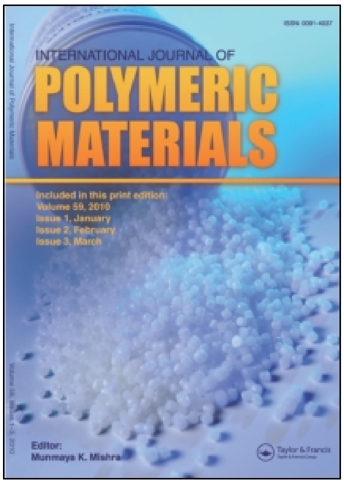

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Viscoelastic and Ultimate Behaviour of Swollen Poly (2-hydroxyethyl methacrylate) Networks Filled with Poly (2-hydroxyethyl methacrylate) in the Rubbery Region

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Viscoelastic and Ultimate Behaviour of Swollen Poly (2-hydroxyethyl methacrylate) Networks Filled with Poly (2-hydroxyethyl methacrylate) in the Rubbery Region

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Composite systems of the crosslinked and soluble poly(2-hydroxyethyl methacrylate) (PHEMA) matrix with various contents of crosslinked PHEMA particles containing 0.4, 1.0 and 20.0 wt. percent ethylenedimethacrylate as the crosslinking agent were prepared. Stress relaxations at the elongation $\lambda = 1.1$, stress–strain curves, Poisson's ratios, the degree of swelling and ultimate characteristics of samples swollen in water at 25°C were measured. With increasing filler content the time effects in the systems and the stress-at-break σ_b, and strain-at-break, ϵ_b, also increase; these results corroborate the viscoelastic concept of the ultimate behaviour. An agreement was found between the experimentally determined course of the initial modulus G_0 and that predicted by Van der Poel as a function of the volume fraction of filler v_f only for those systems in which the content of the crosslinking agent in the filler is smaller than in the matrix; systems with a higher content of the crosslinking agent in the filler than in the matrix require $v_f^* = 3v_f$ to fit the theory. Water present during the formation of filled systems preferentially swells the filler particles and reduces the polymer–filler interaction, which has a negative effect on the modulus G_0 and on σ_b and ϵ_b.

INTRODUCTION

One of the methods used for modifying mechanical properties of the polymer is to fill it with suitable particles.[1] Dispersed particles usually enhance the ability of the material to dissipate energy, which leads to more pronounced time dependences of the viscoelastic functions (broadening of the main transition region). The particles can also stop or bend growing cracks in the deformed sample, thus favourably influencing the ultimate characteristics of the system. These changes in the polymer properties due to the presence of filler depend on physical and chemical interactions between polymer molecules and filler particles.

Wide uses of poly(2-hydroxyethyl methacrylate) networks (further, PHEMA) in biomedical applications[2] call for changes in their structure and improvement of their mechanical properties. It has been shown in an earlier paper[3] that some mechanical characteristics of PHEMA can be greatly affected by the incorporation of 10 vol. percent of particles of the same polymer having different network density. It was found that in some cases mechanical properties of such hydrophilic composite systems resemble a system with solid particles, in others a system with network density fluctuations or a heterogeneous system depending on the character of the polymer–filler interface. The possibility of widely changing mechanical properties, especially of the matrix and filler moduli independently of each other, makes this system also suitable for verifying various theoretical predictions of a change in the modulus of the resulting composite system.

In this paper we examine the viscoelastic and ultimate properties of a one-component, two-phase swollen PHEMA–PHEMA system depending on the filler content for various network densities of matrix and filler. An advantage of this system is the possibility of wide variation of interactions between polymeric filler and continuous medium.

EXPERIMENTAL

Polymer filler: Three types of PHEMA filler with 0.4, 1.0 and 20.0 wt. percent ethylenedimethacrylate (EDMA) as the crosslinking agent were used in the preparation of filled PHEMA systems. The technique used in the preparation of filler has been described in detail elsewhere.[3] The diameter of virtually mono-disperse spherical particles of variously crosslinked filler in the dry state was about 2.5 μm; there was a good fit between particle sizes determined by the light, transmission and scanning electron microscopy.

Preparation of filled systems

Three different heterogeneous systems PHEMA filler–PHEMA were prepared:

I) In the first series, two-stage process has been used. Firstly, the viscous prepolymer of PHEMA with 1 wt. percent EDMA was prepared.[3] This prepolymer was used to prepare three series of samples containing 0.4, 1.0 and 20 wt. percent of the crosslinking agent in the filler (samples 1–12, Table I). The required amount of the filler was added to the prepolymer and the mixture was homogenized in an agate grinding mortar (5–15 min). After that the mixture was deaerated in a dessiccator 5–45 min depending on the mixture viscosity, placed in polymerization moulds and left to polymerize at 70°C for 4 h (90°C in the series with 20 percent of the crosslinking agent in the filler).

TABLE I

Composition of samples and their equilibrium characteristics

Sample	ν_0	c_m wt. %	c_f wt. %	ν_f	ν_2^g	ν_2	G_0 MPa	$2C_1$ MPa
1	1	1	—	0.000	0.225	0.557	0.330	0.215
2	1	1	0.4	0.058	0.226	0.561	0.320	0.180
3	1	1	0.4	0.115	0.224	0.558	0.267	0.166
4	1	1	0.4	0.171	0.233	0.556	0.278	0.152
5	1	1	0.4	0.227	0.249	0.558	0.289	0.179
6	1	1	1	0.058	0.241	0.559	0.336	0.265
7	1	1	1	0.115	0.259	0.566	0.397	0.281
8	1	1	1	0.227	0.276	0.580	0.449	0.314
9	1	1	1	0.334	0.308	0.594	—	—
10	1	1	20	0.058	0.254	0.578	0.510	—
11	1	1	20	0.115	0.303	0.596	0.696	—
12	1	1	20	0.171	0.433	0.616	1.210	—
20	1	0.1	—	0.000	0.058	0.522	0.106	0.019
21	1	0.1	0.4	0.059	0.047	0.520	0.140	0.025
22	1	0.1	0.4	0.117	0.043	0.521	0.150	0.022
23	1	0.1	0.4	0.174	0.058	0.531	0.163	0.023
24	1	0.1	0.4	0.230	0.073	0.528	0.178	0.028
30	0.8	0.1	—	0.000	0.020	0.530	0.112	0.021
31	0.8	0.1	0.4	0.074	0.016	0.519	0.123	0.018
32	0.8	0.1	0.4	0.146	0.022	0.522	0.133	0.020
33	0.8	0.1	0.4	0.216	0.039	0.525	0.146	0.025
34	0.8	0.1	0.4	0.309	0.105	0.530	—	—
41	—	—	0.4	0.050	—	0.436	—	—
42	—	—	0.4	0.100	—	0.436	—	—
43	—	—	0.4	0.150	—	0.437	—	—
44	—	—	1	0.050	—	0.435	—	—
45	—	—	1	0.100	—	0.437	—	—
46	—	—	1	0.200	—	0.437	—	—
47	—	—	20	0.050	—	0.435	—	—
48	—	—	20	0.100	—	0.437	—	—

II) In the second case, ordinary one-stage process was used. The matrix was prepared from the HEMA monomer which contained 0.1 wt. percent EDMA. In the first series of samples the filler with 0.4 percent of the cross-linking agent was ground in the mortar, the monomer was added, and after stirring (10 min) the mixture was deaerated (10 min). An initiation redox-system (0.03 vol. percent of 1 percent aqueous solution of sodium persulphate and ammonium pyrosulphite) was added to a mixture of the monomer, filler and 20 vol. percent diluent (water), the mixture was deaerated again and filled into the mould; the polymerization proceeded at room temperature 24 h (samples 30–34, Table I). In the second series the same monomer was used, with an initiator (0.1 wt. percent azobisisobutyronitrile) added. After stirring of the monomer–filler mixture (10 min), the mixture was deaerated and filled into the moulds. The polymerization took 4 h at 70°C (samples 20–24, Table I).

III) In the third series, a solution of uncrosslinked PHEMA[4] was used as the matrix. Twenty percent PHEMA solution in the methanol–ethanol (1:1 by weight) mixture was used in the preparation of filled systems. The filler was mixed with ethanol and the necessary amount of the PHEMA solution was added. After homogenization (3 h), the samples were prepared by gradual evaporation of solvent (samples 41–48, Table I).

By choosing these three types of samples, we wanted to have a scale of interactions of polymeric filler with continuous medium: starting from monomer, which swells filler particles during polymerization, thus forming interpenetrating networks, and ending with loose physical interactions of embedded PHEMA particles in the uncrosslinked matrix.

The volume fractions of filler, v_f, given in Table I, were related to the dry state; in calculations it was assumed that the densities of the dry polymer matrix and of the filler were the same ($\rho = 1.29$ g/cm^3).

Degree of swelling The samples were swollen in water and in diethyleneglycol at 70° for seven days. After that they were cooled to T = 25°C and weighed. Drying proceeded in the oven at 70°C and then over P_2O_5 to constant weight. The volume fraction of the polymer, v_2, was calculated from the weights of the dry and swollen samples assuming additivity of volumes. An average v_2 was calculated for each sample from swelling of three test pieces. The same test pieces were again swollen and dried. New v_2 values do not virtually differ from the original ones (Table I).

Swelling of fillers The particle diameters were measured with a Zetopan microscope with a planachromatic objective. Thirty-five to forty particles in the dry state were measured; after that the swelling agent was added dropwise between the micro-cover slip and the mount, and 35–40 particles were measured again after some time. The results were treated by selecting the most frequent particle diameters in the dry and swollen states and also by calculating the average particle size in the dry and swollen states. The particles did not aggregate. The increase in volume with swelling, V_n/V_0, was calculated as the average of the ratio of third powers of the above diameters in the swollen and dry states. During the swelling of the filler in the prepolymer it was found that $V_n/V_0 = 1.40$, 1.69 and 1.60 respectively for a filler with 0.4, 1.0 and 20 wt. percent EDMA after one hour of swelling. If filler with 0.4 wt. percent EDMA was swollen in the monomer, a volume ratio $V_n/V_0 = 1.48$ was observed after 105 min of swelling.

Measurement of mechanical characteristics All mechanical characteristics were measured on samples swollen in water at 25°C with an Instron type TM-M apparatus. The ultimate characteristics were measured on dumbbell-shaped samples at the rate of deformation 0.88 min^{-1}; tensile strength, σ_b, and strain-at-break, ϵ_b, were determined as an average from three values (average scatter in σ_b was $\pm$ 10 percent and in ϵ_b was $\pm$ 15 per cent).

The equilibrium properties were characterized by the Mooney–Rivlin constants C_1, C_2, determined from the stress–strain curves at a slow rate of deformation 0.02 min^{-1} using the equation:[5]

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

where σ is the stress related to the initial cross-section, λ is the relative elongation. For samples with which only small elongations $\lambda \leq 1.2$ could be obtained, only values of the initial modulus G_0 were calculated using:[6]

$$\sigma = G_0(\lambda - \lambda^{-2}) \tag{2}$$

The constants $2C_1$, $2C_2$ and G_0 were calculated by the least squares method[7] (accuracy of values was $\pm$ 5 percent). Table I gives the values of G_0, $2C_1$; for $2C_2$ it holds $2C_2 = G_0 - 2C_1$.

The dependence of the volume V on deformation has also been measured with some samples, and the dependences thus obtained were used in the determination of Poisson's ratio, μ. The sample was deformed, and after five-minutes' relaxation its length, l, and width, w, were determined. After that the sample was deformed again, and the whole procedure was repeated. At least 10 values of l_i and w_i were measured; the sample length was measured between two fixed points on the surface of the sample. Poisson's ratio μ was determined from

$$\mu = \left(1 - \frac{d\ln V}{d\ln \lambda}\right)/2 = -\frac{d\ln w/w_0,}{d\ln l/l_0} \tag{3}$$

where l_0, w_0 respectively are the initial length and width of the sample.

Stress relaxation, $\sigma(t)$, at constant strain $\epsilon = \lambda - 1 = 0.1$ within the time range 3–1800 s was also measured on all samples; $\sigma(t)$ was used to calculate the Young modulus $E(t) = \sigma(t)/\epsilon$ (accuracy $\pm$ 5 percent). The rate of relaxation, i.e. the viscoelastic part of deformation, was characterized by log $[E(6)/E(1800)]$ (accuracy in $E(6)/E(1800)$ much higher about $\pm$ 0.3 percent). A detailed dependence of the Young modulus $E(t)$ on time could be described by[8]

$$E(t) = E_\infty[1 + (t_0/t)^m], \tag{4}$$

where t_0, m are constants characterizing the magnitude of the viscoelastic component of the modulus, E_∞ is the equilibrium modulus. The constants

E_∞, t and m were calculated by using an iterative numerical method described elsewhere.[7]

RESULTS AND DISCUSSION

Viscoelastic characteristics

The viscoelastic part of the total deformation in the rubbery region is influenced mainly by the network density of the matrix (Table II). While for 1 percent of the crosslinking agent in the matrix the log $[E(6)/E(1800)]$ values lie within 0.03–0.05, for 0.1 percent of the crosslinking agent in the matrix they have increased to the range between 0.12–0.20; for uncrosslinked systems this

TABLE II

Viscoelastic and ultimate characteristics of samples

Sample	σ_b MPa	ϵ_b	$\log \frac{E(6)}{E(1800)}$	m	$\log t_0$	E_∞ MPa
1	0.356	0.65	0.027	0.079	−7.22	0.680
2	0.522	0.84	0.043	0.078	−5.43	0.676
3	0.499	0.78	0.044	0.080	−4.95	0.650
4	0.702	1.10	0.038	0.075	−4.66	0.695
5	0.750	1.10	0.050	0.095	−3.92	0.726
6	0.380	0.61	0.027	0.083	−6.68	0.771
7	0.695	0.91	0.043	0.087	−4.82	0.881
8	0.930	1.08	0.047	0.074	−3.49	0.946
10	0.580	0.54	0.023	0.069	−7.92	1.000
11	0.972	0.56	0.032	0.080	−6.17	1.500
12	1.040	0.39	0.043	0.078	−4.03	2.404
20	2.330	2.77	0.135	0.110	3.90	0.122
21	4.260	3.52	0.110	0.105	1.86	0.176
22	6.590	3.88	0.104	0.104	1.36	0.213
23	8.560	3.65	0.114	0.107	2.15	0.214
24	10.000	3.51	0.119	0.105	2.45	0.234
30	4.760	5.50	0.100	0.104	1.32	0.143
31	4.530	4.26	0.153	0.110	4.92	0.173
32	5.160	3.35	0.151	0.106	3.45	0.187
33	4.950	2.42	0.132	0.104	2.78	0.190
34	—	—	0.137	0.115	2.23	0.225
41	—	> 10	1.242	—	—	—
42	—		0.729	—	—	—
43	—		0.684	—	—	—
44	—		1.000	—	—	—
45	—		0.848	—	—	—
46	—		0.706	—	—	—
47	—		1.060	—	—	—
48	—		0.946	—	—	—

fraction is particularly high, 0.6–1.2. These results are in agreement with those obtained with unfilled PHEMA networks earlier.[7]

With increasing filler content in the prepolymer containing 1 percent of the crosslinking agent, time dependences of the modulus become more pronounced; the log $[E(6)/E(1800)]$ values increase virtually at the same rate regardless of the network density of the filler (Figure 1a). The independence of the time effects of the filler structure indicate that they are mainly due to the detailed character of the intermediate layer, and thus to the polymer–filler interaction, which for the fillers used need not be markedly different. Such conclusion is also corroborated by virtually the same degree of swelling of fillers after one hour of swelling in the prepolymer regardless of their structure.

On the other hand, the dependences of log $[E(6)/E(1800)]$ on the filler content determined for systems prepared from the monomer are more complicated (Figure 1b). At the low concentration of the filler in the pure monomer the filler reduces the time effects; for a filler concentration higher than 10 vol. percent the time effects increase similarly to the prepolymer–filler system. With the system monomer–water–filler the dependence of log $[E(6)/E(1800)]$ on v_f is reversed (Figure 1b). First fractions of the filler lead to rather pronounced time dependences, which later on decrease with increasing filler content. The generally greater time effects observed with the monomer–water system compared with monomer alone could be explained by the cosolvent character of the monomer–water mixture for PHEMA and by the preferential water sorption in filler particles if the monomer is present in the mixture in excess.[9] With increasing filler content the effect of water becomes gradually weaker, owing to the decreasing fraction of water in the filler particle.

The same conclusions as those obtained by analyzing the dependence of the log $[E(6)/E(1800)]$ values on filling may be reached by analyzing the constants m and t_0, Eq. (4) (Table II). In the case of samples prepared from the prepolymer (samples 1–12) the m values are virtually constant ($m \doteq 0.08$), and the different time dependence of the modulus is given by different values of log t_0 (Table II); log t_0 increases with increasing v_f. With samples prepared from the monomer (samples 20–34), m is also virtually constant ($m \doteq 0.105$) and somewhat higher than with samples from the prepolymer matrix; the generally stronger time dependence of samples 20–34 compared with samples 1–12 is predominantly given by an increase in the log t_0 values (Table II). A strong dependence of the constant t_0 and a weak dependence of the constant m on structure have been observed earlier with unfilled PHEMA networks.[7] Detailed log t_0 vs. v_f dependences are similar to those of log $[E(6)/E(1800)]$ on v_f (Figure 1) and lead to the same conclusions. By comparing equilibrium values of the Young modulus E_∞, Eq. (4) (Table II) with G_0 values obtained from the stress–strain curves at the deformation rate 0.02 min^{-1}, one arrives at a conclusion that G_0 values are higher by some 40 percent than the respective equilibrium G_∞

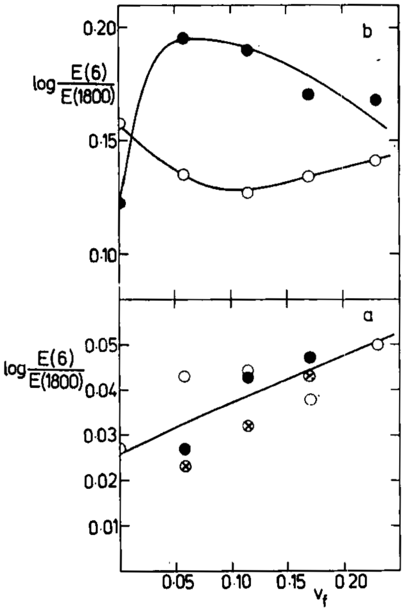

FIGURE 1 Dependence of the time decrease of the modulus on filler content, v_f.
a. $c_m = 1$ percent, $\nu_0 = 1$: ○ sample 1–5, $c_f = 0.4$ percent; ● sample 6–9, $c_f = 1$ percent; ⊗ sample 10–12, $c_f = 20$ percent.
b. $c_m = 0.1$ percent, $c_f = 0.4$ percent: ○ sample 20–24, $\nu_0 = 1$; ● sample 30–34, $\nu_0 = 0.8$.

values ($G_\infty = E_\infty/3$) for samples 1–12, and by some 120 percent than the respective equilibrium G_∞ values for samples 20–34.

With increasing filler content in the uncrosslinked matrix there is both an increase in the absolute values of the modulus $E(t)$ and a decrease in the rate of relaxation characterized by log $[E(6)/E(1800)]$ (Table II, Figure 2). In this case the effect of the filler is similar to that of physical bonds between entanglements and can be explained by assuming that cooperative motions of molecules in contact with the filler require a higher activation energy.[18] This means that these motions occur at longer times. The magnitude of the decrease of log $[E(6)/E(1800)]$ is virtually independent of the filler structure (Table II), similarly to systems prepared from the prepolymer.

Equilibrium characteristics

Degree of swelling The volume fractions of polymers in the swollen state in diethyleneglycol, $v_2{}^g$, are much smaller than the respective v_2 values in water

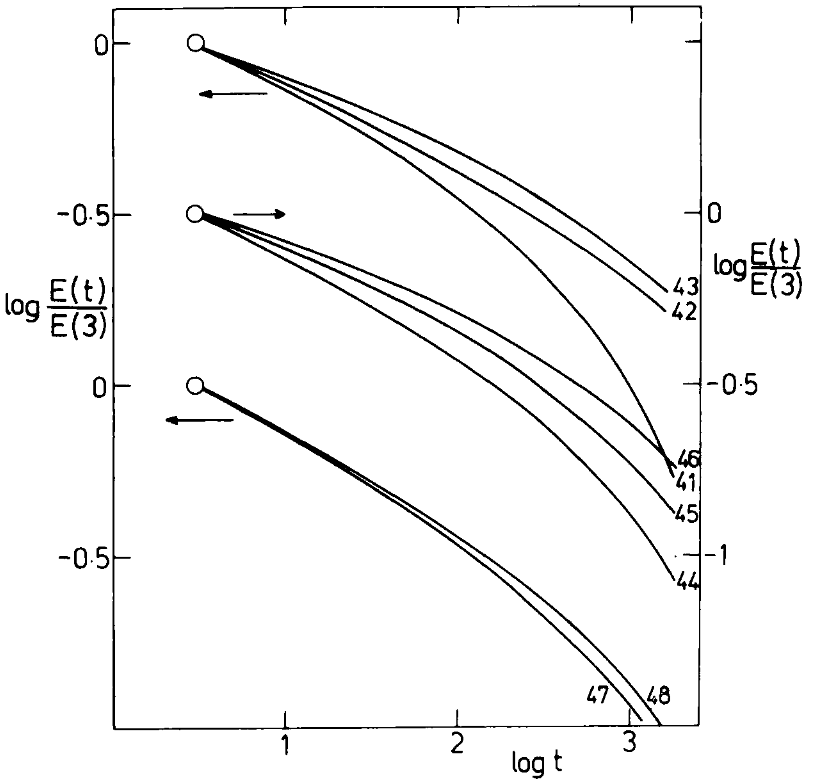

FIGURE 2 Time dependence of the Young modulus for systems prepared from soluble matrix. Figures at curves correspond to samples in Table I: 41–43, $c_f = 0.4$; 44–46, $c_f = 1$ percent; 47 and 48, $c_f = 20$ percent.

(Table I). With samples prepared from the prepolymer matrix both ν_2 values similarly depend on the filler concentration and structure; the respective ν_2 values increase with increasing filler concentration and with increasing content of the crosslinking agent in the filler. The general character of the increase in ν_2 with the filler content, especially the increase in $\nu_2{}^g$ in glycol in the case of a filler with the lowest content of the crosslinking agent (less than in the matrix) suggest that composite networks are formed in the filler particles. Such conclusion is also supported by the degrees of swelling of filler particles in the prepolymer and in the monomer.

The generally lower ν_2 of systems prepared from the monomer compared with those obtained from the prepolymer (Table I) are due to the lower content of the crosslinking agent in the monomer. The higher swelling in glycol of samples prepared from the monomer–water mixture compared with samples of the monomer alone (Table I) is in agreement with the view that in the crosslinking copolymerization the diluent (water) leads to a generally lower network density of the matrix owing to the formation of intramolecular rings on a larger scale.

With filled systems prepared from the soluble matrix, higher degrees of swelling in water were found compared with crosslinked samples; but no effect of structure or of the amount of filler on v_2 could be observed. This leads to a conclusion that the v_2 values are mainly given by swelling of the matrix and that interaction of the soluble polymer matrix with filler particles of various types is of similar nature.

Dependence of volume on deformation Poisson's ratios were determined for samples having a constant filler content $v_f = 0.1$ (samples 1, 3, 7, 11, 22, 32, and 48). The dependences ln w/w_0 on ln l/l_0 are linear within the whole deformation range under investigation in all cases in which the crosslinked matrix is used; their slopes were used in the determination of μ from Eq. (3). The following values were obtained: sample 1 $\mu = 0.5$, sample 3 $\mu = 0.47$, sample 7 $\mu = 0.50$, sample 11 $\mu = 0.44$, sample 22 $\mu = 0.49$, and sample 32 $\mu =$ 0.475. Hence it follows that while for a homogeneous sample, or for a sample in which the filler has the same network density as the matrix (samples 1, 7), $\mu = 0.5$, μ decreases with increasing heterogeneity of the sample. In the case of sample 48, prepared from the soluble matrix, there is a slope change in the ln w/w_0 on ln l/l_0 dependence. While the initial slope leads to $\mu = 0.5$, in the following part μ decreases to 0.18; the slope changes at an elongation $\lambda = 1.32$. After this deformation has been reached, the matrix is torn away from the filler in the sample of the soluble matrix; a similar effect has been observed also with other filled systems.[11] With samples prepared from the crosslinked matrix no such effect takes place, which suggests good adhesion between the matrix and the filler, probably owing to composite networks formed in the latter.

Mechanical behaviour The general character of the effect of network density of the filler on the dependence of the initial modulus $G_0 = 2C_1 + 2C_2$ on filler concentration can be seen in Table I. While filler having a network density lower than that of the matrix causes a decrease in G_0, filler whose network density is the same as, or higher than, that of the matrix leads to an increase in G_0. An increase in G_0 in the case of samples prepared from a filler having the same density of the crosslinking agent as the matrix also suggests that composite networks are formed in filler particles. With systems prepared from monomers there also is an increase in the modulus with the filler content; in this case the increase in G_0 is due to an increase in C_2 of the networks (Table I). The fact that for the monomer–water mixture this increase is slower than for the monomer alone indicates that water present in the crosslinking copolymerization is probably preferentially swollen in filler particles, which leads to a less dense composite network, and thus to a smaller polymer–filler adhesion. This conclusion is in accord with selective sorption measurements of PHEMA networks in a cosolvent monomer–water mixture.[9] The generally lower G_0 values of samples prepared from the monomer compared with those prepared from the prepolymer are given by the lower concentration of the crosslinking agent in the matrix.

The dependence of the modulus on the volume fraction of the filler can be expressed in the form

$$G_0(v_f) = G_0^0 X(v_f) \qquad (5)$$

where G_0^0 is the modulus of the matrix and X is the multiplication factor. Attempts to solve the problem of a theoretical calculation of the X factor of filled systems from the knowledge of the moduli of the filler and matrix have been made by various authors.[12–16] It has been shown that various theoretical approaches in the range of small v_f values lead to almost identical X. To compare in detail our results with theory we shall use a corrected Van der Poel equation for calculations of X, given by[16]

$$A(X-1)^2 + B(X-1) + C = 0 \qquad (6)$$

where the coefficients A, B, C are functions of the modulus of the matrix G_0^0 and of the filler G_f, and of Poisson's ratios of the matrix μ_m, of the filler μ_f and of the volume fraction of the filler, v_f. Detailed relationships for the coefficients A, B, C can be found in Ref.16 [Eqs. (36–38)].

Assuming that the moduli of filler particles are the same as those of macroscopic samples of the same network densities the following values were used for fillers swollen to equilibrium in water: for fillers with 0.4 percent, 1 percent and 20 percent crosslinking agent, G_f is 0.2 MPa, 0.33 MPa and 2.3 MPa respectively. Since Poisson's ratio μ only slightly influences theoretical results[16] and μ's measured by us for systems with different fillers vary from 0.44 to 0.50, $\mu_m = \mu_f = 0.5$ was used in our calculations.

The dependence of the experimentally and theoretically determined X values on v_f is given in Figure 3. Good fit between theory and experiment is obtained only for samples in which the filler exhibits a lower network density than the matrix, which leads to $X < 1$. In all the other systems the experimentally determined effect of the rise in the modulus due to the filler is higher than theoretical. The values of X are higher than those predicted by current theories;[12–16] they are also out of the region of lower and upper bounds found by Hashin and Shtrikman[12] (HS). E.g., for sample 12 $X_{\mathrm{exp}} = 3.7$ whereas the upper bound HS gives $X^{+}_{HS} = 1.71$ and Eq. (6) leads to $X_{VP} = 1.42$. Similar results were obtained earlier for the system PHEMA–SiO_2[18]

and PHEMA–glass beads.[19] To explain these results, two effects may be considered:

a) Formation of interpenetrating networks in the filler particles (due to their swelling in monomer or prepolymer) causes an increase in network density in the particles and, consequently, a higher G_f/G_0^0. Such procedure makes possible a quantitative description of the X vs. v_f dependence by Eq. (6) for the system prepolymer–filler with 1 percent EDMA (if $G_f/G_0^0 = 5$ instead of $G_f/G_0^0 = 1$), for the system monomer + water–filler with 0.4 percent EDMA (if $G_f/G_0^0 = 4$ instead of $G_f/G_0^0 = 2$), and for the system monomer–filler with 0.4 percent EDMA (if $G_f/G_0^0 = 20$ instead of $G_f/G_0^0 = 2$). The system prepolymer–filler with 20 percent EDMA cannot be described at all.

b) Effective volume fraction of the filler, v_f^*, in the system is higher than the values v_f due to the immobilisation of polymer matrix chain on the surface of filler particles. The observed dependence of X on v_f for the system prepolymer–filler with 20 percent EDMA can be quantitatively described by Eq. (6) assuming that $v_f^* = 3v_f$ (while maintaining the experimental ratio $G_f/G_0^0 = 7$).† The value of $v_f^* = 3v_f$ allows to describe also the system monomer–filler with 0.4 percent EDMA; the same value of v_f^* has already been used[18] for the system PHEMA–SiO_2. With the system monomer + water–filler containing 0.4 percent EDMA a smaller increase is sufficient, $v_f^* = 1.5\,v_f$.

In reality, both effects are probably operative simultaneously, but it is difficult to separate quantitatively their influence.

Ultimate characteristics

While stress-at-break values, σ_b, are similar for all samples under investigation (0.3–1 MPa), strain-at-break values, ϵ_b, of samples prepared from the prepolymer are much lower (0.6–1) than the respective values found for samples prepared from the monomer (2.5–5.5, Table I). The difference is mainly due to the higher network density of the pregel matrix compared with the monomer.[21] The generally higher moduli of samples obtained from the pregel matrix lead to an agreement between all the resulting σ_b.

The stress values, σ_b, of samples prepared from the pregel matrix increase with increasing filling, v_f (Table I); the rate of increase of σ_b/σ_{b0} (σ_{b0} refers to an unfilled sample) with v_f increases with increasing network density of the filler (Figure 4). The ratio ϵ_b/ϵ_{b0} as a function of v_f increase at virtually the same rate for systems prepared with a filler having the same or smaller

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†The value of 3 is rather high and leads to a roughly 40 percent increase of filler diameter. One can expect, that the high v_f^* can be effected by swelling of the filler at composite formation (cf. p. 96).

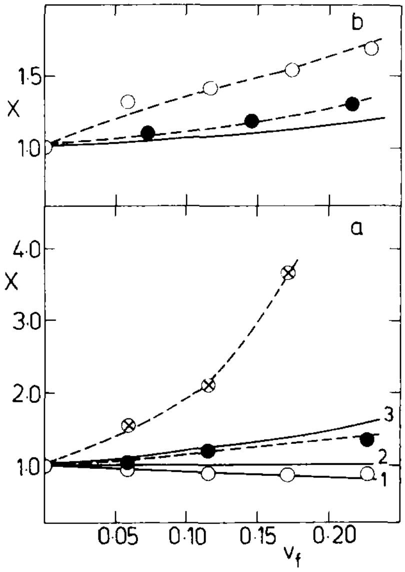

FIGURE 3 Dependence of $X = G_0/G_0^0$ on filler content, v_f.
a. ○ sample 1–5, $c_f = 0.4$ percent; ● sample 6–8, $c_f = 1$ percent; ⊗ sample 10–12, $c_f = 20$ percent; theoretical dependences (Eq 6): 1 sample 1–5, 2 sample 6–8, 3 sample 10–12.
b. ○ sample 20–24, $v_0 = 1$; ● sample 30–34, $v_0 = 0.8$; theoretical dependence [Eq. (6)].

network density; in the case of a filler with 20 percent crosslinking agent ϵ_b/ϵ_{b0} decreases with v_f (Figure 5). It is of interest that the reinforcement of true tensile strength $Y = (\sigma_0\lambda_b/\sigma_{b0}\lambda_{b0})$ increases with v_f practically in the same way regardless of the filler structure (Figure 6), similarly to the viscoelastic characteristics of the same systems. This result suggests that the increase in Y with v_f is related to the increase in local viscosity and to the increase of time effects in the system, in agreement with the viscoelastic conception of the destruction behaviour.[10,22] Also the extent of the effect of filler on the initiation and growth of the crack does not depend to any important degree on the detailed structure of filler particles.

The presence of water in the crosslinking copolymerization of the monomer has led to a twofold increase in ϵ_b, and consequently in σ_b (Table I). Since the degree of swelling in water is the same for both networks, this fact is due to different reference states of the two networks. Owing to the presence of water in the crosslinking copolymerization, the network in the isotropic state (state during measurement) is less deformed than the network prepared from the monomer alone, which leads to the differences observed in ϵ_b and σ_b. The increasing filler content in samples 21–24 leads to a considerable increase in

σ_b/σ_{b0} (Figure 4); the dependence of ϵ_b/ϵ_{b0} on v_f passes through an unpronounced maximum (Figure 5), similarly to samples obtained from the prepolymer matrix. With samples 31–34 the dependences of σ_b and ϵ_b on v_f are completely different; the filler leads to a drop in ϵ_b/ϵ_{b0} (Figure 5), and hence σ_b/σ_{b0} is virtually constant (Figure 4). Similar differences can also be found in the Y vs. v_f dependence (Figure 6); they can be interpreted by assuming that water present in the monomer–water mixture preferentially interacts with the filler particles, thus giving rise to a less densely crosslinked composite network in the filler and to weaker polymer–filler interactions (cf. discussion of the effect of water on the modulus G_0). As a result, the filler which in the monomer alone has a positive effect on the ultimate characteristics of the system, has a negative effect in the presence of monomer and water.

While with samples prepared from the crosslinked matrix stress was increasing within the whole range of strain, a more or less pronounced yield point can be seen on the stress–strain curves of samples with the soluble matrix

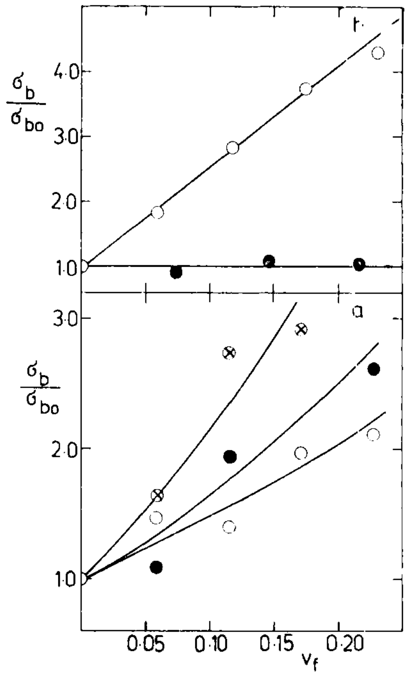

FIGURE 4 Dependence of the strengthening factor σ_b/σ_{b0} on filler content, v_f.
a. $v_0 = 1$, $c_m = 1$ percent: ○ sample 1–5, $c_f = 0.4$ percent; ● sample 6–8, $c_f = 1$ percent; ⊗ sample 10–12, $c_f = 20$ percent.
b. $c_m = 0.1$ percent, $c_f = 0.4$ percent: ○ sample 20–24, $v_0 = 1$; ● sample 30–34, $v_0 = 0.8$.

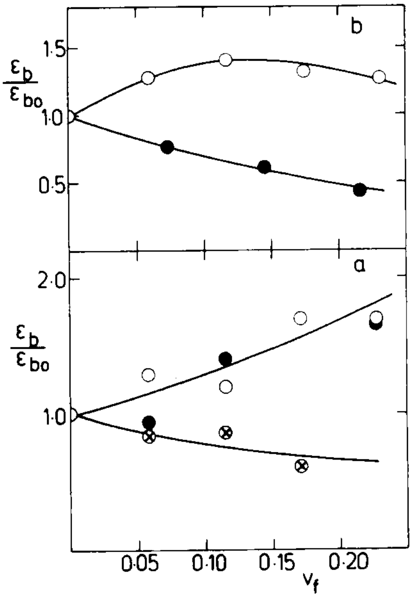

FIGURE 5 Dependence of ϵ_b/ϵ_{b0} on filler content, v_f. Samples denoted as in Figure 4.

(Figure 7). The position of this point on the stress–strain curve is shifted to lower ϵ with increasing filler content and decreasing network density. All samples sustained a more than tenfold elongation, with deformation proceeding via gradual diminishing of the cross-section in the central part of the sample without necking, similarly to poly(methyl methacrylate)[23] at temperatures above 160°C.

CONCLUSIONS

1) With increasing content of PHEMA filler, v_f, in crosslinked PHEMA matrices the time dependence of the Young modulus $E(t)$ in the rubbery region increases. The magnitude of viscoelastic decrease in the modulus $\Delta = \log [E(6)/E(1800)]$ is determined mainly by crosslink density of the matrix, c_m, being independent of crosslink density of the filler, c_f. Water present at composite formation leads to more pronounced time effects; this fact is caused by the preferential sorption of water in filler particles. For an uncrosslinked PHEMA matrix, the increasing v_f gives a lower value of Δ.

2) If $c_f < c_m$, a decrease in the initial modulus, G_0, with v_f was observed; the magnitude of the decrease is in agreement with the theoretical prediction

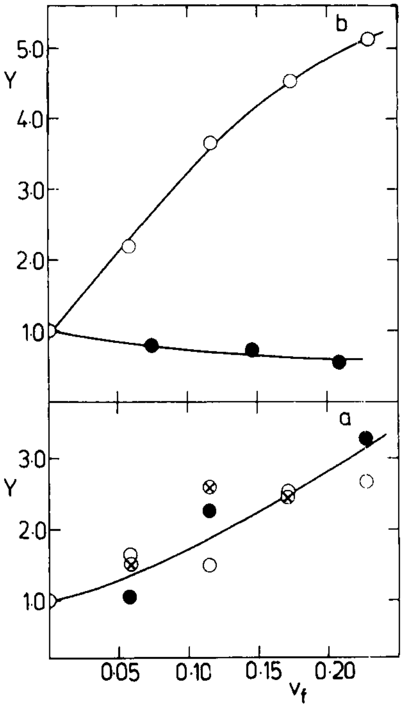

FIGURE 6 Dependence of the factor $Y = \sigma_b \lambda_b / \sigma_{b0} \lambda_{b0}$ on filler content, v_f. Samples denoted as in Figure 4.

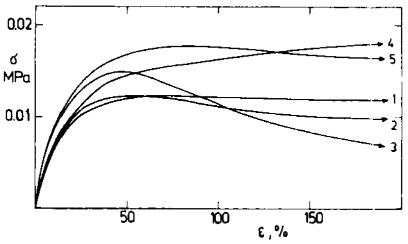

FIGURE 7 Stress–strain curves of systems prepared from the soluble matrix. Samples denoted as in Figure 2.

of the Van der Poel theory.[15] For systems where $c_f \geq c_m$, the G_0 was found to increase with v_f. This increase is higher than prediction based on current theories. This can be due to either interpenetrating network formation in filler particles or higher value of effective filler content due to immobilization of the matrix chains. Presence of water at composite formation leads to a slower increase in G_0 with v_f.

3) Composite systems prepared from crosslinked matrices exhibit a constant value of Poisson's ratio, μ, in the whole region of deformation. If $c_f = c_m$, it was found that $\mu = 0.5$; for systems where $c_f \neq c_m$, $\mu < 0.5$. For a system prepared from uncrosslinked matrix, the separation of filler particles from matrix takes place at extension $\lambda \doteq 1.32$, and μ changes from 0.5 to 0.18. In this region, the stress–strain curves show a more or less pronounced yield point.

4) Filler in a composite system acts favorably on both tensile strength, σ_b, and strain-at-break, ϵ_b, values. Reinforcement of true tensile strength, $Y = \sigma_b\lambda_b/\sigma_{b0}\lambda_{b0}$, increases with v_f independently of crosslink density of filler; this supports the viscoelastic concept of ultimate behaviour. Presence of water at composite formation leads to Y being independent of v_f.

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