a_T is the shift factor which displaces the viscoelastic curves from T to T_o. From the temperature dependence of the shift factors, a_T, which corresponded to the WLF equation,[8]

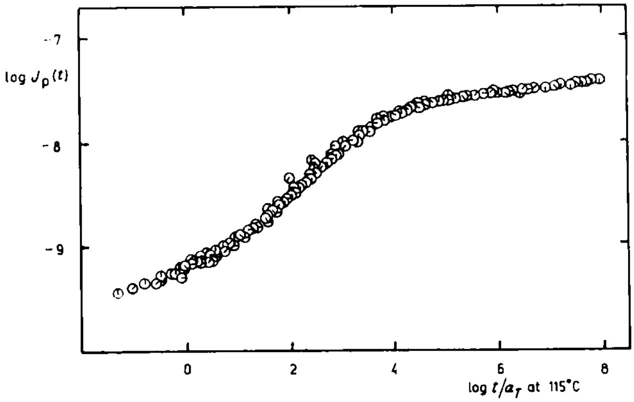

FIGURE 1 An example of the dependence of $J_p(t)$ (cm^2 dyn^{-1}) vs. $t/a_T(s)$ of Sample 7. Temperatures of measurement: ⦶ 99.6, ⊘ 103, ⊖ 106.7, ⦸ 110, ⦶ 114, ⊘ 117.5, ⊖ 122.3 ⦸ 126.9, ⦶ 132.5, ⊘ 136.8, ⊖ 141.2, ⦸ 155.8, ⦶ 167.5°C.

the characteristic temperatures T_S were determined (T_S^0 in the case of unfilled samples) (Table I). Retardation spectra, $L(\tau)$ were calculated from the superimposed curves, using the second approximation method suggested by Schwarzl-Stavermann.[9]

Stress-strain measurements of polymers in the rubberlike state. The stress-strain measurements were made on a simple device[3] with samples in the dry state (temperature of measurement $T = 180°$) and with samples swollen with water to equilibrium (temperature of measurement $T = 25°C$). The samples, 60 × 10 × 1 mm in size, with two points marked on them, were fixed in clamps and subjected to constant load. The distance between the points was read each time after five minutes' loading; the load was then increased, and the procedure repeated. 10–15 points were measured for each sample; from these, elastic parameters C_1 and C_2 of the Mooney-Rivlin equation[10] in the form

$$\sigma v_2^{1/3} = 2(C_1 + C_2/\lambda)(\lambda - \lambda^{-2}) \tag{1}$$

were calculated by means of the least squares method;[3,7] σ is the stress referred to the original dry cross-section of the samples, v_2 is the volume fraction of the filled polymer in an equilibrium swollen state, and λ is relative elongation. For dry samples, crosslinked or filled to a higher degree, which cracked already at smaller elongations ($\lambda \approx 1.1$), only modulus G_o was measured (G_o^0 in the case of unfilled samples), calculated with the aid of the relationship $\sigma v_2^{1/3} = G_o(\lambda - \lambda^{-2})$, assuming that $G_o = 2(C_1 + C_2)$.

Degree of swelling. v_2 (v_2^0 in the case of unfilled samples) was determined from the relationship $v_2 = (G_d/\rho_d)/(G_s/\rho_s)$, where G_d and G_s are weights,

ρ_d and ρ_s are densities of the dry and swollen samples, respectively. The value of the equilibrium degree of swelling of a filled system referred to the pure polymer, v_2^p, was defined by the relationship $v_2^p = (G_d/\rho_d - G_f/\rho_f)/(G_s/\rho_s - G_f/\rho_f)$, where G_f is the weight of the filler in the sample and ρ_f is the density of the filler (for SiO_2, $\rho_f = 1.95$ g/cm^3). The sample densities were determined by double weighing; dry samples were weighed in cyclohexane, the swollen ones in water. The density of the filler was determined pycnometrically in water.

RESULTS AND DISCUSSION

1 Effect of Concentration of the Filler

Dry polymers. With increasing content of the filler the transition parts of the superimposed curves and retardation spectra are shifted toward longer times, and their slopes decrease in dependence on log t/a_T, resp. log τ. At the same time there is a decrease in the reduced compliance values, log $J_p(t)$, and also a decrease in the maxima of the retardation spectra in the rubberlike region (Figures 2a, 3a). The shift of viscoelastic curves in the main transition region by an order of about 1.5 is correspondingly reflected in an increase of T_S by 7°C (Table I). An approximately double value of the volume fraction, v_f, of the glass beads in polyisobutylene corresponds to the same increase of T_S (or the same shift of viscoelastic spectra toward longer times).

A decrease in compliance in the rubberlike region, $J_p(t)$, with increasing concentration of the filler corresponds to an increase in the modulus G_o in the dry state (Table I), which can be represented by the relationship

$$G_o(v_f) = G_o^0(v_f) \tag{2}$$

where X is the multiplication factor. The function X rapidly increases with increasing v_f; this increase is much faster than in the case of filled rubbers[1] (for instance, in comparison with natural rubber filled with the HAF carbon black[12]). To describe the dependence of X on v_f, an empirical expression was suggested[13] for the viscosity of suspensions:

$$X = \left(1 + \frac{a v_f}{1 - b v_f}\right)^2 \tag{3}$$

where the constants $a = 1.25$ and $b = 1.28$ describe well also the behaviour of rubbers filled with inactive filler,[1] such as e.g. the system polyurethane—NaCl.[14] For $v_f \rightarrow 0$, Eq. (3) acquires the form of Einstein's equation: $X = 1 + 2.5\, v_f$, which was derived theoretically for similar systems (cf. Ref. 1); $X \rightarrow \infty$ for $v_f \rightarrow 0.78$, which is approximately the limit value of a volume fully occupied by spheres of the same diameter ($v_f = 0.74$). In the concentration

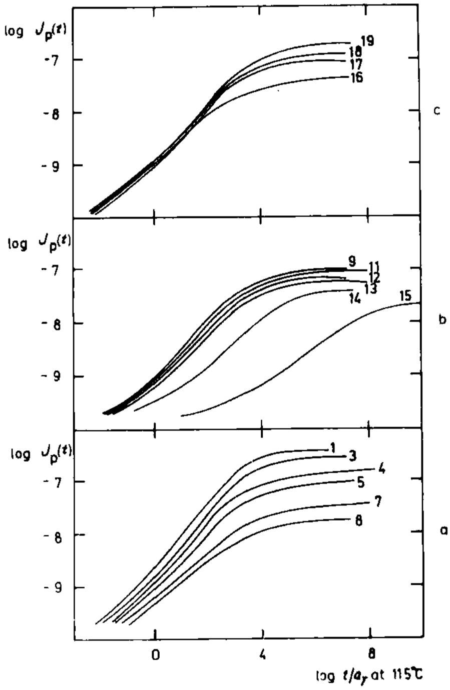

FIGURE 2 Dependence of $J_p(t)$ (cm^2 dyn^{-1}) on $t/a_T(s)$, referred to the reference temperature T_0 = 115°C.

a—effect of concentration of the filler; b—effect of concentration of the crosslinking agent; c—effect of dilution during polymerization. Designation of samples is given in Table I.

region $v_f \leqslant 0.50$ and for the modulus of the filler $G_f \geqslant 10^5 . G_o^0$ the X values in Eq. (3) agree with sufficient accuracy with the theoretical prediction.[15] Relationship (3) proved to be suited for a description of the dependence of X on v_f established by the authors, either if approximately triple constants are used: $a = 4.26$ and $b = 4.05$ (Figure 4), or under assumption that for the apparent SiO_2 fraction in PHEMA, v_f^*, it holds that $v_f^* \approx 3v_f$. The increase in v_f can be visualized, e.g., as caused by an immobilization of the polymer in the surroundings of the filler due to the strong interactions between the filler and the polymer, which in its turn leads to an apparent increase by 1.44 times in the radius of the filler particles. This result is in qualitative agreement with the previously established changes in T_S and the displacements of viscoelastic functions toward longer times.

Swollen polymers. The variation of the G_0 modulus of a filled polymer in the swollen state with v_f is much smaller (Table II, Figure 4); if the same procedure is used, it can be stated that $v_f^* \approx 1.5\, v_f$. In this case, the effect of the

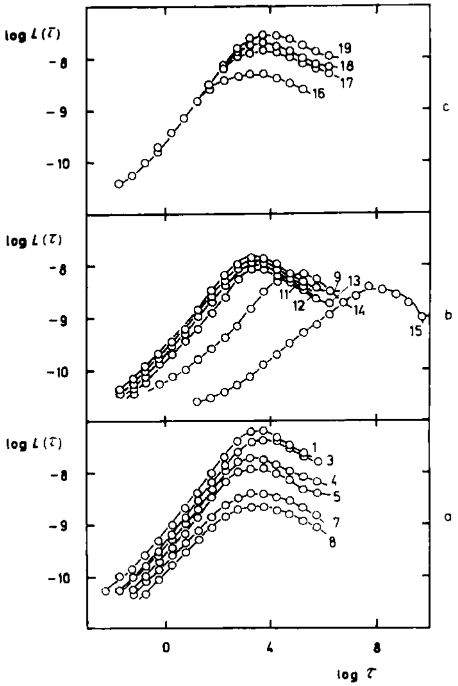

FIGURE 3 Retardation spectra $L(\tau)$ ($cm^2\ dyn^{-1}$) of samples in Figure 2.

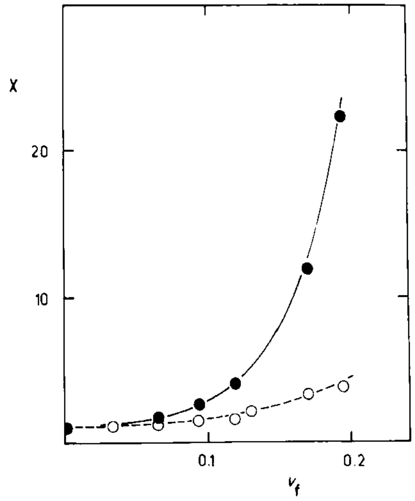

FIGURE 4 Dependence of X on v_f.

Values obtained by measuring samples: (●) in the dry state, $T = 180°C$; (○) in a state swollen with water to equilibrium, $T = 25°C$; (——) and (- - -): calculated courses according to Eq. (3) and (4), respectively.

TABLE II

Equilibrium parameters of swollen poly(2-hydroxyethyl methacrylate) gels containing Ultrasil VN-3

Sample	G_o kp cm^{-2}	G_o^0 kp cm^{-2}	v_2	v_2^0	v_{2p}	C_1 kp cm^{-2}	C_2 kp cm^{-2}
Effect of concentration of the filler							
1	—	1.47	—	0.527	0.527	0.65	0.82
2	1.58	1.47	0.534	0.527	0.526	0.71	0.87
3	1.77	1.47	0.541	0.527	0.525	0.81	0.96
4	2.18	1.47	0.550	0.527	0.526	0.84	1.34
5	2.38	1.47	0.561	0.527	0.528	0.70	1.68
6	3.10	1.47	0.564	0.527	0.529	0.69	2.32
7	4.80	1.47	0.581	0.527	0.535	—	—
8	5.60	1.47	0.588	0.527	0.536	—	—
Effect of concentration of the crosslinking agent							
9	2.38	1.47	0.561	0.527	0.529	0.70	1.68
10	2.98	1.53	0.559	0.526	0.528	0.97	2.01
11	3.91	1.61	0.565	0.532	0.534	1.87	2.04
12	5.01	2.32	0.575	0.536	0.544	3.87	1.14
13	8.06	3.66	0.549	0.553	0.563	7.03	1.03
14	15.80	6.84	0.620	0.588	0.590	—	—
15	33.60	16.60	0.667	0.631	0.638	—	—
Effect of concentration of water during polymerization							
16	5.03	2.21	0.587	0.544	0.563	1.79	3.24
17	3.95	2.24	0.569	0.542	0.545	1.28	2.67
18	2.18	1.47	0.550	0.527	0.526	0.84	1.34
19	1.37	1.23	0.531	0.509	0.507	0.50	0.87
20	1.14	1.08	0.520	0.475	0.496	0.26	0.88

filler is comparable with the effect of the carbon black in natural rubber and satisfies Guth's equation[16]

$$X = 1 + 0.67 f v_f + 1.62 f^2 v^2_f \tag{4}$$

better than Eq. (3); f being an empirical constant related to the assymmetry of the filler particles. In our case, $f = 4.5$ (Figure 4), whereas in the case of natural rubber filled with carbon black[12] of the MT and HAF types, $f = 1$ and $f = 6.5$, respectively.

In the case of samples swollen to equilibrium the increase in X is connected with the increase in the constant C_2 (Table II), similarly to natural rubber.[12] On the other hand, C_1, which is a measure of the number of permanent crosslinks, is independent of the filler content. It can be concluded, therefore, that the dependence of X on v_f, similarly to the increase in T_S and the shift of superimposed curves toward longer times, are determined, in the first place, by physical interactions polymer-filler, whereas the changes in the concentration of crosslinks is probably minimum. The equilibrium degree of swelling, v_2, increases with increasing concentration, v_f, while $v_2{}^p$, i.e. the degree of swelling of the pure polymer in a filled system, remains almost constant and identical with $v_2{}^0$. This means that either the surface of the filler does not absorb any water during swelling of the filled polymer, and that the filler also does not limit the swelling of the polymer, or that the absorption on one part of the surface of the filler (which e.g. in the case of monolayer would reduce v_2 by 0.02 for $v_f = 0.12$) is compensated by a decrease in the swelling of the polymer in a close vicinity of the remaining part of the surface of the filler. The former explanation can be considered more likely, owing to the agreement between the values of $v_2{}^p$ and $v_2{}^0$, which has also been established for another two series of samples (Table II). The decrease in the activity of the filler, reflected in a decrease of the dependence of X on v_f due to swelling can be explained by the fact the interaction polymer-water is stronger than the interaction polymer-filler. Swelling leads to an interaction of the bonds polymer-filler, and thus to a smaller effect of filler upon $v_f{}^*$. A similar, although much less pronounced effect, was observed with natural rubber.[12]

Viscoelastic functions. To obtain a more detailed characterization of the filler effect upon the shape and position of viscoelastic functions in the main transition region the superimposed curves (Figure 2a) must be compared at corresponding temperature states, i.e. they all must be shifted to the same distance from T_S in the WLF equation. The volume effect of the filler in the system can be excluded, if the superimposed curves are reduced to unfilled polymer by plotting[11]

$$J_p{}^0(t) = J_p(t)\,(T_o\rho_o/T_x\rho_x)\rho_x/\rho_x{}^0 \tag{5}$$

where $T_x = T_o + (T_S - T_S{}^0)$, $T_o = 115°\mathrm{C}$, ρ_o and ρ_x, are densities of the filled polymer at temperatures T_o and T_x, respectively; $\rho_x{}^0$ is the density of the unfilled polymer at T_x. The curves of compliance $J_p{}^0(t)$ coincide well in the region of short times (in the vicinity of the glassy region); the differences between $J_p{}^0(t)$ increase with increasing time (Figure 5).

The volume effect of the filler upon viscoelastic functions thus plays a decisive role in the glass transition region. The effect of the filler-polymer interactions gradually appears with increasing time and a release in the mobility of the main chain; as a consequence, the slope $\log J_p{}^0(t)$ vs. $\log t/a_T$ in the main transition region decreases with increasing content of filler. The observed change in the slope of the system PHEMA-SiO$_2$ is much more pronounced than in the case of filled polyisobutylene.[11] Reduced compliances $J_p{}^0(t)$ differ most in the region of long times; this means that the effect of the filler-polymer interactions in this region is at its highest. The changes in the compliances $J_p(t)$ in the rubberlike region are quantitatively determined by the multiplication

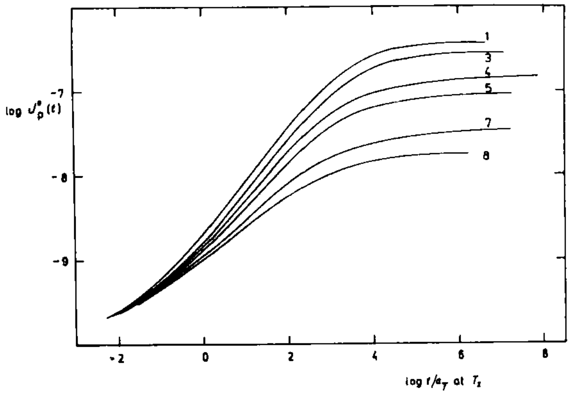

FIGURE 5 Dependence of $J_p^0(t)$ (cm^2 dyn^{-1}) on log $t/a_T(s)$ of samples prepared with a varying concentration of the filler.
Reduced to T_X.

factor X in Eq. (3), and the curves $J_p^*(t) = J_p(t)XT_0\rho_0/T_x\rho_x$, reduced to the corresponding temperatures T_x, coincide (Figure 6). The effect of the filler volume could manifest itself in the magnitude of X by 11% at the utmost within the concentration range used by the authors; which means that this magnitude is determined, in the first place, by the polymer-filler interaction. It can be said, therefore, that the volume effect of the filler included in Eq. (5) and the effect of the filler described by the factor X in Eq. (3) are limit cases of the total effect of the filler upon the course of the viscoelastic functions from the glassy into the rubberlike region.

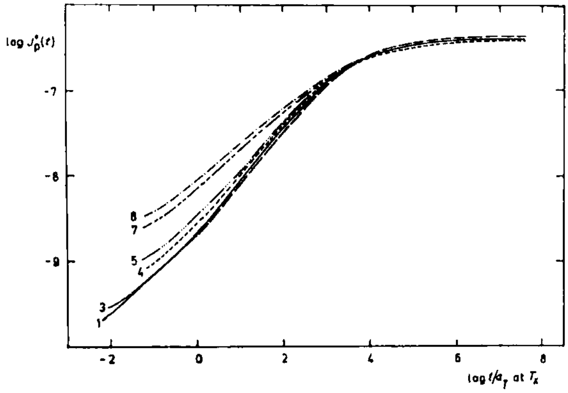

FIGURE 6 Dependence of $J_p^*(t)$ (cm^2 dyn^{-1}) on t/a_T (s) of samples in Figure 5.
Reduced to T_X.

2 Effect of Concentration of the Crosslinking Agent

Stress-strain properties. It holds, on the basis of the kinetic theory of rubber-like elasticity,[18] that

$$G_o^0 = \langle \alpha^2 \rangle_o \nu_e^0 RT; \tag{6}$$

here, ν_e^0 is the content of the effective chains in the dry polymer network, R is the gas constant, T is absolute temperature and $\langle \alpha^2 \rangle_o$ is the dilatation factor. In accordance with the kinetic theory, ν_e^0 should be constant irrespective of the experimental conditions (that is, temperature or the degree of swelling). Figure 7 shows the plot of the G_o/T and G_o^0/T values in dependence on the concentration of the crosslinking agent, c, for filled and unfilled samples, respectively. The rate of increase in G_o^0/T with c, as well as the absolute values of G_o^0/T are higher in the case of unfilled swollen samples at a lower temperature than with the same samples measured in the dry state at a higher temperature. It follows from the temperature dependence of $\langle \alpha^2 \rangle_o$ of PHEMA measured elsewhere[5] that the values of G_o^0/T, corresponding to $T = 25°C$, are 1.8 times higher than the values of G_o^0/T corresponding to $T = 180°C$. The coefficient 1.8 approximately corresponds to the ratio G_o^0/T, measured for high c values. In the case of low c this correction is too great, which can be explained by a decrease in the constant C_2 with the degree of swelling and the concentration of the crosslinking agent.[5-7]

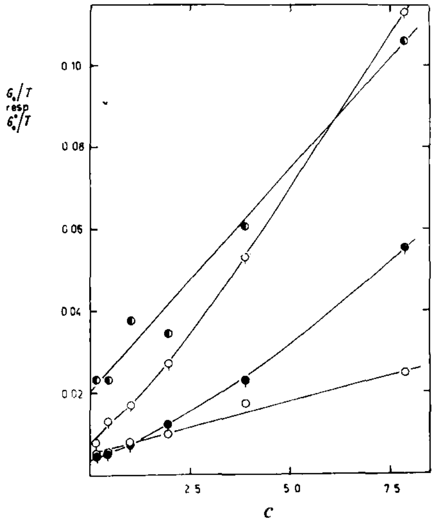

FIGURE 7 Dependence of G_o/T and G_o^0/T (kp cm^{-2} grad^{-1}) on the concentration of the crosslinking agent c.

Unfilled samples: (○) dry, $T = 180°C$; (●) swollen, $T = 25°C$; samples filled with a volume concentration of the filler $v_p = 0.09$: (◐) dry, $T = 180°C$; (○) swollen, $T = 25°C$.

The G_o/T values of filled samples are always higher than the G_o^0/T values of unfilled samples (Figure 7, Tables I, II), their ratio $X = G_o/G_o^0$ being approximately independent of the concentration of the crosslinking agent. Whereas $X \approx 4$ in the case of dry samples, it decreases to 2 in the case of swollen polymers. For the system investigated by the authors, Eq. (2) can therefore be written in a general form

$$G_o(c,\mathrm{v}_f) = G_o^0(c)X(\mathrm{v}_f). \qquad (7)$$

Even though the X value of a polymer in the dry state is twice as high as that of a polymer in the swollen state, numerical values of G_o/T are still close to each other irrespective of the degree of swelling and temperature of measurement (Figure 7), which can be explained, on the one hand, in terms of the above-mentioned effect of the temperature dependence of the dilatation factor $<\alpha^2>_o$, and on the other in terms of the concentration dependence of the constant C_2 in the region of lightly crosslinked networks.

Viscoelastic functions. With increasing concentration of the crosslinking agent there is a shift of the transition parts of reduced compliances $J_p(t)$ and retardation spectra of filled samples toward higher times by approximately five orders (Figures 2b, 3b). The characteristic temperatures T_S increase by approximately 30°C, and agree for both filled and unfilled samples (Table I) within the limits of experimental error; the effect of the crosslinking agent is thus not affected by the presence of the filler. A shift of the transition parts of the $J_p(t)$ curves and spectra toward longer times is caused by an increase in the monomeric friction coefficient ζ_o of the modified Rouse's theory,[8] which is connected with a decrease in the free volume with increasing concentration of the crosslinking agent.[2,19] It is easy to show that the concentration of the crosslinking agent does not virtually affect the viscoelastic functions of filled polymers in the glassy state, just the same as those of unfilled polymers.

3 Effect of Concentration of the Diluent

Stress-strain properties The concentration dependence of the dilatation factor, $<\alpha^2>_o$, which depends on the content and nature of the diluent during polymerization[19,20] can be expressed by the relationship $<\alpha^2>_o = \mathrm{v}_o^{2/3}$, where v_o is the ratio of the polymer volume to the polymer and water volume during polymerization. The $G_o/<\alpha^2>_o T$ values of filled systems are higher than the $G_o^0/<\alpha^2>_o T$ values of unfilled systems; this difference decreases with increasing dilution during polymerization (Figure 8), and a similar effect is produced by the degree of swelling. If the polymerization is carried out in the dry state, there is a maximum effect of filler upon its course, and thus also upon v_f^*. A decrease in the effect of filler with increasing water content during polymerization corroborates the conclusion mentioned above, namely, that

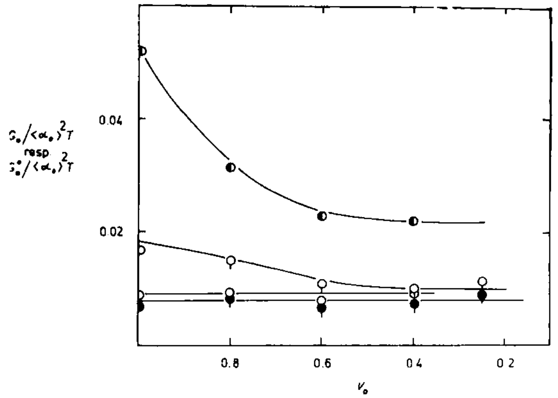

FIGURE 8 Dependence of $G_o/<\alpha^2>_o T$ and $G_o^0/<\alpha^2>_o$ (kp cm^{-2} grad^{-1}) on the water content during polymerization, v_o.
Designation of samples as in Figure 7.

the interaction polymer-water is more advantageous than the interaction polymer-filler.

If we consider the effect of dilution during polymerization, the total effect of the filler upon the modulus G_o of the systems investigated by the authors can be represented by the relationship

$$G_o(v_o,c,v_f) = G_o^0(c,v_o)Z(v_o,v_f) \tag{8}$$

in which the factor Z determines the increase in the modulus of the unfilled system, G_o^0, due to the filler. Assuming that for all v_o the dependence of the modulus G_o on the filler content v_f is given by the factor $X(v_f)$, it can be written that $Z(v_f,v_o) = X(v_f)\,Y(v_o)$. Eq. (8) can then be written as

$$G_o(v_o,c,v_f) = G_o^0(c,v_o)X(v_f)\,Y(v_o) \tag{9}$$

where the factor $Y(v_o)$ represents a change in the effect of the filler in dependence on v_o. The experimentally established values of $\log Y(v_o) = \log(G_o/G_o^0X)$ plotted against v_o ($v_f = 0.09$ and $c = 0.13$, samples measured in both dry and swollen state) lie practically on one and the same curve (Figure 9), which can be described by the relationship

$$Y(v_o) = 0.57 \times 10^{0.42v_o}. \tag{10}$$

It follows from the above that Eq. (9) together with Eq. (3) (the system PHEMA-SiO$_2$ in the dry state) or Eq. (4) (the system PHEMA-SiO$_2$ in the swollen state) describe an increase in the modulus G_o^0 due to the filler for all the networks studied by the authors in both the dry and swollen states.

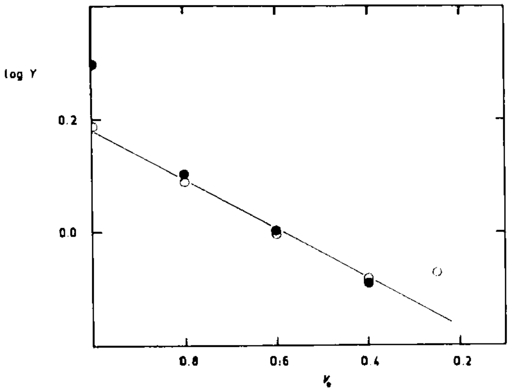

FIGURE 9 Dependence of the factor Y in Eq. (9) on v_0 of samples prepared at various concentrations of the diluent.

(●) dry samples, $T = 180°C$; (○) samples swollen with water to equilibrium, $T = 25°C$; the curve corresponds to the course described by Eq. (10).

Viscoelastic functions. Positions of the transition parts of superimposed curves $J_p(t)$ of filled samples are independent of the diluent content during polymerization; the same effect was also observed with unfilled samples. This means that a change in the water content during polymerization does not affect the structure of the short segments in the chain which contribute to the course of the viscoelastic functions in the transition region, and also that the monomeric friction coefficient, ζ_0, does not depend on v_0. This conclusion is corroborated by the independence of the characteristic temperatures T_S on v_0, in the case of both filled and unfilled systems. On the other hand, an increase in v_0 leads to a decrease in compliance $J_p(t)$ in the rubberlike region, which corresponds to an increase in the equilibrium modulus; this in its turn leads to a decrease in the maximum of the spectrum and to a smaller representation of longer times in the retardation spectrum. It can easily be shown that a change in compliance $J_p(t)$ with v_0 in the rubberlike state corresponds quantitatively to a change in the modulus G_0 with the variable v_0.

CONCLUSIONS

1 The presence of SiO_2 manifests itself in an increase of the modulus G_0 of poly(2-hydroxyethyl methacrylate) in the rubberlike region in a more pronounced manner than the presence of an active filler in natural rubber. The increase in G_0 is due to a restriction of the mobility of the PHEMA chains, owing to the physical interactions SiO_2-polymer; the effect of filling is therefore greater in the case of a polymer measured in the rubberlike state than in that of a polymer measured in the glassy and transition regions.

2 Swelling, as well as the presence of water during polymerization, has as its consequence a decrease in G_0 in comparison with a dry polymer or a polymer prepared in the absence of the diluent.

3 The presence of SiO_2 in the main transition region manifests itself in a shift of the retardation spectra of PHEMA toward longer times and a decrease in their slope; similarly to rubbers, this effect is not pronounced.

4 The effects of the crosslinking agent and water during polymerization on the position of the viscoelastic functions are identical for both filled and unfilled PHEMA. With increasing concentration of the crosslinking agent the transition parts of the retardation spectra are shifted toward longer times, without, however, any changes in their shapes. The presence of water during polymerization does not have any influence upon the position and shape of the transition parts of the retardation spectra.

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