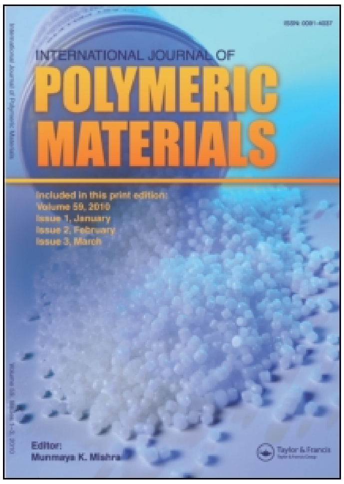

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Effect of Chemical Crosslinks on Ultimate Tensile Properties of Water Swollen Poly(2-Hydroxyethyl Methacrylate) Gels

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Tensile properties were measured of poly(2-hydroxyethyl methacrylate), swollen with water to equilibrium and prepared in the presence of ethylene dimethacrylate as the crosslinking agent within the concentration range from $c = 0.0855$ to 5.65×10^{-4} mol cm^{-3} and water as the diluent during polymerization up to the volume fraction of the polymer $v_0 = 0.2$. Tensile strength and strain-at-break were determined at 5°C and crosshead speed 10 mm s^{-1}, and also at 25°C and 1 mm s^{-1}. Both tensile strength and strain-at-break depended with good approximation on the effective crosslinking density only, irrespective of the crosslinking agent and diluent contents during polymerization. An exception occurs in heterogeneous systems polymerized in the presence of a large volume of water ($v_0 < 0.6$). The temperature and time dependences of the strength characterictics of samples having three different crosslinking densities were summarized in a universal failure envelope. The points pertaining to samples having the lowest crosslinking density ($c = 0.085 \times 10^{-4}$ mol cm^{-3}) departed from the failure envelope towards larger deformations. This effect was explained in connection with the time and temperature dependence of the elasticity modulus of lightly crosslinked elastomers.

INTRODUCTION

Hydrophilic 2-hydroxyethyl methacrylate polymers (further PHEMA) have been applied in medicine to a still increasing degree, especially as material for soft contact lenses.[1,2] In a state swollen with water to equilibrium, these polymers become rubberlike, thus allowing the existing theoretical models of the failure mechanism of amorphous rubbers to be used for the description of their behaviour. Among various theoretical viewpoints, an important place is held by the viscoelastic conception of strength, based on an experimentally proved relation between the ultimate and viscoelastic behaviour of elastomers[3,4] and considering the failure process as a non-equilibrium one, being both time- and temperature-dependent. Smith[5] has shown that by plotting the tensile strength values, σ_b, against strain-at-break, ϵ_b, in the coordinates $\log \sigma_b \lambda_b T_0/T$ vs. $\log \epsilon_b E_e T_0/T$, a characteristic failure envelope may be obtained for every polymer, independent of temperature, strain rate, and network density. $\lambda_b = \epsilon_b + 1$ is the ultimate extension ratio, T is the absolute temperature, T_0 is the reference temperature, and E_e is the equilibrium modulus.

The non-equilibrium time-dependent processes also determine the shape of the dependence of tensile strength on the crosslinking density of elastomers. For the natural and butadiene-styrene rubbers and some other crystalline and amorphous rubberlike polymers the dependence of strength on the crosslinking agent content is non-monotonous as a rule, having a maximum in the region of lightly crosslinked networks.[6-8] The differences between the position and shape of maxima of amorphous and crystalline rubbers suggest various mechanisms of their formation. It has been suggested[8] that the strength maximum appears as a consequence of varying rate of change in σ_b and ϵ_b with crosslinking density, which assumes that strain-at-break ϵ_b is the primary critical quantity which accounts for break. The maximum goes on decreasing with increasing temperature and content of the low-molecular weight compounds and with decreasing crosshead speed, until it disappears completely, and the tensile strength then increases monotonously with crosslinking density.[7] Bueche and Dudek[7] assumed that tensile strength consists of an equilibrium part, increasing monotonously with crosslinking density, and a non-equilibrium part, which accounts for the occurrence of maximum. They described the dependence of tensile strength, σ_b, on the effective crosslinking density, ν_e, by equation

$$\sigma_b = \nu_e \left\{kT(\lambda_b - \lambda_b^{-2}) + \psi(1 - \mathrm{erf}\, X^{1/2})\right\}, \qquad (1)$$

where k is Boltzmann's constant and X is a function of the effective crosslinking density, ν_e. The second term in brackets describes the non-equilibrium process and accounts for the formation of the maximum on the curve; the fall of strength with increasing temperature and decreasing crosshead speed is expressed by the parameter ψ, which decreases when the system under investigation approaches equilibrium. Eq. (1) prescribes, at higher crosslinking densities and under equilibrium conditions, an increase in tensile strength with the first or a lower power of ν_e (ultimate extension ratio, λ_b, decreases with increasing ν_e). In the case of the polyether-polyurethane elastomers, a proportionality has been established[9] between tensile strength, σ_b, and $\nu_e^{1/2}$. The behaviour of these systems has been described by relations

$\sigma_b = K_1(T)\nu_e^{1/2}$ and $\lambda_b = K_2(T)\nu_e^{-1}$, in which $K_1(T)$ and $K_2(T)$ are temperature-dependent parameters.

The aim of the current work has been to determine the dependence of strength characteristics of poly(2-hydroxyethyl methacrylate), swollen with water to equilibrium, on the concentration of the crosslinking agent and water during polymerization. These polymeric networks, whose topological structure can be varied over a wide range by varying the preparation conditions, represent a system interesting from both the experimental and theoretical points of view.

EXPERIMENTAL

Preparation of Samples

The polymerization of 2-hydroxyethyl methacrylate (cf. Ref. 10) in the presence of water as the diluent and ethylene dimethacrylate as the crosslinking agent was initiated with isopropyl percarbonate (1×10^{-2} mol/l) proceeded at 60°C four hours between two glass plates. The sheets thus obtained were approximately $10 \times 19 \times 0.1$ cm in size. Two series of samples were prepared. The first series (A) was polymerized in the presence of 40% water (volume fraction of the polymer $v_o = 0.60$) and 25 different concentrations of ethylene dimeth acrylate over the range $c = 0.0855$ to 5.65×10^{-4} mol cm^{-3} (Table I). The second series (B) was prepared with a constant content of ethylene dimethacrylate ($c = 1.08 \times 10^{-4}$ mol cm^{-3}) and at 11 different concentrations of water during polymerization ($v_o = 0.20$ to 0.99) (Table II).

From the polymer sheets swollen with water to equilibrium, the dumb-bell test pieces were cut out. The width and length of the working part of these samples were 4.1 and 22.5 mm, respectively. All samples were extracted by boiling in water for 6–8 hours before measurements.

Tensile Measurements

The tensile strength and strain-at-break measurements were carried out on a tensile strength tester ZT-4 (VEB Thüringen Industriewerke, Rauenstein). Throughout the tensile test, the samples were immersed in distilled water, which was maintained at constant temperature by means of a thermostatting jacket, moving together with the lower clamp and connected with the thermostat. The temperature of water surrounding the test-piece was controlled with a mercury thermometer; the test was started when the temperature became stabilized at the required value, but not sooner than 5 min. after the sample had been immersed into water. The tensile strength, σ_b, was determined with respect to the initial cross-section of an unstretched swollen sample; strain-at-break, ϵ_b, was determined as the ratio of the maximum length of the sample

TABLE I

Characteristics of samples with constant diluent content on polymerization

For values of σ_b, ϵ_b probable errors of the mean value are indicated. Polymerization was initiated with isopropyl percarbonate, 1 × 10^{-2} mol/l, volume fraction of polymer during polymerisation $v_0 = 0.60$.

A 5°C, 10 mm s^{-1}; B 25°C, 1 mm s^{-1}.

				A		B	
Sample	$\nu_c 10^4$[a] mol cm^{-3}	$\nu_e 10^4$[b] mol cm^{-3}	v_r[c]	σ_b[d] kp cm^{-2}	ϵ_b[e] %	σ_b kp cm^{-2}	ϵ_b %
A-1	0.17	0.73	0.525	7.4 ± 0.3	479 ± 8	3.4 ± 0.1	480 ± 40
A-2	0.47	0.89	0.528	6.6 ± 0.2	390 ± 10	4.1 ± 0.1	300 ± 10
A-3	0.53	0.92	0.529	6.4 ± 0.2	376 ± 7	3.3 ± 0.1	230 ± 10
A-4	0.73	1.02	0.531	8.1 ± 0.3	370 ± 10	3.3 ± 0.1	196 ± 6
A-5	0.79	1.05	0.532	6.7 ± 0.2	320 ± 10	3.1 ± 0.1	170 ± 6
A-6	0.87	1.09	0.533	7.8 ± 0.2	306 ± 4	2.8 ± 0.1	130 ± 5
A-7	1.05	1.19	0.535	8.0 ± 0.4	280 ± 10	3.6 ± 0.3	130 ± 10
A-8	1.25	1.23	0.536	7.1 ± 0.2	280 ± 6	3.0 ± 0.1	113 ± 7
A-9	1.24	1.29	0.537	8.4 ± 0.3	252 ± 5	4.0 ± 0.1	149 ± 3
A-10	1.69	1.52	0.544	10.3 ± 0.4	224 ± 7	4.1 ± 0.1	112 ± 4
A-11	2.10	1.73	0.549	8.9 ± 0.3	189 ± 5	3.4 ± 0.2	77 ± 5
A-12	2.59	1.99	0.554	10.9 ± 0.3	172 ± 4	2.8 ± 0.1	50 ± 1
A-13	3.14	2.27	0.559	12.0 ± 0.3	159 ± 2	3.2 ± 0.2	47 ± 2
A-14	3.18	2.39	0.560	14.3 ± 0.2	134 ± 2	3.3 ± 0.1	42 ± 1
A-15	4.05	2.75	0.569	22.8 ± 0.7	140 ± 6	4.3 ± 0.2	48 ± 2
A-16	4.52	2.99	0.573	26.0 ± 0.7	146 ± 1	5.4 ± 0.2	58 ± 2
A-17	4.87	3.15	0.575	28.5 ± 0.2	138 ± 1	6.0 ± 0.2	62 ± 2
A-18	5.18	3.33	0.577	24.1 ± 0.7	133 ± 3	4.6 ± 0.1	41 ± 1
A-19	5.37	3.43	0.579	30.0 ± 0.6	128 ± 2	6.7 ± 0.1	60 ± 1
A-20	5.54	3.52	0.580	30.8 ± 0.8	128 ± 2	6.1 ± 0.1	46 ± 1
A-21	5.99	3.76	0.583	35.5 ± 0.5	120 ± 1	7.4 ± 0.1	61 ± 1
A-22	6.78	4.17	0.589	39.5 ± 0.2	102 ± 1	7.8 ± 0.1	52 ± 1
A-23	8.00	4.80	0.596	54.5 ± 0.3	93 ± 1	10.5 ± 0.2	55 ± 1
A-24	8.73	5.18	0.599	56.0 ± 0.1	84 ± 1	11.3 ± 0.1	54 ± 1
A-25	11.30	6.51	0.696	49.0 ± 0.2	55 ± 1	18.6 ± 0.3	48 ± 1

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[a] Chemical crosslinking density $\nu_c = 2c$. [b] Effective crosslinking density. [c] Volume fraction of polymer in equilibrium swollen system. [d] Tensile strength. [e] Strain-at-break.

TABLE II

Characteristics of tensile samples with variable diluent content on polymerization
For values of σ_b, ϵ_b probable errors of the mean value are indicated. Polymerization was initiated with isopropyl percarbonate, 1×10^{-2} mol/l.

Chemical network density $\nu_c = 2c = 2.16 \times 10^{-4}$ mol cm^{-3} with all samples. A 5°C, 10 mm s^{-1}, B 25°C, 1 mm s^{-1}.

				A		B	
Sample	ν_0[a]	$\nu_e 10^4$ mol cm	ν_r	σ_b kp cm^{-2}	ϵ_b %	σ_b kp cm^{-2}	ϵ_b %
B-1	0.20	0.92	0.229	0.29 ± 0.02	107 ± 3	0.20 ± 0.01	100 ± 9
B-2	0.26	1.05	0.291	1.86 ± 0.04	150 ± 2	1.06 ± 0.05	107 ± 3
B-3	0.29	1.13	0.335	1.62 ± 0.02	108 ± 1	0.88 ± 0.08	68 ± 5
B-4	0.40	1.35	0.449	5.50 ± 0.1	178 ± 2	1.70 ± 0.1	64 ± 2
B-5	0.51	1.58	0.566	7.90 ± 0.1	179 ± 2	2.40 ± 0.1	63 ± 4
B-6	0.60	1.76	0.574	10.90 ± 0.2	168 ± 2	3.20 ± 0.1	63 ± 3
B-7	0.60	1.76	0.574	9.70 ± 0.1	—	2.70 ± 0.1	—
B-8	0.68	2.00	0.580	12.40 ± 0.3	170 ± 4	3.20 ± 0.1	54 ± 1
B-9	0.79	2.20	0.588	13.40 ± 0.7	145 ± 5	3.60 ± 0.2	47 ± 2
B-10	0.80	2.22	0.589	14.30 ± 0.3	153 ± 2	—	—
B-11	0.99	2.63	0.604	22.20 ± 0.5	150 ± 2	4.70 ± 0.5	47 ± 3

[a] Volume fraction of polymer during polymerization. The other symbols are the same as in Table I.

to the initial distance between the clamps. The ϵ_b values thus calculated are somewhat lower than the real ones. In some cases, the data obtained with the tester were compared with the cathetometric measurement of the distance between two marks; the experimental error of ϵ_b did not exceed 10%. The tensile strength and strain-at-break measurements were in most cases repeated five times under the same conditions. From the values thus measured, the arithmetic mean value and the probable error of the mean value were calculated, with the exclusion of cases when the sample broke in the clamps.

RESULTS AND DISCUSSION

Effect of the Network Density and Water Content During Polymerization

The tensile strength and strain-at-break of PHEMA samples swollen to equilibrium are very sensitive to temperature and crosshead speed (Figure 1). Moreover, the testing conditions affect the dependences of the strength

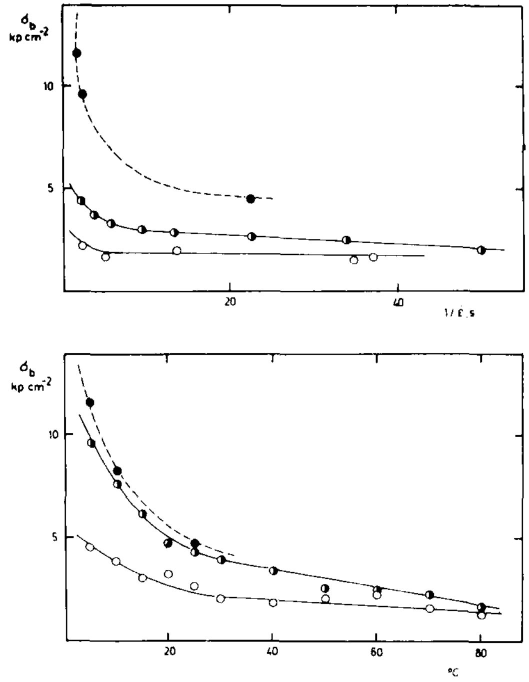

FIGURE 1 Dependences of tensile strength, σ_b, on the reciprocal strain rate and temperature for sample B-7 ($\nu_e = 1.76 \times 10^{-4}$ mol cm^{-3}).

a (●) 5, (◑) 25, (○) 60°C; b (●) 0.74, (◑) 0.44, (○) 0.044 s^{-1}.

characteristics on the network density, as assumed also by the theoretical relation (1). In the temperature region which, at the crosshead speed values used, is sufficient for attaining equilibrium with respect to the modulus, the tensile strength still distinctly decreases. Only at temperatures above 40°C is it possible to attain the equilibrium conditions also with respect to strength. (The samples swollen with water to equilibrium cannot be measured at temperatures lower than 0°C, because the ice formed in the polymer as a separate phase changes its properties.)

The investigation of the measuring conditions allows an evaluation of the participation of the non-equilibrium effects in the failure mechanisms. For this reason, the tensile measurements with all samples of the series A and B were carried out both at 25°C and crosshead speed 1 mm s^{-1} and under conditions more remote from the equilibrium (5°C, 10 mm s^{-1}). The tensile strength, σ_b, and strain-at-break, ϵ_b, values thus obtained, along with the corresponding probable errors are summarized in Tables I and II; within the experimental range used, the tensile strength monotonously increases, whereas strain-at-break decreases with network density. The effect of the network density on the shape of the stress-strain curves can be seen in Figure 2. A bilogarithmic plot of our results, log σ_b vs. log ν_e, and log λ_b vs. log ν_e (Figures 3 and 4) allowed a comparison between the ultimate behaviour of the measured networks and the empirical relations derived earlier.[9] The degree of crosslinking of the PHEMA samples is represented in Figures 3 and 4 by means of the effective network density ν_e, which is directly proportional to the modulus of elasticity. The ν_e values were calculated from a known concentration of the crosslinking agent, c, using an empirical relation[10] suggested earlier and derived for the PHEMA networks prepared at different concentrations of the diluent in the form

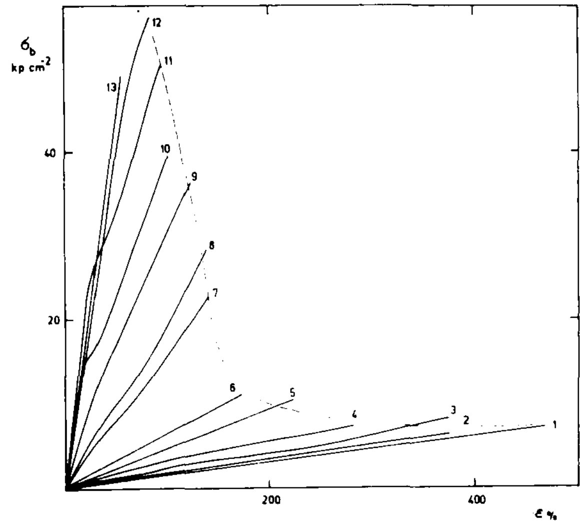

FIGURE 2 Influence of the effective network density, ν_e, on the shape of the stress-strain curves.

5°C, 10 mm s^{-1}; 1 $\nu_e = 0.73 \times 10^{-4}$, 2 0.89×10^{-4}, 3 1.02×10^{-4}, 4 1.23×10^{-4}, 5 1.52×10^{-4}, 6 1.99×10^{-4}, 7 2.75×10^{-4}, 8 3.15×10^{-4}, 9 3.76×10^{-4}, 10 4.17×10^{-4}, 11 4.80×10^{-4}, 12 5.18×10^{-4}, 13 6.51×10^{-4} mol cm^{-3}.

$$\nu_e = 2Kc + Q = K\nu_c + Q; \qquad (2)$$

ν_c is the chemical degree of crosslinking determined under the assumption $\nu_c = 2c$. The values of the constants K and Q for different dilution during polymerization, ν_0, were determined with more precision later.[11]

The points corresponding to the series A and B lie on one curve within limits of experimental scatter. Therefore, under the given experimental conditions only elastic effective chains, which determine the modulus of elasticity, are

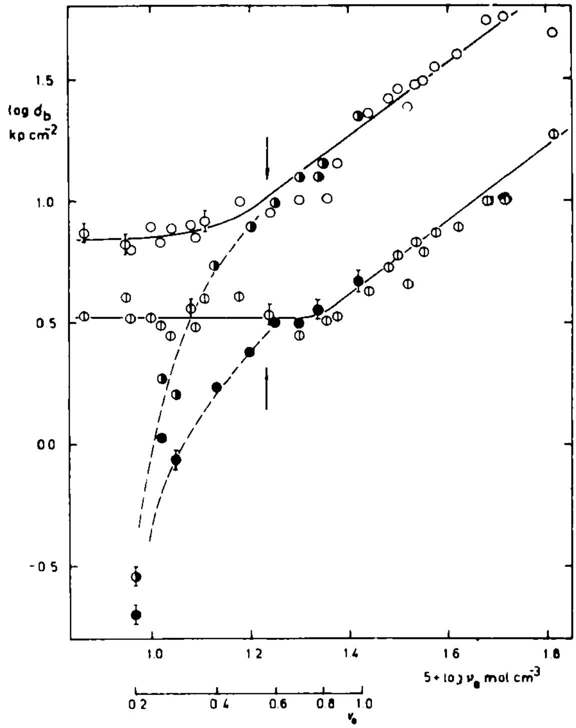

FIGURE 3 Influence of the effective network density, ν_e, on tensile strength, σ_b, in bilogarithmic plot.

The scale of values, ν_0, is related to the samples of series B. (○) series A, 5°C, 10 mm s^{-1} ($0.44 s^{-1}$); (◐) series A, 25°C, 1 mm s^{-1} ($0.044 s^{-1}$); (◑) series B, 5°C, 10 mm s^{-1}; (●) series B, 25°C, 1 mm s^{-1}.

relevant for the ultimate behaviour. An exception is made only by heterogeneous gels prepared in an excess of water ($\nu_0 < 0.57$), in which separation of phases occurs and turbidity develops.[12,13] A local stress concentration appears on microscopic or macroscopic cavities in a sample under load, which has an unfavourable effect on the ultimate behaviour (dashed curves on Figures 3 and 4; boundary conditions for the development of syneresis are marked with arrows). In the region of low crosslinking densities the tensile strength, σ_b, almost does not change with network density. Starting approximately from $\nu_e = 2.0 \times 10^{-4}$ mol cm^{-3} the dependence σ_b vs ν_e is linear in the bilogarithmic coordinates, and can be represented by

$$\sigma_b = a\,\nu_e^{3/2}, \tag{3}$$

where $a = 4.57 \times 10^6$ and 1.05×10^6, respectively, for the experimental conditions 5°C, 10 mm s^{-1} and 25°C, 1 mm s^{-1}. Also on the curves of the

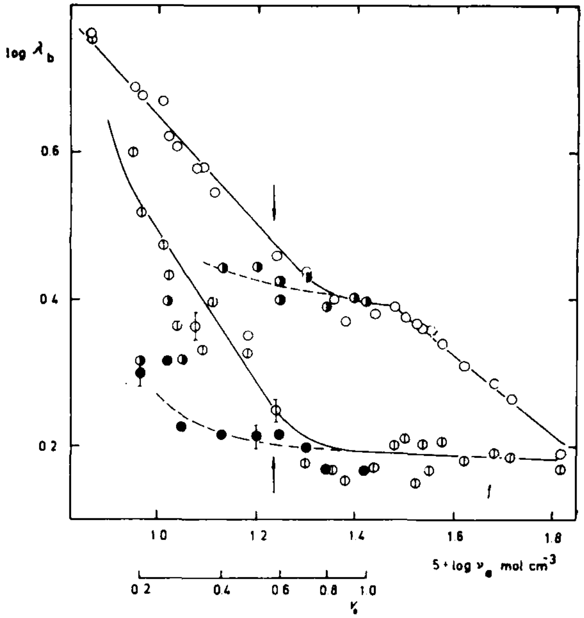

FIGURE 4 Influence of the effective network density, ν_e, on the ultimate extension ratio, λ_b, in bilogarithmic plot.

The scale of values ν_0 is related to samples of the series B; points are designated as in Figure 1.

ultimate extension ratio, λ_b vs. ν_e, two parts can be distinguished, indicating different failure mechanisms in the regions of low and high network densities. Within the range of validity of Eq. (3) a change in the experimental conditions has as its consequence a greater change in tensile strength, σ_b, than in the region of low network densities. This effect is still more pronounced in heterogeneous systems and can be connected in this case with a drop in the hypothetical glass transition temperature, T_g, due to the orientation in the surroundings of the fracture initiators.[14] In the case of the ultimate extension ratio, λ_b, the effect of discontinuities also manifests itself by a departure of λ_b values from the dependence valid for homogeneous samples, directed towards lower extensibility. The decrease in λ_b with increasing ν_e remains preserved, however; only in the cases of values corresponding to macroscopic sponges ($\nu_0 < 0.30$) lower values of λ_b were found under less equilibrium conditions, which indicates a specific fracture mechanism of these systems.

The region in which tensile strength, σ_b, is insensitive towards changes in the network density is larger under experimental conditions closer to equilibrium. As to strain-at-break, the region of low sensitivity to the degree of crosslinking appears only in experiments carried out closer to equilibrium. In accordance with Figure 3, the region of insensitivity of σ_b to ν_e lies at low ν_e, whereas for λ_b it lies at high ν_e. The results described demonstrate, therefore, that the ultimate behaviour of the PHEMA networks is determined by a combined action of the equilibrium and viscoelastic factors.

The exponent 1.50 in Eq. (3) has the same value for both levels of testing conditions, and is higher than both the data published earlier and those predicted by theory. The cause should probably be seen in a decrease in the equilibrium degree of swelling with network density, leading to a gradual increase in the glass transition temperature of the systems under investigation. The course of typical dependences $\sigma_b - \nu_e$, determined for various elastomers, has been compared with our results in Figure 5. The amorphous elastomers have a maximum,[7,9] lying in the region from $\nu_e = 4 \times 10^{-6}$ to 2×10^{-5} mol cm^{-3}, whereas the strength of the crystallizing natural rubber passes through a maximum[6] at $\nu_e = 1.5$ to 3.0×10^{-4} mol cm^{-3} (the ν_e values were estimated from the M_c values by means of a graphical dependence published earlier[15]). Although our results have been somewhat affected by certain changes in the degree of swelling with network density, it seems that the monotonous character of the PHEMA curves is related to the fact that the strength maximum lies

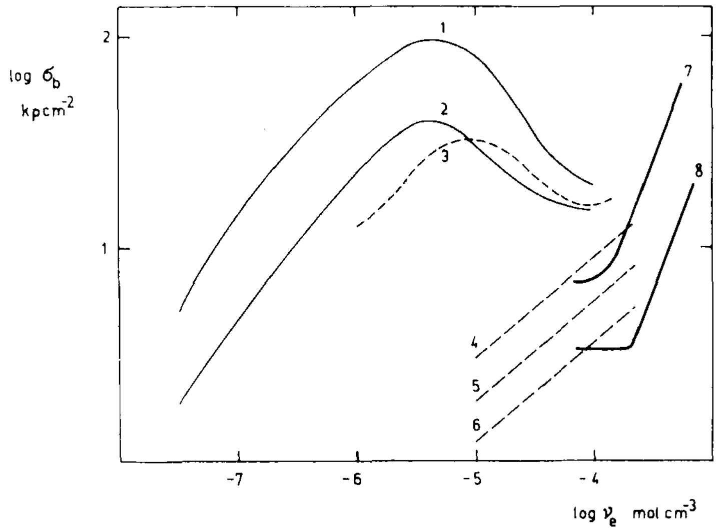

FIGURE 5 Influence of the effective network density, ν_e, on tensile strength, σ_b, of various amorphous elastomers.

Ethylene propylene rubber[7]: 1 25°C, 0.83 s^{-1}; 2 25°C, 0.008 s^{-1}; 3 styrene butadiene rubber,[7] 25°C, 0.083 s^{-1}; polyether polyurethane elastomer[9]: 4 4.5°C, 0.052 s^{-1}; 5 25°C, 0.052 s^{-1}; 6 71°C, 0.052 s^{-1}; PHEMA: 7 5°C, 0.44 s^{-1}; 8 25°C, 0.044 s^{-1}.

beyond the interval under investigation, probably in the direction of low network densities in analogy with other amorphous polymers.

Failure Envelope

The effect of temperature and experimental time scale on tensile strength, σ, and strain-at-break, ϵ_b, was studied in more detail using samples A-1, A-7 and B-7 ($\nu_c = 0.17 \times 10^{-4}$; 1.05×10^{-4} and 2.16×10^{-4} mol cm^{-3}, resp.) prepared at constant dilution during polymerization, $v_o = 0.6$. The values σ_b and ϵ_b obtained at different temperatures and strain rates were plotted in the coordinates log ($\sigma_b\ \lambda_b\ 273/T$) vs. log ($\epsilon_b E_e\ 273/T$) in the universal failure envelope (Figure 6). Since $E_e = 3\ \nu_e RT\ v_o{}^{2/3}$, it holds

$$\log \epsilon_b\ E_e\ 273/T = \log \epsilon_b + \log z, \tag{4}$$

where $z = 3R\,\nu_e 273\ v_o{}^{2/3}$ is a shift factor, which reduces the failure envelopes of the individual samples into a universal curve. For samples A-1, A-7 and B-7, respectively, we obtain $\log z = 0.558, 0.715$ and 0.940 kp cm^{-2}. It follows from

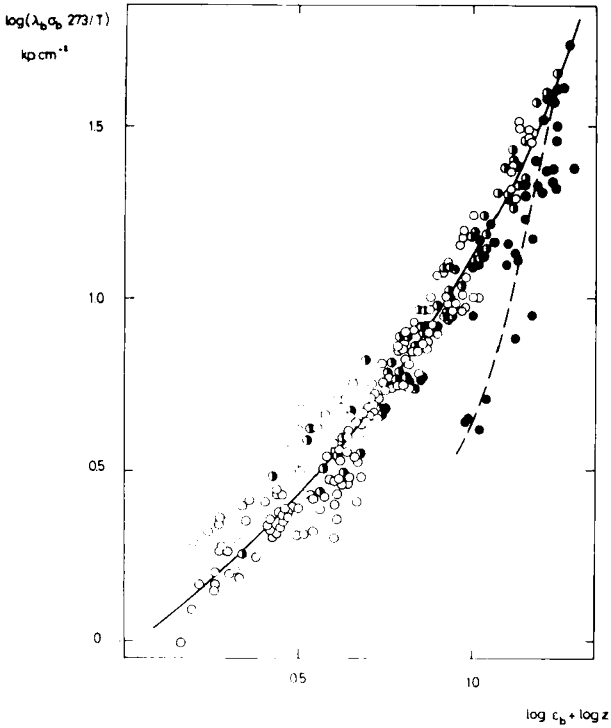

FIGURE 6 Universal failure envelope of PHEMA swollen with water to equilibrium. (●) $\nu_e = 0.73 \times 10^{-4}$, (◑) 1.19×10^{-4}, (○) 1.76×10^{-4} mol cm^{-3}.

Figure 6 that the points pertaining to samples A-7 and B-7 actually form a continuous failure envelope. However, the failure envelope of the sample A-1 having the lowest network density distinctly departs in its high-temperature part from the curve corresponding to the other two samples. This means that the shift factor z used was too great. To superimpose the points in the high-temperature part of the failure envelope of the sample A-1 into a general curve, the shift factor $\log z = 0.238$ ought to be used, which corresponds to $\nu_e = 0.35 \times 10^{-4}$ mol cm^{-3}. The attaining of equilibrium deformation (if at all possible) in elastomers with a very low crosslinking density takes a long time, and the modulus of elasticity goes on decreasing with increasing temperature. In the dynamic experiments, the characteristic secondary relaxation process is often observed with such systems; it is usually ascribed to the effect of entanglements.[16] The lightly crosslinked networks cannot therefore be superimposed into the universal failure envelope, with respect to the fact that their experimentally determined modulus of elasticity, and consequently their shift factor z, are temperature and time-dependent.

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