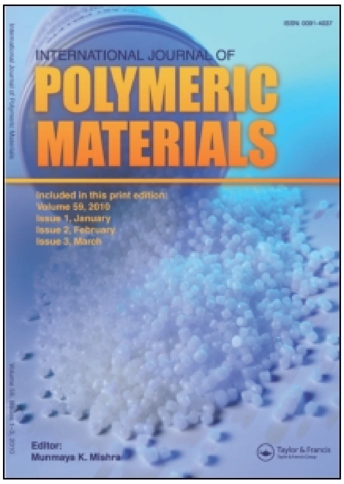

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Janáĉek, J. , Kola, J. , ík, Vacík, J. and Kopeĉek, J.(1976) 'Mechanical Responses of 2-Hydroxyethyl Methacrylate-Methacrylonitrile and 2-Hydroxyethyl Methacrylate-Acrylonitrile Copolymer Networks', International Journal of Polymeric Materials, 5: 1, 59 — 70

To link to this Article: DOI: 10.1080/00914037608072389

URL: http://dx.doi.org/10.1080/00914037608072389

Intern. J. Polymeric Mater., 1976, Vol. 5, pp. 59–70

Printed in Reading, England

Mechanical Responses of 2-Hydroxyethyl Methacrylate–Methacrylonitrile and 2-Hydroxyethyl Methacrylate–Acrylonitrile Copolymer Networks

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(*Received January, 1975*)

The mechanical behaviour of 2-hydroxyethyl methacrylate–methacrylonitrile (HEMA–MAN) and 2-hydroxyethyl methacrylate–acrylonitrile (HEMA–AN) copolymer networks of various composition prepared in presence of 0.6×10^{-4} mol cm^{-3} ethylene dimethacrylate and 20 vol.-% dimethylformamide were investigated. The viscoelastic and stress–strain behaviour of samples swollen in water to equilibrium and the dynamic relaxation behaviour of dry polymers from liquid nitrogen temperature onwards was investigated.

It was found that with increasing concentration of the MAN or AN component the equilibrium degree of swelling in water decreases, which on the other hand is accompanied by a simultaneous decrease in the glass transition temperature, T_g, of copolymers in the dry state. T_g passes through a minimum in this case. The HEMA–AN copolymers become swollen to a higher degree; their T_g temperatures in the dry state are lower compared to the HEMA–MAN copolymers. The effect of the decreasing degree of swelling with increasing content of the MAN or AN comonomers is predominantly reflected in shifting the viscoelastic data toward the main transition region, that is in the increasing distance from the mechanical equilibrium of networks measured at room temperature. In the molar concentration range of nitrile comonomers $n \cong 0.2$ a minimum of the equilibrium modulus was observed, probably related to changes in the effectivity of crosslinking reaction with increasing content of the MAN or AN groups.

The tensile strength increased with increasing content of acrylonitrile and methacrylonitrile, while strain-at-break passed through a maximum, the position of which depended on temperature and on the strain rate. The failure envelopes plotted as $\sigma_b \lambda_b T_0 T^{-1}$ vs. $\log \epsilon_b + \log 3(C_1 + C_2)$ shows that the ultimate behaviour of both types of copolymers is very similar, while the differences in behaviour can be predominantly attributed to different distances from the equilibrium.

INTRODUCTION

Poly(2-hydroxyethyl methacrylate) (PHEMA) is an important polymer, mainly in view of surgical applications; its mechanical behaviour has been studied in a number of papers.[1] The tensile strength of this polymer, σ_b, is comparatively low and varies around 5 kpcm^{-2} for polymer networks swollen in water to equilibrium and measured under usual conditions, while strain-at-break, ϵ_b, reaches 1–2. An increase in the ultimate characteristics can be obtained either by using fillers, such as SiO_2,[2] or by copolymerization of HEMA with appropriate monomers, which however have a complex effect on both T_g of the copolymers obtained and on their equilibrium degree of swelling.

In this paper we investigated the basic stress–strain characteristics, σ_b and ϵ_b in the first place, and the equilibrium and relaxation behaviour of the 2-hydroxyethyl methacrylate–methacrylonitrile (HEMA–MAN)[3] and 2-hydroxyethyl methacrylate–acrylonitrile (HEMA–AN)[3] copolymers swollen in water to equilibrium in order to find out to what extent these properties are affected by the presence of comonomer at a constant crosslinking agent (ethylene dimethacrylate) concentration. The low-temperature relaxation behaviour of some PHEMA copolymers has been studied earlier; this paper has therefore been devoted to a more detailed study of the effect of the CN and CH_3 groups on secondary transitions.

EXPERIMENTAL

2-Hydroxyethyl methacrylate (HEMA). The monomer was prepared by alkaline reesterification of methyl methacrylate with glycol.[8] The ethylene-dimethacrylate formed was removed from the water-diluted reaction mixture by several extractions with hexane, after which HEMA was repeatedly extracted from its aqueous solution by shaking with ether. The raw HEMA was twice redistilled in vacuo. Purity 99.9%. B.p. 79°C/4 mm Hg. $n_D^{20} = 1.4525$. The methacrylonitrile and acrylonitrile monomers were rectified on a 20-plate column and were chromatographically pure. B.p. 90.5° and 77 respectively.

Ethylenedimethacrylate was extracted five times with a 5% NaOH solution, then 20 times with a twofold volume of water, distilled twice in vacuo and was chromatographically pure. B.p. 84°C/1 mm Hg, $n_D^{20} = 1.4549$.

Methyl 2,2′-azo-bis-isobutyrate used as initiator was obtained by saponification of 2,2′-azo-bis-isobutyronitrile with hydrogen chloride in methanol solution. The separated iminoether hydrochloride was hydrolyzed with lukewarm water (35°C). The raw product was purified by repeated crystallization from petroleum ether. M.p. 30°C.

Dimethylformamide was rectified in vacuo and redistilled in vacuo immediately before the experiment.

The polymerization was carried out by radical mechanism[9] in the presence of 20 vol.-% of dimethylformamide. Methyl 2,2′-azo-bis-isobutyrate in a concentration of 3×10^{-3} mol/l was used as initiator. The composition of polymers is given in Table I.

A mixture of monomers, crosslinking agent and initiator was weighed into an Erlenmeyer flask, flushed for 20 min. with purified nitrogen to remove the dissolved oxygen, and pressed under an inert atmosphere into a mould consisting of two plane-parallel brass plates provided with a polypropylene coating and sealed with silicone. After this mould was placed in a thermostat heated to 60°C for 16 h. After completion of polymerization the samples were removed from the mould and washed for several weeks in distilled water which was changed every second day in order to remove the residues of the monomer, diluent, and initiator.

Test samples preparation

The ultimate characteristics were measured on dumbbell samples, 4.1 mm wide (ultimate characteristics) and on strips, c. 10 mm wide and 100 mm long (stress relaxation and the C_1, C_2 constants of the Mooney–Rivlin equation[10]). The test samples were cut out from films 1 mm thick and swollen in water to equilibrium.

Measurement of mechanical characteristics

The ultimate characteristics were measured with an Instron (Table type) apparatus at 3°C (crosshead speed 100 cm min^{-1}), 25°C (100 cm min^{-1} and 2 cm min^{-1}), and also at 60°C (2 cm min^{-1}). By using different temperature and strain rate various distances from the mechanical equilibrium were obtained. The working length of samples fixed in the clamps was 22.5 mm. The constants of the Mooney–Rivlin equation were calculated from the stress–strain curves obtained at a constant crosshead speed 0.05 cm min^{-1}; the effect of different deformation of samples near the clamps was regarded as negligible. Stress relaxation was measured on the same samples during 30 min at a deformation $\epsilon \doteq 0.2$. The deformation was determined optically with a cathetometer and calculated from the distance between two points on the sample. In all experiments the samples were swollen in water to equilibrium and immersed into a cylinder with thermostated distilled water.

Measurement of the equilibrium degree of swelling

The equilibrium degree of swelling in water was measured gravimetrically and calculated from the weights of dry and swollen to equilibrium samples assuming additivity of the contributions of the individual components.

Measurement of low-temperature relaxation behaviour

Temperature dependences of the components G' and G'' of the complex shear elasticity modulus were determined by means of a torsional pendulum with digital recording of damped oscillations.[1] The measurements were carried out at increasing temperature (approx. 1°C/2 min) from liquid nitrogen temperature to the main transition region of the polymers. The samples were dried over P_2O_5 to constant weight at 80–90°C, annealed at some 130°C before measurement with the torsional pendulum and then gradually cooled in order to remove internal stress, if any.

RESULTS AND DISCUSSION

Relaxation behaviour

The main transition temperature T_a (1 Hz) decreases with decreasing molar fraction n_H HEMA for both series of copolymers over the whole concentration range investigated (Figures 1, 2). T_a read off for the highest value of the loss modulus G'' in the main transition region is by about 15°C higher for PHEMA than T_g determined dilatometrically.[11,12] Since T_g values given in the literature are 90°C for PHEMA,[11,12] about 105°C for PAN[13–16] (two glass transition temperatures, 87°C and 140°C, are also given[17]) and about 110°C for PMAN,[18,19] one can see that T_g's of the copolymers studied are lower than T_g of the respective homopolymers. A minimum of T_g for a certain copolymer composition was found earlier,[14] predominantly when the difference between T_g of components was small. Also for copolymers of AN with MMA a minimum T_g was found, at an approximately equimolar participation of both components.[13–15] In the qualitative explanation[14] it was borne in mind that the relatively high T_g of PAN is a consequence of a strong electrostatic interaction of the —CN groups, which reduces flexibility of the main chains. If the AN monomeric units are incorporated into PMMA—into PHEMA in our

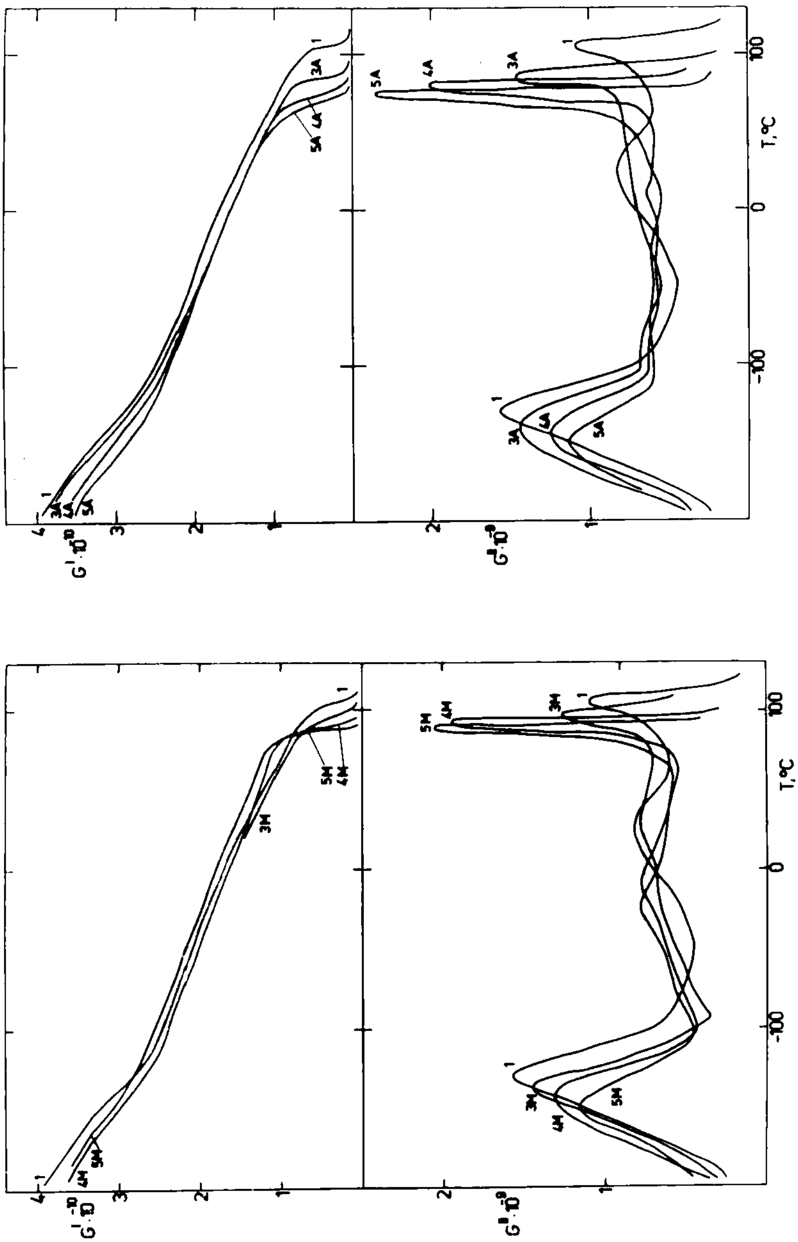


FIGURE 1 Temperature dependence of moduli G' and G'' (dyn/cm^2) of copolymers of 2-hydroxyethyl methacrylate and (a) methacrylonitrile; (b) acrylonitrile (composition of copolymers is given in Table I).

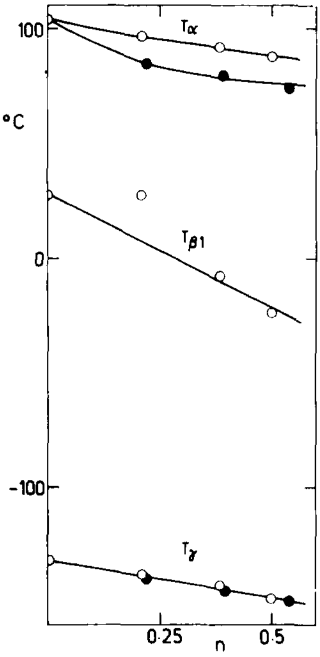


FIGURE 2 Dependence of dispersion temperatures of 2-hydroxyethyl methacrylate on molar fraction *n* of methacrylonitrile (○) or acrylonitrile (●).

case—main chains, the —CN dipoles are isolated from each other and their interaction is suppressed to a great deal. The resulting effect of the incorporation of AN then consists in a decrease in steric hindrances, because the absence of the α methyl group means an increase in the flexibility of the main chains, and thus also a decrease in their T_g. A general cause of extremes on the T_g-composition dependence consists in that in the copolymers there is no additive combination of properties (free volume, chain flexibility, cohesive energy, etc.) of the respective homopolymers. It has been calculated from the copolymerization parameters[15] that the highest concentration of the AN–MMA diads is found in copolymers having a composition close to the equimolar one. It may be inferred as a consequence that the lowest T_α values for the molar fraction of HEMA $n_H \simeq 0.5$ (Figure 2) approximately indicate minima on the total T_α vs. n_H dependences.

As a rule, the T_g temperatures of polymethacrylates are higher by 70–100°C[13,20] than those of polyacrylates with the same side group —R.

Since the T_g temperatures of PAN and PMAN are only little different, one may conclude that the flexibility of the main chains is controlled rather by an interaction between the —CN dipoles than by steric hindrances. We therefore believe that the observed decrease in T_g with the content of MAN may be interpreted similarly as to the HEMA–AN copolymers. The weaker effect of MAN can be explained somewhat speculatively by the presence of the α methyl groups.

As to the β_1 dispersion (28°C; 1 Hz) which is assigned[20–22] to the hindered rotation of the side chains —COO—CH_2—CH_2—OH, the incorporation of MAN is reflected in a shift of the loss maximum in the direction of lower temperatures (Figure 1a). Since PMAN does not exhibit[19] any dispersion in the region of -150°C to T_g, the β_1 dispersion of copolymers must be regarded as a consequence of motion of the remaining HEMA side chains; this is also the most plausible explanation of the decrease in the magnitude of the β_1 maximum. Taking into account that the —CN groups are able to act as proton acceptors in the formation of hydrogen bonds or interact with other dipolar groups,[14] the cause of an increased mobility of the remaining side chains can be seen in a decrease in steric hindrances. This effect can be expected to become operative prevailingly for side chains adjacent to the —CN groups. A qualitatively similar explanation was also used for the decrease in $T_{\beta 1}$ in the series of the HEMA–MAAc copolymers.[6] On the other hand the β_1 maximum cannot be identified already at a molar fraction AN 0.22 (Figure 1b); a further increase in the AN content is not reflected in any systematic changes in the course of the loss modulus G'' with temperature within the interval from -100 to 50°C. The discontinuity of parameters, i.e. of the height and temperature of the β_1 dispersion with decreasing HEMA content has been observed earlier for the HEMA–AAm[7] and HEMA–HEA[8] copolymers. These results allow some earlier conclusions to be confirmed,[7,8] viz., that acrylate comonomers do not affect the parameters but rather the molecular mechanism of the β_1 relaxation process.

The effect of MAN and AN on the parameters of the γ dispersion (-133°C; 1 Hz) which is assigned to the rotational isomerism of the hydroxyethyl groups[5–8,20,23] is very similar to the effect of other comonomers[5–7,24] which do not exhibit a low-temperature relaxation process themselves. The γ loss maximum reduces proportionately to the decrease in the HEMA content (Figure 1); its simultaneous shift toward lower temperatures (Figure 2) can similarly to the β_1 process be attributed to a gradual decrease in the steric hindrances of the motion of remaining side groups —CH_2—CH_2—OH. The presence of the α methyl groups on the main chains does not affect the parameters of the γ dispersion to any considerable degree, in agreement with earlier findings.[7,8,20] The decrease in the intensity of the γ dispersion can also be seen in the diminishing magnitude of drop in the loss modulus G' within the temperature interval of the γ dispersion (−196 to −100°C) (Figure 1). Generally, however, the effect of the comonomer content on the temperature dependence of the storage moduli G' in both series of copolymers is very small.

The equilibrium degree of swelling in water

The equilibrium degree of swelling of copolymers characterized by the volume fraction of polymer, ν_2, in a swollen gel as a function of MAN and AN is given in Table I. In both cases ν_2 increases approximately linearly with increasing molar concentration of these components, but the increase is faster for the methacrylonitrile copolymer. Hence it follows that for the same content of the nitrile comonomer the copolymers HEMA–MAN are swollen to a lower degree, and consequently their T_g is higher than T_g corresponding to the copolymer HEMA–AN.

TABLE I

Composition of copolymers of 2-hydroxyethyl methacrylate (HEMA) with methacrylonitrile (MAN) and acrylonitrile (AN)

Sample No.	HEMA (mol %)	MAN (mol %)	AN (mol %)	ν_2[a]	C_1[b] (kg cm^{-2})	C_2[b] (kg cm^{-2})	log E(300s) (dyn cm^{-2})
1	100	—	—	0.545	1.78	0.46	6.799
2M	89.7	10.3	—	0.611	1.42	1.15	6.731
3M	79.1	20.9	—	0.678	1.11	0.49	6.627
4M	61.3	38.7	—	0.769	0.80	0.83	6.622
5M	50.3	49.7	—	0.804	0.70	1.66	6.775
2A	88.9	—	11.1	0.591	1.57	0.43	6.768
3A	78.1	—	21.9	0.630	0.97	0.42	6.574
4A	60.4	—	39.6	0.736	1.57	0.59	6.755
5A	46.0	—	54.0	0.774	1.80	0.97	6.906

[a] Volume fraction of polymer in swollen gel.

[b] Constants of Mooney–Rivlin equation.

Stress relaxation

Stress relaxation measured at a deformation $\epsilon \doteq 0.2$ and 25°C (Figure 3) indicates an increasing distance of the measured systems from the mechanical equilibrium with increasing content of the comonomers MAN and AN, which is mainly a result of decreasing degree of equilibrium swelling. The results also suggest that the HEMA–MAN copolymer networks are measured at a larger distance from the equilibrium than those of copolymers HEMA–AN, which is in relation with a comparatively higher degree of swelling and a correspondingly lower T_g of swollen copolymers HEMA–AN.

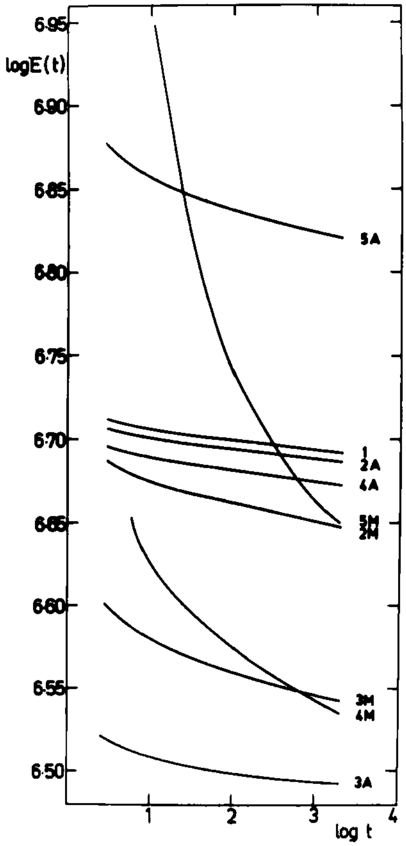


FIGURE 3 Time dependence of $E(t)$ measured by stress relaxation at 25°C (Polymer composition is given in Table I).

Moduli and constants of the Mooney–Rivlin equation

The C_1, C_2 values of the Mooney–Rivlin equation are also given in Table I: copolymers HEMA–MAN exhibit lower constants C_1 and higher constants C_2 than corresponding copolymers with AN. The C_1 values decrease with increasing content of MAN while for copolymers with AN they pass through a minimum. The $C_1 + C_2$ values pass through a minimum, just the same as the moduli $E(t)$ corresponding to stress relaxation during 300 sec.

The constants C_2 probably reflect specific features of forming networks. Since the same concentration of crosslinking agent was used in the preparation of all copolymers, the initial decrease in C_1 with the concentration of hydrophobic groups in systems swollen in water may be related to a decrease in the chemical degree of crosslinking owing to the formation of rings or of pendent vinyl groups, and also to a decrease in the number of permanent entanglements. The increase in the modulus which prevails at higher concentrations of nitrile comonomers is probably related to the increasing distance from the equilibrium in experiments carried out at 25°C.

Ultimate characteristics

Tensile strength, σ_b, and strain-at-break, ϵ_b, increase with increasing content of nitrile comonomers the faster the larger the distance between the experiments and the equilibrium (Figures 4, 5). Strain-at-break (Figure 5) in the system HEMA–MAN passes through a maximum in the region $n_{\mathrm{MA}} = 0.4$, and at a lower n_{A} for the copolymers HEMA–AN. The resulting dependences are again very sensitive to the distance from the mechanical equilibrium. It can be seen from the results that the effect of nitrile comonomers is generally reflected in an increase in the ultimate characteristics. The plot of log $\sigma_b\ \lambda_b\ T_0/T$ vs. log ϵ_b + log 3 ($C_1 + C_2$) (Figure 6) show that the forms of failure envelopes according

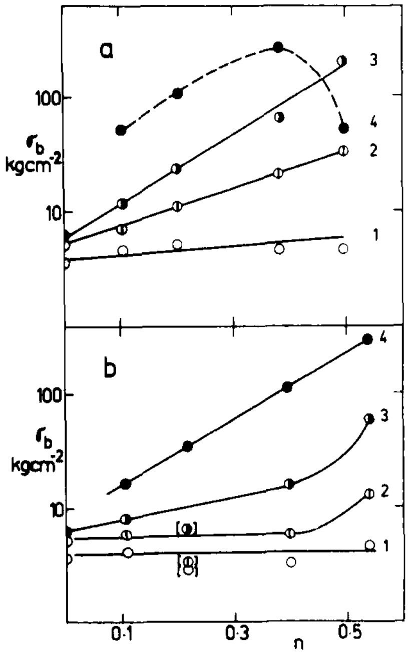


FIGURE 4 Dependence of tensile strength, δ_b, on molar fraction n of comonomer in HEMA.
Conditions of experiments: 1 — $T = 60$°C, $\dot{\epsilon} = 0.148$; 2 — $T = 25$°C, $\dot{\epsilon} = 0.148$; 3 — $T = 25$°C, $\dot{\epsilon} = 7.7$; 4 — $T = 3$°C, $\dot{\epsilon} = 7.4$.
Copolymers (a) HEMA–MAN, (b) HEMA–AN.

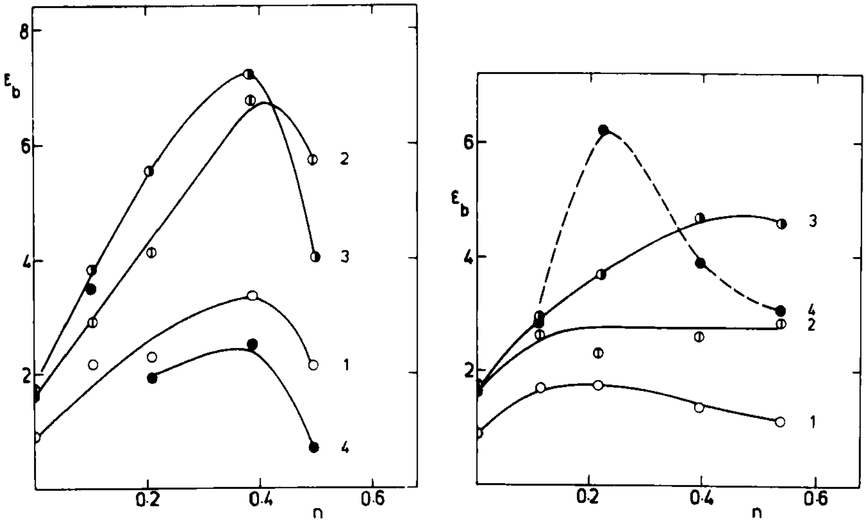


FIGURE 5 Dependence of strain-at-break, ϵ_b, on content of comonomers inH EMA. Copolymers (a) HEMA-MAN, (b) HEMA-AN.
Curves described as in Figure 4.

to Smith[25] are roughly similar, which indicates that the ultimate characteristics of both types of copolymers differ mainly by the contribution of viscoelastic mechanisms, and thus by their distance from the equilibrium.

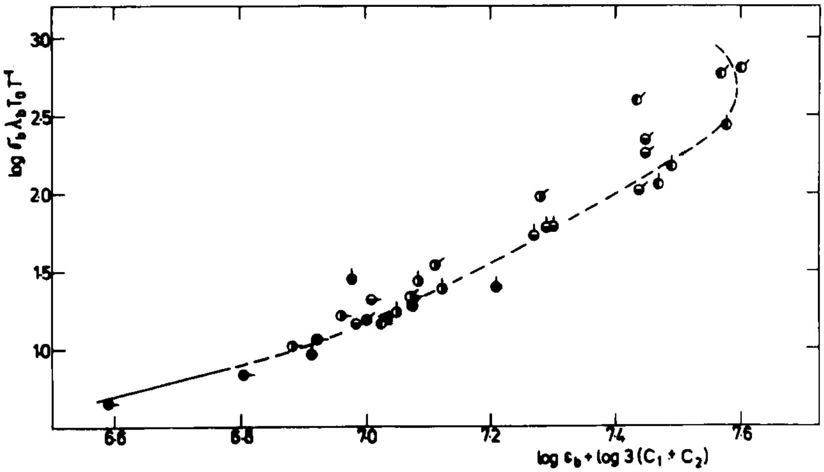
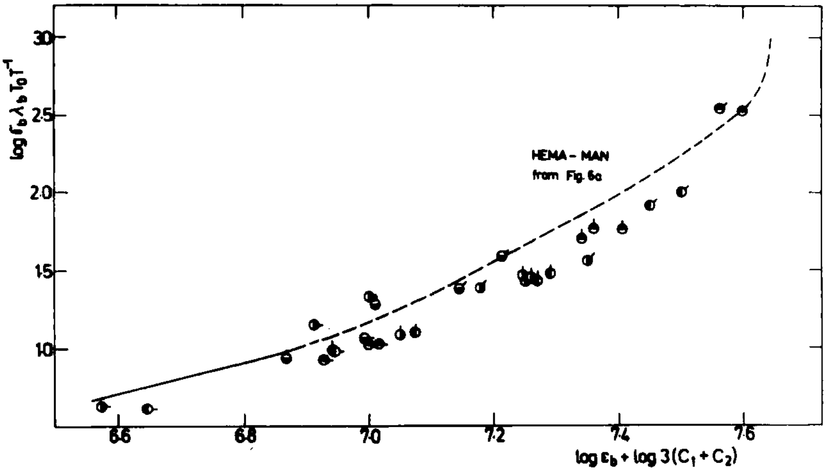


FIGURE 6 Failure envelopes of the system HEMA–MAN (a) and HEMA–AN (b). Points described as in the Experimental Conditions, Figure 4: 1 (⫯), 2 (⌀), 3 (⊸); 4 (⟍). samples Table I: 1 (●); 2A, 2M (◑); 2A, 3M (◒); 4A, 4M (◐); 5A, 5M (◓).

(FIGURE 6B OVERLEAF)



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