Tear propagation resistance of semicrystalline polymeric networks

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The tear resistance behaviour of semicrystalline polymeric networks is characterized by noted variations from the behaviour of amorphous polymers, due to the existence of crosslinks and crystallites. A theoretical analysis and experimental investigation of this phenomenon was undertaken using crystalline poly(vinyl alcohol) hydrogels which were prepared by electron beam irradiation of aqueous PVA solutions followed by a two-stage dehydration–annealing process. The tear propagation resistance depended on the time–temperature history, the crosslinking density and the crystallinity of the hydrogels; the values varied between 700 and 1400 J/m^2 (4–8 ppi) depending on the above parameters. A relationship between tear resistance and degree of crystallinity was obtained, within the range of experimentation of this work. The tearing energy of the same films was a function of the crosslinking density; a theory for prediction of the tearing energy was established. Typical values for semicrystalline networks were higher (up to 1500 J/m^2) than those reported for amorphous networks, mainly due to the crystallites introduced in the network after annealing.

INTRODUCTION

Among the desirable mechanical properties of polymers as potential biomaterials tear propagation strength is of importance, especially in cases of practical applications where the material is subjected to shear stress[1]. The force necessary to propagate a tear in plastic films and thin sheets or in tubings is a means of evaluating the tear propagation strength; this force depends on the thickness and the extensibility of the torn films.

A quantitative expression of the stresses arising from a tear test can be given by the 'tearing energy' T parameter[2], which refers to the stored elastic energy W per surface area A of one face of a crack c of a plastic film of thickness t at constant extension l:

$$T = -\left(\frac{\partial W}{\partial A}\right)_l = -\left(\frac{\partial W}{\partial c}\right)_l \times \frac{1}{t} \qquad (1)$$

The tearing energy can be calculated from force–deformation experiments. Typical stress–strain curves for high and low extensibility films differ in that a highly extensible film is characterized by an initial tear and a maximum load of tearing (smooth tear : *Figure 1*, curve A), while a less extensible film shows almost constant load as a function of time (steady tear : *Figure 1*, curve B).

The tear resistance and threshold fracture energy of crosslinked polymeric networks has been the subject of recent work by Ahagon *et al.*[3,4] who reported that the degree of crosslinking is an additional parameter affecting the tear strength. According to Lake and Thomas[5], the predicted dependence of the fracture energy T on the number-average molecular weight between crosslinks $\bar{M}_c$ can be expressed as:

$$T = K\left(\frac{1}{\bar{M}_c} + \frac{1}{\bar{M}_e}\right)^{-1/2} \times \left(1 - \frac{2\bar{M}_c}{\bar{M}_n}\right) \qquad (2)$$

where K is a constant depending on the density of the polymer, the flexibility and the length of the monomeric unit, and $\bar{M}_e$ is the number-average molecular weight characteristic of the presence of entaglements in the chains; these entanglements usually behave as additional crosslinking points.

Crystalline crosslinked poly(vinyl alcohol) hydrogels have been recently reported as materials with satisfactory biomedical properties[6,7]. The mechanical properties of these hydrogels[8] are within the limits established by Akutsu[1], i.e. the ultimate tensile strength varies between 2500 and 3000 psi and the elongation at break can increase up to 600% depending on the degree of crystallinity. Although the importance of the physical behaviour of biomaterials as determined by the above mentioned mechanical properties has been previously stressed[1], the effect of tear strength on practical applications has been neglected in most related studies.

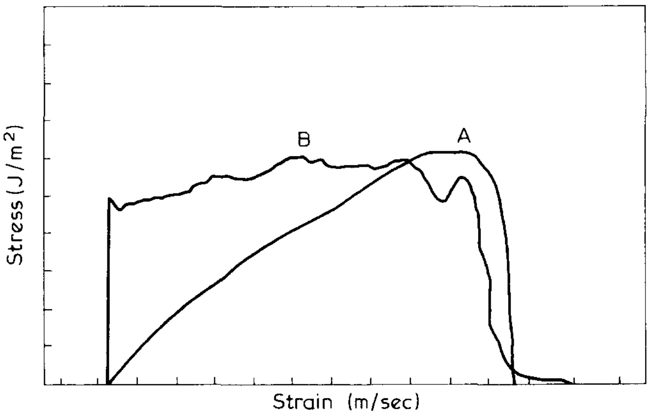

Figure 1 Typical tear strength test stress–strain curves of smooth (A) and steady tear (B)

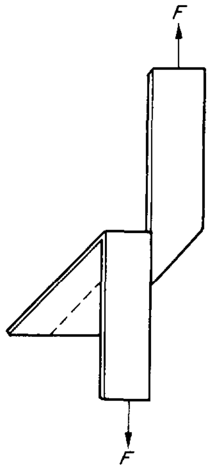

Figure 2 Simple extension tear experimental set-up

The variation of the mechanical properties of high polymers with temperature is an important characteristic, since the physical behaviour of these materials is a function of the temperature of practical applications. For biomedical applications in extra- or intra-corporeal uses, this temperature varies between 20° and 37°C; in addition, the temperature–time history of the materials significantly affects their physical behaviour.

It is the purpose of this contribution, to study the effect of the temperature–time history and the crosslinking density of crystalline crosslinked polymeric networks on their tear propagation resistance using PVA hydrogels as an experimental model. This study can be of further interest in obtaining additional information about the structure and morphology of these polymers.

EXPERIMENTAL

This section deals with the determination of the force necessary to propagate a tear in polymeric networks. The crosslinked PVA samples were prepared by electron beam irradiation of 10 and 15% aqueous PVA solutions with 3 and 5 Mrads at 0° and 30°C using a Van de Graaff generator. The PVA used was Elvanol 73-125 G of Du Pont[9] with $\bar{M}_n$ = 88 800 as calculated by gel permeation chromatography. The crosslinking density ρ (mol/cm^3) was calculated after determination of the average molecular weight between crosslinks $\bar{M}_c$ from swelling experiments using the following relations[10]:

$$\rho = \frac{1}{v\bar{M}_c} \tag{3}$$

where

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \frac{\dfrac{\bar{v}}{V_1}\left[ln(1-\nu_{2,s}) + \nu_{2,s} + \chi_1\,\nu_{2,s}^2\right]}{\nu_{2,r}\left[\left(\dfrac{\nu_{2,s}}{\nu_{2,r}}\right)^{1/3} - \dfrac{1}{2}\left(\dfrac{\nu_{2,s}}{\nu_{2,r}}\right)\right]} \tag{4}$$

where $\nu_{2,r}$, $\nu_{2,s}$ are the initial and final polymer volume fractions, respectively, i.e. before and after swelling; V_1 is the molar volume of solvent = 18 cm^3/mol; $\bar{v}$ is the specific volume of amorphous polymer = 0.788 cm^3/g and χ_1 is the Flory polymer–solvent interaction parameter[9].

Annealing processes at 90°, 105° and 120°C for 30–90 min introduced crystallites in the polymer chains[6]. The samples were subsequently swollen in water at 30°C until thermodynamic equilibrium. It has been proven by i.r. spectroscopy[11] and X-rays analysis[12] that this swelling process does not dissolve the already formed crystalline regions. Thus the weight swelling ratio q, defined as in equation (5), is characteristic of the degree of crystallinity x:

$$q = \frac{\text{Weight after swelling}}{\text{Weight before swelling}} \tag{5}$$

The degree of crystallinity x was calculated using these swelling experiments and applying equation (6) under the assumption of additivity of volumes[6]:

$$x = \frac{\dfrac{1}{\rho_h} - \dfrac{1 - W_{\text{PVA}}}{\rho_w} - \dfrac{W_{\text{PVA}}}{\rho_a}}{\left(\dfrac{1}{\rho_c} - \dfrac{1}{\rho_a}\right) W_{\text{PVA}}} \tag{6}$$

where W_{PVA} is the polymer weight content in the hydrogel; ρ_h is the density of the swollen crystallized hydrogel at 30°C; ρ_a is the density of 100% amorphous[13] PVA = 1.269 g/cm^3; ρ_c is the density of 100% crystalline[13] PVA = 1.345 g/cm^3 and ρ_w is the density of water at 30°C = 0.996 g/cm^3.

Specimens were cut from these films in strips of 7.5 cm long by 2.5 cm wide with a clean longitudinal slit of 5.0 cm and they were cut in the middle with a sharp razor blade (*Figure 2*). Thus, the experiments performed were of the 'trousers' type[14,15], where the simple extensions tear theory applies[16]. The thickness of the specimen was measured below the slit with a Dial Comparator and the average of three values was reported; it varied between 4.83 x 10^{-2} and 5.33 x 10^{-2} cm.

All the tests were run in a water bath at 30°C. The tongues of the specimen were secured in the two grips of the constant grip rate separation testing machine, using an initial grip separation of 5.0 cm. The major axis of the specimen was aligned with the imaginary line joining the centres of the grips. The grip separation used was 4.23 x 10^{-2} cm/sec. Although the crystalline hydrogels were not stress oriented, the specimens were cut in different directions of the major axis, to test the homogeneity of the samples with respect to physical behaviour.

The fracture energy T was calculated as:

$$T = 2F/t \tag{7}$$

where

$$t' = (2)^{1/2}t \tag{8}$$

where F was the applied load and t was the thickness of the film. It was observed that the tear path was inclined by approximately 45°. Our finding is in accord with previously reported observations by Ahagon *et al.*[4].

The load necessary for the propagation of a crack was recorded as a function of time. For PVA films all the diagrams were of the 'low extensibility' type (elongation at break 400–600%[6] and followed the general shape of curve B of *Figure 1*.

Table 1 Dependence of tear strength on the annealing conditions. Initial solution 10% in PVA

Crosslinking density (mol/cm^3)	Annealing conditions T (°C)	Annealing conditions t (min)	Degree of crystallinity x (%)	Elongation at break (%)	Tear resistance (J/m^2)	Tear resistance (ppi)	Tearing energy (J/m^2)
1.35×10^{-4}	105	30	43.72	320	905	5.17	1280
($\bar{M}_c = 9370$)	105	60	–	365	1079	6.16	1525
	105	90	–	405	1175	6.71	1662
	90	30	24.56	215	424	2.42	599
	90	60	43.10	305	786	4.49	1116
	90	90	48.50	320	1072	6.12	1472
3.37×10^{-4}	105	30	38.15	185	1173	6.70	1658
($\bar{M}_c = 3765$)	105	60	–	275	821	4.69	1161
	105	90	51.65	305	1198	6.84	1694
	90	30	26.72	110	359	2.05	479
	90	60	28.16	155	250	1.43	354
	90	90	31.18	195	373	2.13	527

Table 2 Dependence of tear strength on the annealing conditions. Initial solution 15% in PVA

Crosslinking density (mol/cm^3)	Annealing conditions T (°C)	Annealing conditions t (min)	Degree of crystallinity x (%)	Elongation at break (%)	Tear resistance (J/m^2)	Tear resistance (ppi)	Tearing energy (J/m^2)
1.51×10^{-4}	105	30	46.18	390	1510	8.62	2135
($\bar{M}_c = 8420$)	105	60	–	470	2254	12.87	3187
	105	90	–	485	1946	11.11	2751
	90	30	33.75	300	674	3.85	987
	90	60	–	380	1201	6.86	1699
	90	90	–	430	1368	7.81	1934
2.22×10^{-4}	120	30	61.17	–	2854	16.30	4186
($\bar{M}_c = 5715$)	120	60	–	480	3149	17.98	4410
	120	90	–	–	3756	21.45	5312
	105	30	43.50	–	1515	8.65	2171
	105	60	–	460	1368	7.81	1934
	105	90	–	–	1732	9.89	2425
	90	30	33.20	–	595	3.40	835
	90	60	–	330	585	3.34	827
	90	90	–	–	616	3.52	872

RESULTS AND DISCUSSION

In the tear propagation experiments the load was recorded and reported as a function of different parameters characterizing the temperature–time history of the hydrogels.

In *Tables 1* and *2*, the tear resistance defined as the load necessary to tear a sample normalized for the thickness of the film is presented as a function of the annealing time for different temperature conditions and crosslinking densities.

The same Tables include the tearing energies at break as calculated from equation (7) for maximum l, i.e. at the elongation at break, and reported as J/m^2. The values of crosslinked crystallized samples are of the order of 500–5000 J/m^2 depending on the different degrees of crystallinity and they are much higher than values reported for amorphous networks[3].

The tear energy is a function of the crosslinking density as reported in *Figure 3*. Using the theory of Lake and Thomas and equation (2), the values of $\bar{K}$ for different films could be evaluated. For this calculation $\bar{M}_e$ was assumed to be 7000; this is a reasonable average value in comparison to $\bar{M}_c$ since, in radiation induced crosslinking, entanglements are not prominent. The values of K varied between 15 and 75 J/m^2/(g/mol)$^{1/2}$ while the corresponding values for amorphous networks were as low as 0.2–1.0 J/m^2/(g/mol)$^{1/2}$.

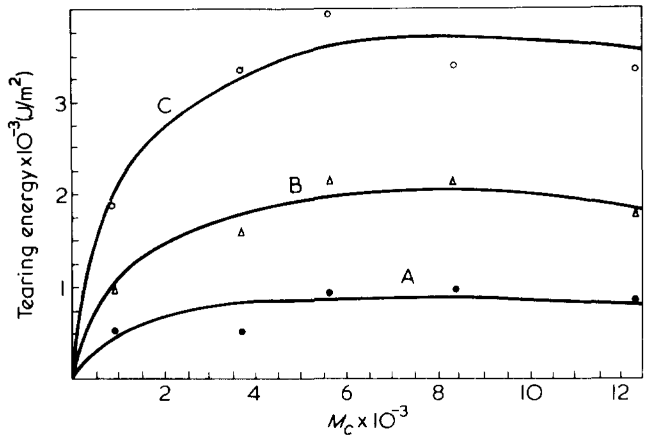

Figure 3 Tear energy (J/m^2) at break as a function of $\bar{M}_c$. Annealing conditions: time 30 min. A, 90°C (K = 16.55); B, 105°C (K = 39.75); C, 120°C (K = 73.85), ——, Theory

Similarly the tear resistance is a function of the crosslinking density as shown in *Figure 4*.

For high crosslinking densities ρ ($>2.2 \times 10^{-4}$ mol/cm^3) the tear strength decreases and the hydrogels become more

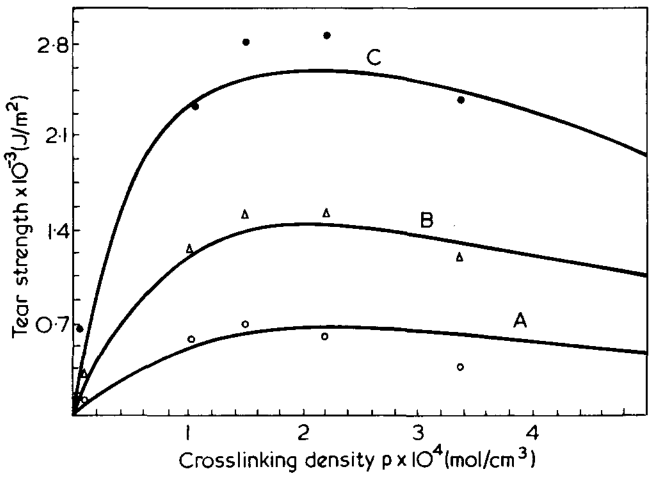

Figure 4 Dependence of tear strength (ppi) on the crosslinking density ρ (mol/cm^3). Annealing conditions: time 30 min. A, 90°C; B, 105°C; C, 120°C. ——, Theoretical prediction

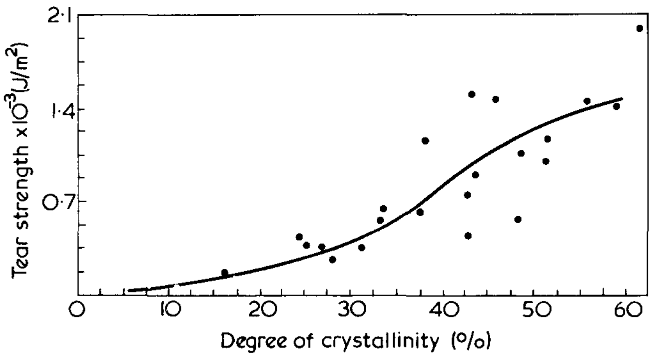

Figure 5 Effect of degree of crystallinity (crystalline PVA/total PVA) on the tear strength for crosslinked semicrystalline PVA hydrogels

brittle. There is a characteristic crosslinking density (2×10^{-4} mol/cm^3) with maximum tear strength and for lower crosslinking densities the tear strength decreases due to lower degree of crystallinity (see *Table 1*). Increasing degrees of crystallinity lead to higher values of tear strength because the crystalline regions act as additional crosslinks reinforcing the hydrogel. For the same reasons, increasing $\overline{M}_c$ favours the formation of more crystallites with larger size and increases the tear strength. The values of tear strength in *Tables 1* and *2* are reported in *SI* as well as imperial units to facilitate the comparison with other values reported in biomaterials oriented research by other investigators. Typical values of tear strength are between 700–1400 J/m^2 or 4 and 8 ppi (lbs per inch of thickness of semicrystalline PVA hydrogels), whereas uncrosslinked crystallized materials have values below 700 J/m^3 (4 ppi) and crosslinked amorphous PVA hydrogels below 80 J/m^2 (0.5 ppi). The values for amorphous PVA hydrogels are in the area reported by others[17,18] for similar amorphous polymeric networks.

In the tear tests the material fails at a specially created stress concentration artificially localized in a small volume where the probability of occurrence of dangerous defects is naturally low. Irrespective of the method of stress raising, tearing begins when certain values of the stresses and strains are reached in the area of stress concentration. In these films a state of simple tension always exists at the tip of a growing nick.

It is now evident that the input energy density to failure is not a material property; the energy density at the tear zone is the strength determining property.

The reinforcement of PVA hydrogels by crystallization is due to the increase of both the input energy (the intrinsic strength) and the tear diameter, with the latter being the predominant factor. Thus this tear method can be used also as a method of estimating the structural quality of networks[19] Equation (2) was derived for what was termed the 'cracked growth limit', and is the minimum tearing energy necessary for any crack growth to take place. At finite rates of crack growth the effect of viscoelasticity increases the tearing energy necessary for steady propagation by, typically, a factor of 100 or more. The approximate agreement with experiment shown in *Figure 3* suggests, perhaps surprisingly that the viscoelastic effect is slightly dependent on the degree of crosslinking. This is not the case if the degree of crystallinity is considered. Therefore, *Figure 5* shows the dependence of tear strength on the degree of crystallinity for all the samples reported in this investigation.

The variation of tear strength has to be viewed as an integral part of the dependence of the physical behaviour of hydrogels on the degree of crystallinity[20]. Along the same lines recently reported theories claim a possible estimation of ultimate tensile properties of networks through simple tear tests[17].

CONCLUSIONS

In biomedical applications and especially in the cases of biomembranes[20] or artificial cartilage uses[7], the tear resistance of semicrystalline PVA hydrogels is of importance due to the shear stresses applied.

The ultimate tearing energy and the tear strength are functions of the crosslinking density and the degree of crystallinity; experimental results for hydrogels show the variation of the physical behaviour as a function of these parameters.

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REFERENCES

1 Akutsu, T. and Kantrowitz, A. *J. Biomed. Mater. Res.* 1967, **1**, 33
2 Rivlin, R. S. and Thomas, A. G. *J. Polym. Sci.* 1953, **10**, 291
3 Ahagon, A. and Gent, A. N. *J. Polym. Sci. (Polym. Phys. Edn)* 1975, **13**, 1903
4 Ahagon, A., Gent, A. N., Kim, H. J., and Kumagai, Y. *Rubber Chem. Technol.* 1975, **48**, 896
5 Lake, G. J. and Thomas, A. G. *Proc. Roy. Soc. (A)* 1967, **300**, 108
6 Peppas, N. A. and Merrill, E. W. *J. Polym. Sci. (Polym. Chem. Edn)* 1976, **14**, 441
7 Peppas, N. A. and Merrill, E. W. *J. Biomed. Mater Res.* in press
8 Peppas, N. A. and Merrill, E. W. *J. Appl. Polym. Sci.* 1976, **20**, 1457
9 Peppas, N. A. and Merrill, E. W. *J. Polym. Sci. (Polym. Chem. Edn.)* 1976, **14**, 459
10 Bray, J. C. and Merrill, E. W. *J. Appl. Polym. Sci.* 1973, **17**, 3779
11 Peppas, N. A. *Makromol. Chem.* in press

12 Sakurada, I., Nukushina, Y. and Sone, Y. *Kobunshi Kagaku,* 1955, **12**, 506

13 Sakurada, I., Nukushina, Y. and Sone, Y. *Ric. Sci (A)* 1955, **425**, 715

14 ASTM Method D-1044-66, 'Tear Resistance of Plastic Film and Sheeting' ASTM, 1970

15 ASTM Method D-1922-67, 'Propagation Tear Resistance of Plastic Film', ASTM, 1972

16 Thomas, A. G. *J. Appl. Polym. Sci.* 1960, **3**, 1968

17 Glucklich, J. and Landel, R. F. *J. Appl. Polym. Sci.* 1976, **20**, 121

18 Greensmith, H. W., Mullin, L. and Thomas, A. G. *Trans. Soc. Rheol.* 1960, **4**, 179

19 Lukomskaya, A. I. Upolovnikova, E. M. and Reznikovskii, M. M. *Mekhan. Polim.* 1967, **3**, 846

20 Peppas, N. A. and Merrill, E. W. *J. Polym. Sci. (Polym. Chem. Edn)* 1976, **14**, 441

21 Peppas, N. A. *Polym. Prepr.* in press