An estimate of the strength of polymers

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Based on the kinetic theory of fracture, the equation $\sigma_{th}=(1/s)(4rE_cU/3n)^{1/2}$ was used to calculate the theoretical strength, σ_{th}, of polymers using the crystal lattice modulus, E_c, the activation energy of thermal degradation, U, and the cross-sectional area, s, of a polymer chain with r taken as the length of a C–C bond and n as unity. The influences of stress concentration and thermal fluctuation on the strength were determined and it was found that both of them could not be neglected.

(Keywords: strength; moduli; cross-sectional area of polymer chains; stress concentration; thermal fluctuation)

INTRODUCTION

It is of considerable interest to obtain an estimate of the theoretical strength of a solid, since when this is compared with experimentally determined values it gives valuable insight into the failure process that occurs in such materials. A discrepancy between the theoretical and actual strengths of polymers is apparent. This discrepancy was, according to some points of view[1–4], attributed to flaws, cracks and imperfections, which concentrate stress. However, the kinetic theory, at first, appeared to represent an entirely different account of fracture phenomena[5]. The kinetic theory assumed that the basic fracture event was bond rupture and it was the accumulation of rupture events that lead to failure of the body, i.e. the fracture event was a thermal fluctuation breakage of bonds. Hence, contradictory notions as to the fracture mechanism arose. Recently, it was pointed out that this was not the case[6,7]. It was concluded that thermal fluctuation and stress concentration were to be regarded as initiating a fracture and deciding the strength of solids.

In this paper, we give a method of determining the theoretical strength of polymers based on the literature[8] and then discuss the influence of thermal fluctuation and stress concentration on the strength.

THEORETICAL STRENGTH OF POLYMERS

According to the kinetic theory of Zhurkov[9], the fracture stress is

$$\sigma_f=\frac{1}{V}\left[U-kT\ln\left(\frac{t}{t_0}\right)\right] \tag{1}$$

where U is the activation energy of mechanical breakdown when $\sigma=0$, V is the structurally sensitive coefficient or activation volume, t_0 is the reciprocal of the molecular oscillation frequency (about 10^{-12}–10^{-14} s), t is the time-to-failure of a specimen held under an applied constant stress σ_f, k is the Boltzmann constant and T is absolute temperature. Based on the photon theory of strength[8,10], the activation energy, U, and activation volume, V, are as follows:

$$U=\frac{nkE_c^0}{2\beta} \tag{2}$$

$$V=V_dq=nsq\sqrt{\left(\frac{3k}{8r\beta}\right)} \tag{3}$$

Here n is the number of atoms in the dilation, s is the cross-sectional area of a polymer chain, r is the interatomic distance, q is the stress concentration factor and E_c^0 is Young's modulus of polymer chains at absolute zero, which is given by

$$E_c^2=(E_c^0)^2-2(E_c^0)\beta T \tag{4}$$

where E_c is the Young modulus of polymer chains at temperature T, and

$$\beta=\left.\frac{\partial E_c}{\partial T}\right|_{T=0} \tag{5}$$

From equation (3), equation (1) is changed to

$$\sigma_f=\frac{1}{V_dq}\left[U-kT\ln\left(\frac{t}{t_0}\right)\right] \tag{6}$$

It is found from equation (6) that the maximum fracture stress is $\sigma_{max}=U/V_dq$ and the theoretical stress is $\sigma_{th}=q\sigma_{max}=U/V_d$. The activation volume without considering stress concentration, V_d, can be obtained from equations (2)–(4) (see Appendix) as:

$$V_d=s\sqrt{\left(\frac{3nU}{4rE_c}\right)} \tag{7}$$

Thus, the theoretical stress is

$$\sigma_{th}=\frac{1}{s}\sqrt{\left(\frac{4rE_cU}{3n}\right)} \tag{8}$$

If the parameters in equation (8) can be determined

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experimentally, the theoretical strength of polymers will be obtained.

It has been shown that the values of activation energy of polymer fracture, U, agree closely with the values of activation energy of thermal degradation[9]. The Young modulus of polymer chains, E_c, could be taken as the crystal lattice modulus of polymers[11], which can be measured by X-ray diffraction[12], Raman scattering[13], inelastic neutron scattering[14] and Brillouin scattering[15]. The cross-sectional area of polymer chains could be calculated from the unit cell of polymers obtained by X-ray diffraction[16]. *Table 1* lists the values of crystal lattice modulus[17], activation energy of thermal degradation[18] and cross-sectional area[19] of some polymers. If the r in equation (8) is taken as the length of a C–C bond (1.54×10^{-10} m) and n as unity, the theoretical strengths, σ_{th}, of polymers are obtained (*Table 1*).

When material is treated as a mechanical continuum rather than as an assembly of atoms or molecules, the application of a tensile stress to the body would cause an increase in interatomic separation. The theoretical strength of polymers is then found to be one order of magnitude smaller than the moduli[20]. From our data in *Table 1* it was found (*Figure 1*) that

$$\sigma_{th} = 0.093 E_c \qquad (9)$$

which is in agreement with the relationship obtained from continuum mechanics. It is shown that equation (8) is a practicable method to determine the theoretical strength of polymers as the parameters used can be measured experimentally.

CONTRIBUTION OF STRESS CONCENTRATION AND THERMAL FLUCTUATION TO THE STRENGTH OF POLYMERS

Another formulation of equation (1) is

$$\sigma_f = \sigma_{max}\left[1 - \frac{kT}{U}\ln\left(\frac{t}{t_0}\right)\right] \qquad (10)$$

where $\sigma_{max} = U/V_d q$. It is clear from equation (10) that the actual strength of polymers is lower than the maximum strength due to the influence of thermal fluctuations. This thermal fluctuation component is responsible for the temperature and time dependence of the strength. An estimate of the thermal fluctuation component, for instance in the polymers in *Table 1* at 295 K with a test duration $t = 1$ s and reciprocal oscillation frequency $t_0 = 10^{-13}$ s, shows that it is large enough not to be neglected (*Table 1*). The fluctuation thermal pressure stretches the interatomic bonds and assists their deformation and ruptures by the external load. Therefore, the higher the values of the activation energy of thermal degradation, the less the influence of thermal fluctuation, which is shown in *Table 1*.

It was mentioned in the previous section that the stress concentration factor is $q = V/V_d$. It is necessary to estimate the stress concentration factor to consider the influence of stress concentration on the strength of polymers. There are two methods to achieve the estimate. First, from the experimental dependence of time-to-failure on applied stress for polymers and from equation (3), V and V_d can be obtained, respectively. Secondly, since it has been shown that the actual strength of polymers σ_f falls off with increasing crack length[21], i.e. $\sigma_f \propto L^{-1/2}$, and $\sigma_f = \sigma_{th}/q$ as in the previous section, the stress concentration factor q can be approximetaly taken as $L^{1/2}$. The values of q for most of the polymers, except polystyrene, in *Table 2* were obtained from the first method based on the values of V in the literature[22-27]. Since the natural or inherent flaws of polystyrene are 10^{-3} m,[28] according to the second method the q value for polystyrene is about 30 (*Table 2*).

The fracture strength of some polymers after considering the influence of stress concentration and

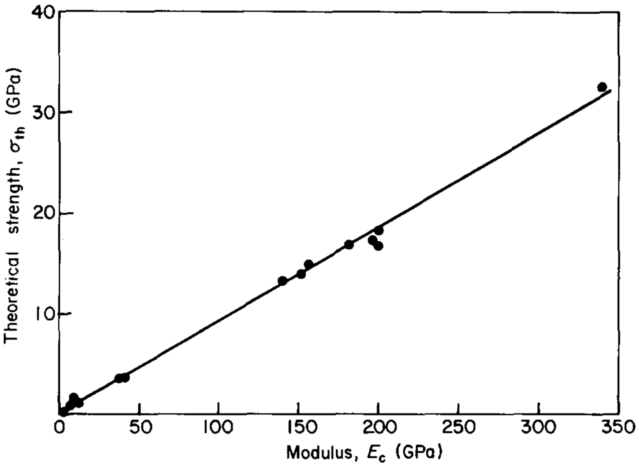

Figure 1 The relationship between theoretical strength and modulus of polymers

Table 1 Theoretical strength of some polymers

Polymer	E_c (GPa)	$s \times 10^{20}$ (m^2)	$U \times 10^{20}$ (J)	σ_{th} (GPa)	$\frac{kT}{U}\ln\left(\frac{t}{t_0}\right)$
Polyethylene	340	18.2	50.0	32.5	0.24
Nylon-6	196	19.9	30.0	17.5	0.41
Nylon-66	200	20.3	28.5	16.9	0.43
Poly(vinylidene fluoride)	181	20.5	33.4	17.1	0.37
Poly(tetrafluoro-ethylene)	156	27.7	56.3	15.3	0.22
Poly(vinyl chloride)	200	28.6	65.9	18.2	0.19
Poly(methylene oxide)	150	17.2	18.9	14.0	0.65
Poly(ethylene terephthalate)	140	20.4	26.4	13.5	0.46
Polypropylene	42	34.3	20.7	3.9	0.30
Poly(vinylidene chloride)	41.5	35.2	21.7	3.9	0.56
Polyisobutene	8.4	43.4	34.0	1.8	0.36
Polystyrene	12	69.8	38.2	1.4	0.32
Poly(4-methyl-pentene-1)	6.7	86.4	37.2	0.83	0.33
Poly(vinyl t-butyl ether)	4.1	88.7	20.1	0.46	0.61

Table 2 Stress concentration factor and fracture strength

Polymer	$V_d \times 10^6$ ($m^3 mol^{-1}$)	$V \times 10^6$ ($m^3 mol^{-1}$)	q	σ_f (MPa)
Polyethylene	9	4390	470	52
Polypropylene	32	213	7	573
Nylon-6	10	113	11	946
Nylon-66	10	50	5	1962
Poly(vinyl chloride)	22	1740	80	185
Polystyrene	–	–	32	30

thermal fluctuation with equation (10) are also listed in *Table 2*. Although the values of fracture strength are larger than those measured for macrospecimens of polymers, they are reliable because they are the fracture strengths of polymers without artificial imperfections. As it is known that some artificial imperfections exist in the macrospecimens of polymers while they are prepared, these artificial defects reduce the strength of macrospecimens of polymers.

DISCUSSION

The activation volume V_d in equation (7) can be approximately taken as the product of the strain of primary bonds at breaking and the cross-sectional area of polymer chains if the fraction of polymers is considered as the primary bond breakage mechanism. From data in the literature[29] the activation volume of nylon-6 is 5.4×10^{-6} m^3 mol^{-1}. From this and the V value in *Table 2* the stress concentration factor of nylon-6 is about 20. This stress concentration factor is comparable to that obtained with the method of the previous section (*Table 2*).

Obviously, the parameters n and r in equations (3), (7) and (8) are the adjustable parameters. The physical meaning of r is the length of activation volume and n is the number of links with the length of r per unit activation volume. According to the literature[8,28,30,31] the ratio of r/n is mr, where m ranges from 1 to 30. It is not unreasonable that r was earlier taken as the length of a C–C bond and n as unity, if the fracture is concerned with primary bond breakage.

It has been shown[32] that, if the primary bonds were broken during fracture, the tensile strength of polymers was of the order of 10^{10} Pa. The theoretical strength of *Table 1* has the same order of magnitude. This means that the fracture of polymers is the process of primary bond breakage. It is not surprising to make such a conclusion, because, first, the kinetic theory of Zhurkov is based on primary bond breakage and, secondly, the modulus used in equation (8) is the theoretical modulus, i.e. it is the resistance to deformation in the direction of the fibre axis of polymer chains. The second point above is in agreement with the point of view of Vincent[33] that one cannot reach the theoretical strength before reaching the theoretical modulus.

APPENDIX

From equation (4)

$$E_c^0/\beta = T + (T^2 + E_c^2/\beta^2)^{1/2} \tag{11}$$

Taking equation (11) into equation (2):

$$\beta^2 = \frac{E_c^2 n^2 k^2}{4U^2 - 4UTnk} \tag{12}$$

According to equations (12) and (3):

$$V_d = s\left(\frac{3nU}{4rE_c}\right)^{1/2}\left(1 - \frac{Tnk}{U}\right)^{1/4} \tag{13}$$

Since T is room temperature, at which the crystal lattice moduli in *Table 1* were measured, and n is unity, then $Tnk/U \ll 1$ and equation (13) is changed to equation (7).

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REFERENCES

1 Griffith, A. A. *Phil. Trans. R. Soc. Lond.* 1921, *A*221, 163

2 Orowan, E., 'Proc. Symp. on Fatigue and Fracture of Metals', John Wiley, New York, 1950, p. 139

3 Benhow, J. J. and Roesler, F. G. *Proc. Phys. Soc. (Lond.) B* 1957, **70**, 201

4 Irwin, G. R. *J. Appl. Mech.* 1957, **24**, 361

5 Zhurkov, S. N., Kuksenko, V. S. and Slutsker, A. I., 'Proc. 2nd Int. Conf. on Fracture', Brighton, Chapman and Hall, London, 1969, p. 531

6 Andrews, E. H. and Reed, P. E. *Adv. Polym. Sci.* 1978, **27**, 1

7 Zhurkov, S. N. *Sov. Phys. Solid State* 1980, **22**, 1958

8 Vettegren', V. I., Kusov, A. A., Korzhavin, L. N. and Frenkel', S. Ya *Polym. Sci. USSR* 1982, **24**, 2241

9 Zhurkov, S. N. *Int. J. Fract. Mech.* 1965, **1**, 311

10 Kusov, A. A. and Vettgren', V. I. *Sov. Phys. Solid State* 1980, **22**, 1962

11 He, Tianbai *J. Polym. Sci., Polym. Phys. Edn.* 1985, submitted

12 Sakurada, I., Ito, T. and Nakame, K. *J. Polym. Sci. C* 1966, **15**, 75

13 Shauffele, R. F. and Shimanouchi, T. *J. Chem. Phys.* 1967, **47**, 3605

14 LaGarde, V., Prask, H. and Trevino, S. *Disc. Faraday Soc.* 1969, **48**, 15

15 Leyer, R. J., Wettling, W. and Wegner, G. *Ber. Bunsenges. Phys. Chem.* 1978, **82**, 697

16 Miller, R. L. and Boyer, R. F. *Polym. News* 1978, **4**, 225

17 Sakurada, I. and Kaji, K. *J. Polym. Sci. C* 1968, **31**, 57

18 Brandrup, J. and Immergut, E. H. (Eds.), 'Polymer Handbook', 2nd Edn., Wiley-Interscience, New York, 1975

19 Privalko, V. P. *Macromolecules* 1980, **13**, 370

20 Kinloch, A. J. and Young, R. J., 'Fracture Behaviour of Polymers', Applied Science, New York, 1983, Chap. 2

21 Andrews, E. H., 'Fracture in Polymers', Oliver and Boyd, London, 1968, Chap. 4

22 Coleman, B. D. *J. Polym. Sci.* 1956, **20**, 447

23 Savitsskii, A. V., Mal'chevski, V. A., Sanfirova, T. P. and Zoshin, L. P. *Polym. Sci., USSR* 1974, **16**, 2470

24 Niklas, H. and Kausch, H. H. *Kunstoffe* 1963, **53**, 839

25 Gaube, E. and Kausch, H. H. *Kunstoffe* 1973, **63**, 391

26 Zhurkov, S. N. and Korskov, V. E. *Sov. Phys. Solid State* 1973, **15**, 1379

27 Zhurkov, S. N. and Korskov, V. E. *J. Polym. Sci., Polym. Phys. Edn.* 1974, **12**, 385

28 Berry, J. P. *J. Polym. Sci.* 1961, **50**, 313

29 Devries, K. L., Lloyd, B. A. and Williams, M. L. *J. Appl. Phys.* 1971, **42**, 4664

30 Peschankaya, N. N., Bershtein, V. A. and Stepanov, V. A. *Sov. Phys. Solid State* 1978, **20**, 1945

31 Bershtein, V. A., Peschankaya, N. N. and Stepanov, V. A. *Polym. Sci., USSR* 1980, **22**, 2462

32 Mark, H., 'Cellulose and Its Derivatives', (Ed. E. Ott), Interscience, New York, 1943, p. 1001

33 Vincent, P. *Proc. R. Soc. Lond. A* 1964, **282**, 113