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Environmental stress cracking of glassy polymers and solubility parameters

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The use of solubility parameters to predict critical stress ($\bar{\sigma}_c^*$) or strains (ε_c) for environmental cracking/crazing in several glassy polymers (e.g. PMMA, PPO, PS, PVC, PSF and PC) is re-examined. It is shown that the enthalpic component (χ_H) of the Flory–Huggins semi-interaction parameter (χ) does not always give a good correlation between ε_c and χ_H even though solvent molar volume and polymer–solvent molecular interactions have already been considered. Re-analysis of available experimental data using Gent's theory shows that there is a general trend for $\bar{\sigma}_c^*$ (or ε_c) to increase with χ. These results, therefore, support Gent's proposed mechanism of environmental stress crazing/cracking. It is finally concluded that unless a definite relationship can be established between ε_c or $\bar{\sigma}_c^*$ with χ_H it is not possible to predict *a priori* ε_c or $\bar{\sigma}_c^*$, given the empirical solubility parameters of a solvent. Unfortunately, there are not many such relationships as discovered in this paper.

1. Introduction

Many glassy polymers when exposed to organic solvents will fail at stresses and strains much below their normal values if these hostile environments were absent [1, 2]. In engineering applications it is important to be able to predict what these stresses and strains are, given the physical properties of the polymer and the solvent. It has been suggested that under an external applied stress the solvent penetrates and swells the polymer at preferential sites of stress concentration such as surface flaws [3, 4]. This gives rise to a reduction in the glass transition temperature (T_g) in the localized material, making crazing or cracking much easier to occur. Different environments have different equilibrium absorptions (ϕ_s) in the polymer and different degrees of T_g reduction.

In a series of papers [5–8], Kambour and co-workers have shown that a definite correlation exists between the critical strain (ε_c) for the onset of crazing or cracking and the equilibrium ϕ_s or T_g for several glassy polymers. Unfortunately, the determination of ϕ_s requires extremely long times not usually permissible in most laboratories. To overcome this problem, Kambour and co-workers [5–8] have used the Hildebrand solvent solubility parameter (δ_s) to correlate with ε_c, but this has produced varying degrees of success. Jacques and Wyzgoski [9] have highlighted the significance of considering both the molar volume (V_s) of the solvent and the types of molecular interaction between polymer and solvent in such empirical δ_s–ε_c correlations. Vincent and Raha [10] as well as Henry [11] are aware of the effects of hydrogen bonding on ε_c and have used two-dimensional solubility parameter mapping techniques to analyse their experimental data. Even so, the prediction of ε_c from such mapping techniques is often complex and not always accurate.

In the present paper, we re-examine the use of solubility parameters to predict critical strains for environmental crazing/cracking in a range of glassy polymers including polymethyl methacrylate (PMMA), polystyrene (PS), polycarbonate (PC), polyphenylene oxide (PPO), polysulphone (PSF) and polyvinyl chloride (PVC). All the experimental data are taken from previous published work [5–10]. Some extensive data for PMMA have been obtained by Neete [12] and are also included in the present analysis. Emphasis is placed on the effects of molar volume and molecular interactions between polymer and solvent.

2. Solubility parameters and environmental stress cracking

An excellent review on solubility parameters is given by Barton [13]. Jacques and Wyzgoski [9] have also given a concise treatment of solubility parameters to predict environmental stress cracking in polymers. In the following, we give only the essential equations which are necessary for this work. According to the Flory–Huggins theory [14, 15], the partial molar free energies of mixing for the solvent and the polymer, ΔG_s and ΔG_p, may be given by:

$$\Delta G_s = RT\left[\ln\phi_s + \left(1 - \frac{1}{m}\right)\phi_p + \chi\phi_p^2\right] \quad (1)$$

$$\Delta G_p = RT\left[\ln\phi_p - (m - 1)\phi_s + m\chi\phi_s^2\right] \quad (2)$$

where R is the universal gas constant, T is the temperature, $\phi_p = (1 - \phi_s)$ and m is the ratio of the molar volumes of polymer and solvent. χ is a semi-empirical interaction parameter between polymer and solvent to fit experimental data and contains both enthalpic (χ_H) and entropic (χ_S) contributions, i.e.

$$\chi = \chi_H + \chi_S \quad (3)$$

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For many systems χ_S is between 0.3 and 0.4 [16]. Now for non-polar, non-hydrogen bonding polymer–solvent systems χ_H may be calculated from the Hildebrand solubility parameters (δ) by

$$\chi_H = \frac{V_s}{RT}(\delta_p - \delta_s)^2 \tag{4}$$

where V_s is the solvent molar volume and δ_p is the solubility parameter for the polymer. For those polymer–solvent systems which are expected to engage in polar–polar interactions without hydrogen bonding, Blanks and Prauswitz [17] give

$$\chi_H = \frac{V_s}{RT}\left[(\lambda_p - \lambda_s)^2 + \frac{T^*}{T}(\tau_p - \tau_s)^2\right] \tag{5}$$

where λ and τ are the non-polar and polar components of the polar polymer (p) or solvent (s) and T^* is the temperature at which τ is measured. The (T^*/T) term allows for the fact that while the non-polar term $(\lambda_p - \lambda_s)^2$ is independent of temperature, the heat of mixing in systems containing polar species varies inversely as T. For polar–non-polar system where hydrogen bonding is not expected [17],

$$\chi_H = \frac{V_s}{RT}\left[(\lambda_p - \lambda_s)^2 + \frac{T^*}{T}(\tau_i^2 - 2\psi)\right] \tag{6}$$

where τ_i is the polar solubility parameter for the solvent or polymer depending on which one is polar and ψ is an empirical term for the induction energy density arising from induction forces between the polar and non-polar components. ψ depends on the product $\lambda\tau_i$ and has been determined [17]. λ is the non-polar solubility parameter of the non-polar substance and is equivalent to Hildebrand's solubility parameter, δ. Methods to measure λ and τ have been discussed by various authors [13, 17] but a comprehensive list for polymers and solvents is lacking. Finally, for those polymer–solvent systems which may engage in hydrogen bonding, we have

$$\chi_H = \frac{V_s}{RT}[(\delta_{np} - \delta_{ns})^2 + (\delta_{pp} - \delta_{ps})^2] \tag{7}$$

where δ_{np} and δ_{pp} are the non-polar or dispersive and "polar" contributions to the total solubility parameter δ_t (which is not necessary equal to Hildebrand's δ) according to Hansen and Skaarup [18]. δ_{ns} and δ_{ps} are the corresponding contributions to δ_t for the solvent, i.e.

$$\delta_t^2 = \delta_{ns}^2 + \delta_{ps}^2 \tag{8}$$

and

$$\delta_{ps}^2 = \delta_{\varepsilon s}^2 + \delta_{hs}^2 \tag{9}$$

where $\delta_{\varepsilon s}$ and δ_{hs} are the polar and hydrogen bonding contributions to δ_t.

At equilibrium absorption or swelling, Equations 1 and 2 for the partial molar free energies must be equal to zero. Thus, we have

$$\Delta G_s = RT\left[\ln\phi_s + \left(1 - \frac{1}{m}\right)\phi_p + \chi_s\phi_p^2 + \chi_H\phi_p^2\right] = 0 \tag{10}$$

$$\Delta G_p = RT[\ln\phi_p - (m-1)\phi_s + m\chi_s\phi_s^2 + m\chi_H\phi_s^2] = 0 \tag{11}$$

where now χ_H is given by any one of Equations 4 to 7 depending on the types of molecular interaction between polymer and solvent. Equation 10 can be solved for ϕ_s which may in turn be used to correlate with ε_c for environmental stress cracking. To avoid complex thermodynamic calculations as required by Equations 10 and 11, it has been suggested that if the enthalpic component of ΔG_s (i.e. $\chi_H\phi_p^2$) is negative or positive but less than the entropic component then mixing can occur. This is equivalent to saying that equilibrium solubility is proportional to χ_H and consequently ε_c should also be proportional to χ_H even though the entropic contribution has not been considered. Thus, for non-polar, non-hydrogen bonding polymer–solvent systems ε_c is least for $\delta_p = \delta_s$ and this has been proved valid to a limited extent [5–9] even though V_s is not considered. For other polymer–solvent systems involving polar to polar and hydrogen bonding interactions, Equations 5 to 7 have to be used for χ_H.

This simple idea of ε_c being directly proportional to χ_H, if it works, will provide an effective method to predict ε_c since χ_H can be calculated from Equations 4 to 7 using empirical solubility parameters available from published data [13, 19]. There is no need then to use the more complex two-dimensional [9, 10] or three-dimensional [11] solubility parameter mapping techniques for those polymer–solvent systems involving polar–polar and hydrogen bonding interactions. Thus, it would be useful to re-examine the experimental data for several glassy polymers [5–10] in the light of this argument.

Thus far we have not considered the influence of external applied stresses or strains on the equilibrium swelling Equations 10 and 11. At the flaw tips the localized material has its T_g reduced by the liquid environment and the dilatent stress, D, present at the tips causes further cavitation and thus crazing to occur. Following Gent [3], Equation 10 can be rewritten as

$$\Delta G_s = RT\left[\ln(1 - \phi_p) + \left(1 - \frac{1}{m}\right)\phi_p + \chi\phi_p^2\right] - DV_s = 0. \tag{12}$$

χ will now be different to that in Equation 1 and can only be obtained by solving the equation. However, this requires ϕ_p to be determined separately. Gent [33] has shown that ϕ_p can be related to the environmental crazing stress $\bar{\sigma}_c^*$ ($= E\varepsilon_c$ where E is Young's modulus) and the crazing stress in air ($\bar{\sigma}_c$) by

$$\bar{\sigma}_c^* = \bar{\sigma}_c - \frac{3\beta T_g(1 - \phi_p)}{k} \tag{13}$$

where k is the stress concentration factor at the tip of the surface flaw and β is a coefficient of about 5 MPa $(^\circ\mathrm{C})^{-1}$. This means that ϕ_p is dependent on the dilatant stress D and it can only be determined from experimentally measured values of $\bar{\sigma}_c^*$ and $\bar{\sigma}_c$. It would not be expected to be the same as that given by solving

Equation 10. Also, D is related to $\bar{\sigma}_c^*$ by [3]

$$\sigma_c^* = 3D/k \tag{14}$$

Thus, using Equations 12 to 14 the Flory–Huggins interaction parameter χ can be determined. Gent has shown theoretically that $\bar{\sigma}_c^*$ is directly related to χ. It is possible, therefore, that a unique correlation between $\bar{\sigma}_c^*$ and χ may exist for all types of solvent independent of their specific molecular interactions with the polymer. This possibility will be studied in the present paper. The problem remains, however, that even if such a correlation exists which, therefore, vindicates Gent's proposed mechanism of environmental stress cracking, the calculation of χ from Equation 12 must depend on $\bar{\sigma}_c^*$ or ε_c which is what we want to know in the first place. Therefore, unlike χ_H, χ cannot here be evaluated independently using empirical solubility parameters such as δ, λ, τ etc.

3. Experimental results and discussion

3.1. Solubility parameters for polymers and organic solvents

The dispersive (δ_{np}) and polar (δ_{pp}) solubility parameters for the glassy polymers are given in Table I and are taken from Shaw [19]. Note that PS is very weakly polar and both PC and PPO are moderately polar. PSF, PMMA and PVC are, however, strongly polar. For the solvents the solubility parameters can be found from heats of vaporization measurements and Table II gives a list of the Hildebrand (δ_s) and Hansen solubility parameters (δ_{ns}, δ_{ps}) taken from Jacques and Wyzgoski [9] and Barton [13]. In the absence of a complete list of values for Blanks and Prausnitz's τ and λ for all polymers and solvents studied here, we have assumed in our calculations that $\lambda_p \equiv \delta_{np}$, $\lambda_s \equiv \delta_{ns}$, $\tau_p = \delta_{pp}$ and $\tau \equiv \delta_{ps}$. These assumptions are not unreasonable.

TABLE I Non-polar and polar solubility parameters for some polymers [19]

Polymer	$\delta_{np}(\mathrm{cal}^{\frac{1}{2}}\,\mathrm{cm}^{-\frac{3}{2}})$*	$\delta_{pp}(\mathrm{cal}^{\frac{1}{2}}\,\mathrm{cm}^{-\frac{3}{2}})$
Polymethyl methacrylate (PMMA)	8.6	2.90
Polyphenylene oxide (PPO)	8.9	0.33
Polystyrene (PS)	9.1	0.10
Polyvinyl chloride (PVC)	7.4	6.10
Polysulphone (PSF)	8.7	5.90
Polycarbonate (PC)	9.5	0.40

*1 cal = 4.187 J.

3.2. Correlation of ε_c and $\bar{\sigma}_c^*$ with solubility parameters

3.2.1. PMMA

Fig. 1 shows the ε_c results from Leete [12] plotted against Hildebrand's solubility parameter δ_s according to Equation 4 for all the organic liquids. The results from Vincent and Raha [10], if plotted on the same figure, would show the same trend. It is observed that in spite of increasing compatibility between δ_p and δ_s, the critical strain increases both for the aliphatic hydrocarbons and primary alcohols as δ_s approaches δ_p. A sharp discontinuity, however, occurs in the curves between octanol and cyclohexane with a minimum at $\delta_p = \delta_s$. Even if the molar volume

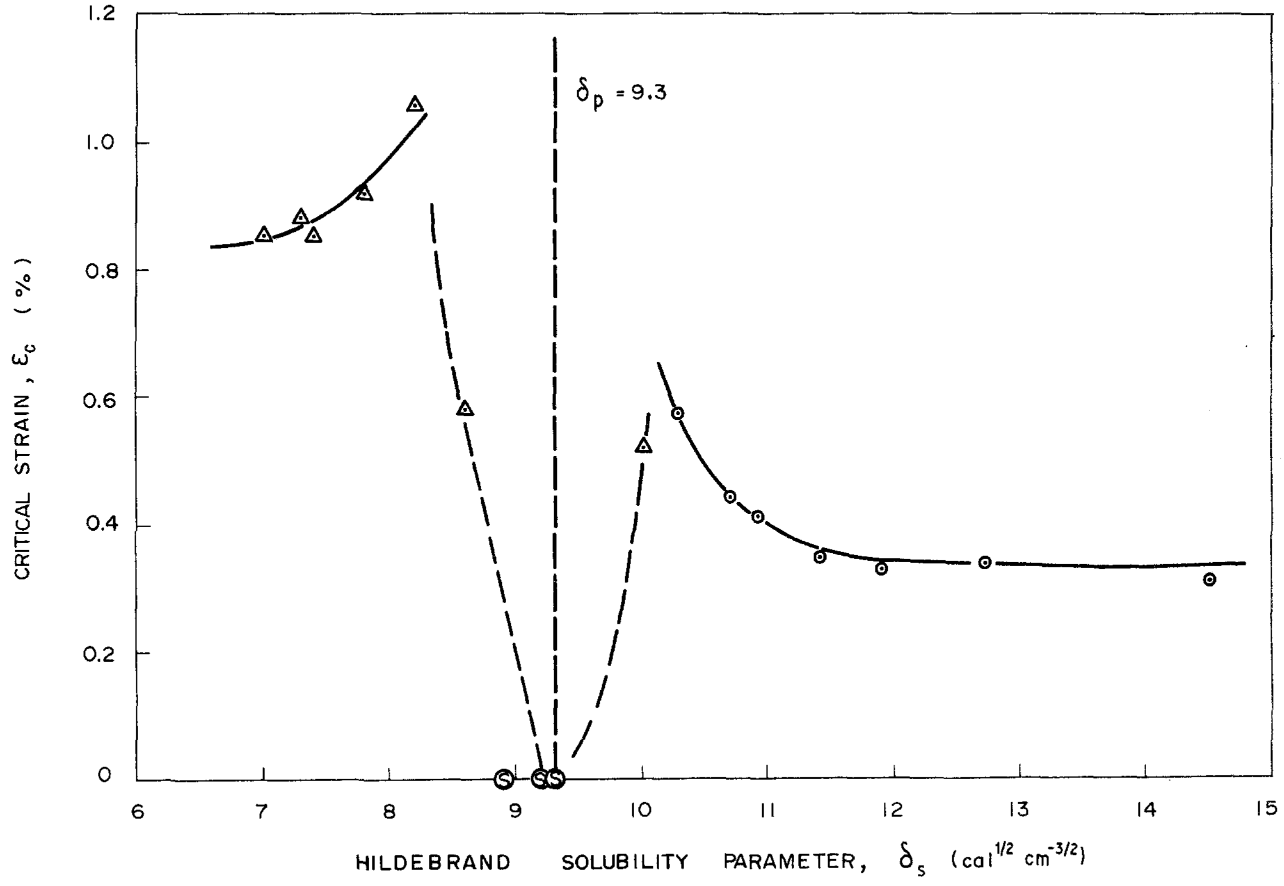

Figure 1 Critical strain (ε_c) against Hildebrand's solubility parameter (δ_s) for environmental stress crazing/cracking in PMMA. (⊙) Primary alcohols, (△) zero hydrogen-bonding liquids, (Ⓢ) solvents (toluene, δ_s = 8.9; benzene, δ_s = 9.2; methyl ethyl ketone, δ_s = 9.3).

TABLE II Solubility parameters for organic solvents and critical strain results for environmental crazing/cracking

Organic Solvent	Solubility parameters ($cal^{\frac{1}{2}}cm^{-\frac{3}{2}}$)				Average critical strain $\varepsilon_c(\%)$*					
	δ_s	δ_{ns}	δ_{ps}	δ_{hs}	PMMA	PPO	PS	PVC	PSF	PC
Alkanes										
n-Pentane	7.0	7.1	0	0	0.87	0.38	0.12	1.23	0.76	0.83
n-Hexane	7.3	7.3	0	0	0.84	0.19	0.10	–	0.97	0.86
n-Heptane	7.4	7.5	0	0	0.86	0.27	0.12	1.18	0.83	0.91
n-Octane	7.6	7.6	0	0	–	0.26	0.17	–	–	0.92
n-Decane	7.74	–	0	0	–	–	–	–	–	1.03
n-Tetradecane	7.9	–	0	0	–	–	–	–	–	1.18
n-Hexadecane	8.0	–	0	0	–	–	–	–	–	1.27
2-Methyl butane	6.75	–	–	–	–	0.37	–	–	–	1.07
2-Methyl pentane	7.03	–	–	–	–	–	0.13	–	–	1.02
2-Methyl hexane	7.29	–	–	–	–	–	–	–	–	1.01
2-Methyl heptane	7.34	–	–	–	–	–	–	–	–	0.99
3-Methyl pentane	7.13	–	–	–	–	–	–	–	–	1.05
2,3-Dimethyl butane	6.97	–	–	–	–	–	–	–	–	1.36
2,2-Dimethyl butane	6.71	–	–	–	–	0.77	–	–	–	1.68
2,3-Dimethyl pentane	7.3	–	–	–	–	–	–	–	–	1.04
2,2,4-Trimethyl pentane	6.86	–	–	–	–	–	–	–	–	1.66
Cyclohexane	8.2	8.2	0.1	0.1	1.08	–	0.13	0.87	0.86	–
Methylcyclohexane	7.8	7.8	0.5	0.5	0.92	–	–	0.73	–	–
Hydrocarbons										
Benzene	9.2	9.0	1.0	1.0	S†	–	–	–	0.07	0.20
Toluene	8.9	8.8	1.2	1.0	S	–	–	–	–	–
Ethyl benzene	8.8	8.7	0.76	0.7	–	–	–	0.19	–	–
Xylene	8.8	8.7	1.60	1.5	–	–	–	–	0.07	0.37
Carbon tetrachloride	8.6	8.7	0.3	0.3	0.50	0.08	–	0.69	0.32	0.46
Chlorobenzene	9.5	9.3	2.33	1.0	S	–	–	–	–	–
Ethers										
Diethyl ether	7.4	7.1	2.90	2.5	0.28	–	0.27	0.23	0.22	–
Ketones										
Acetone	9.9	7.6	6.1	3.4	S	0.50	–	–	0.11	0.51
Methyl ethyl ketone	9.3	7.8	5.1	2.5	S	0.21	–	–	0.11	0.32
Methyl propyl ketone	–	7.7	4.5	–	–	0.09	–	–	–	0.50
Cyclohexanone	9.9	8.7	4.0	2.5	–	–	–	–	0.86	0.15
Methyl butyl ketone	–	7.5	4.2	–	–	0.12	–	–	–	–
Esters										
Methyl acetate	9.6	7.6	5.1	3.7	–	0.31	–	–	0.11	0.59
Ethylene carbonate	14.7	9.5	10.8	2.5	–	–	–	–	–	0.52
Isoamyl acetate	7.8	7.5	3.72	3.4	–	–	–	–	–	–
n-Butyl acetate	8.5	7.7	3.6	3.1	S	0.13	–	–	0.11	0.35
Propylene 1,2-carbonate	13.3	9.8	9.0	2.0	–	–	–	–	–	0.28
Dibutyl phthalate	9.3	8.7	4.6	2.0	0.89	–	–	–	0.40	0.41
Dimethyl phthalate	10.7	9.1	5.8	2.4	0.37	–	–	–	0.29	0.31
α-Butyrolactone	–	9.3	8.9	–	–	–	–	–	0.11	0.30
Dioctyl phthalate	7.9	8.1	3.7	1.5	1.44	–	–	–	–	–
Ethyl formate	9.4	9.6	5.8	4.1	–	0.42	–	–	–	–
Ethyl acetate	–	7.5	5.2	–	–	–	–	–	0.07	–
Nitrogen compounds										
Nitromethane	12.7	7.7	9.5	2.5	–	–	–	0.05	–	0.69
Nitroethane	11.1	7.8	7.9	2.2	–	–	0.24	–	–	0.72
Nitrobenzene	10.0	9.8	4.6	2.0	–	–	–	–	–	0.51
Acetonitrile	11.9	7.5	9.3	3.0	–	–	0.17	–	–	0.57
Formamide	19.2	8.4	15.9	9.3	–	–	0.28	–	1.58	1.55
N,N-dimethyl formamide	12.1	8.5	8.7	5.5	–	0.45	0.42	–	–	1.57
Monohydric alcohols										
Methanol	14.5	7.4	12.7	10.9	0.33	1.34	0.29	0.68	1.12	1.19
Ethanol	12.7	7.7	10.4	9.5	0.32	1.10	0.27	0.72	0.83	1.00
1-Propanol	11.9	7.8	9.1	8.5	0.31	0.84	–	0.79	–	0.91
2-Propanol	11.5	7.7	8.5	8.0	–	–	–	–	–	1.02
1-Butanol	11.4	7.8	8.2	7.7	0.33	0.77	–	0.68	0.47	0.83
1-Pentanol	10.6	7.8	7.1	6.8	0.41	–	0.21	–	–	0.91
1-Octanol	10.3	8.3	6.0	5.8	0.53	0.67	–	–	–	0.93
1-Decanol	–	8.6	5.1	–	–	–	–	–	–	0.97
1-Dodecanol	–	8.5	5.0	–	–	–	–	–	–	1.17
Benzyl alcohol	–	9.0	7.4	–	–	–	0.13	–	–	0.26
Cyclohexanol	–	8.5	6.9	–	–	–	0.23	–	0.94	1.23
2-Ethyl hexanol	9.5	7.8	5.6	5.8	0.37	–	–	–	0.76	0.87
Allyl alcohol	11.8	7.9	9.8	8.2	–	–	–	–	0.58	0.56
1-Hexanol	10.7	7.8	7.1	6.8	0.39	–	–	–	0.59	0.71

TABLE II Continued

Organic Solvent	Solubility parameters ($cal^{\frac{1}{2}}cm^{-\frac{3}{2}}$)				Average critical strain $\varepsilon_c(\%)$*					
	δ_s	δ_{ns}	δ_{ps}	δ_{hs}	PMMA	PPO	PS	PVC	PSF	PC
Polyhydric alcohols										
Ethylene glycol	14.6	8.3	13.8	12.7	0.94	–	0.36	1.16	–	1.90
Glycerol	16.5	8.5	15.4	14.3	1.40	–	–	1.36	–	0.77
Propylene glycol	12.6	8.2	17.2	11.4	–	–	–	–	–	1.46
Triethylene glycol	10.7	7.8	10.8	9.1	–	–	0.27	–	–	0.98
Diethylene glycol	12.1	7.9	12.3	10.0	–	–	0.21	–	–	–
Others										
Carbon disulphide	10.0	10.0	0.3	0.3	0.50	–	–	–	–	–
Dimethyl sulphoxide	12.0	9.0	9.4	5.0	–	–	0.18	–	0.07	–
Freon 113	–	7.2	0.8	–	–	–	0.14	0.35	–	–
Acetic acid	10.1	7.1	7.7	6.6	–	–	–	0.31	0.33	–

*Data from source as follows: PMMA, Leete [12] and Vincent and Raha [10]; PPO, Bernier and Kambour [5]; PS, Kambour, Gruner and Romagosa [7]; PVC, Vincent and Raha [10]; PSF, Kambour, Romagosa and Gruner [6]; PC, Kambour *et al.* [8] and Jacques and Wyzgoski [9].

†S^1 = dissolves.

V_s is included in Equation 4 it is still not possible to show that ε_c varies directly with χ_H for the zero hydrogen bonding liquids and the alcohols [12].

It has been shown in Section 2 that the Hildebrand solubility parameter plotting technique cannot be expected to apply for all PMMA–solvent systems and that the relevant χ_H value has to be used in the correlation between ε_c and χ_H, depending on the molecular interactions between PMMA and the solvents. Since PMMA is polar and the alkanes and hydrocarbons are non-polar and non-hydrogen bonding (see Table II), χ_H can be evaluated from Equation 6 and the ε_c against χ_H results are shown in Fig. 2. Similarly, for the PMMA–alcohol systems where both polar to polar and hydrogen bonding interactions occur χ_H has been calculated from Equation 7 and the results are

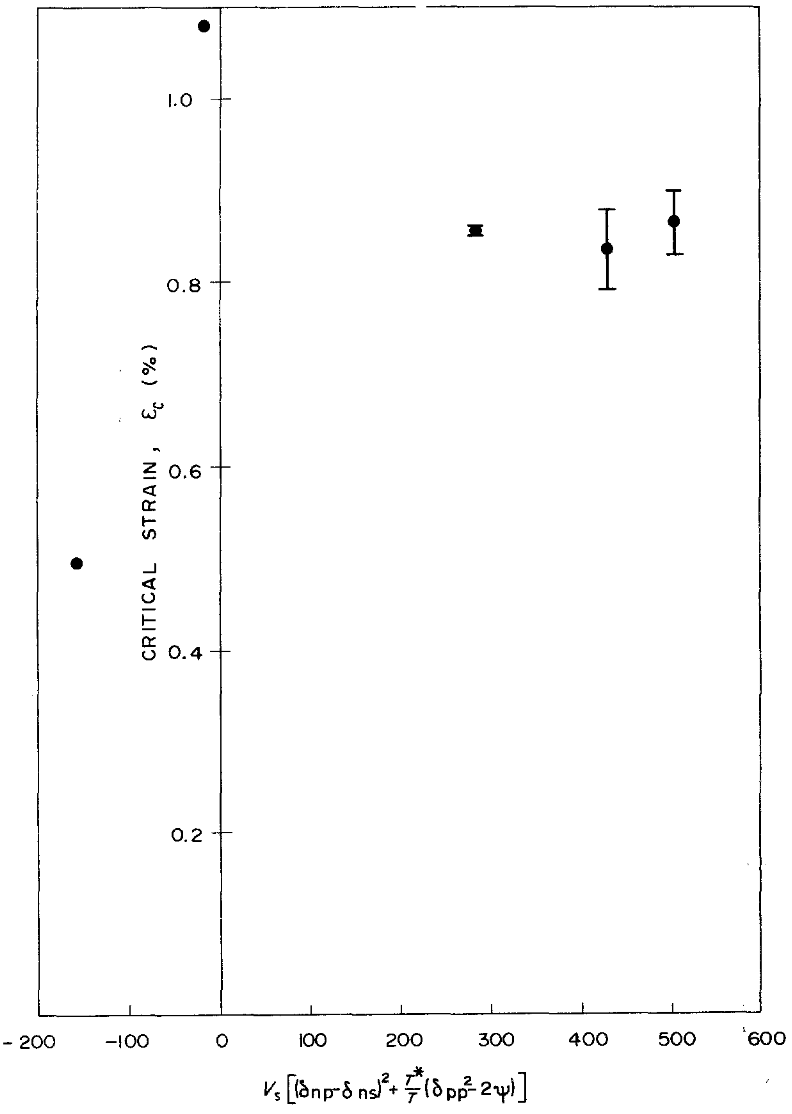

Figure 2 Critical strain (ε_c) against χ_H (Equation 6) for PMMA–(alkanes and hydrocarbons).

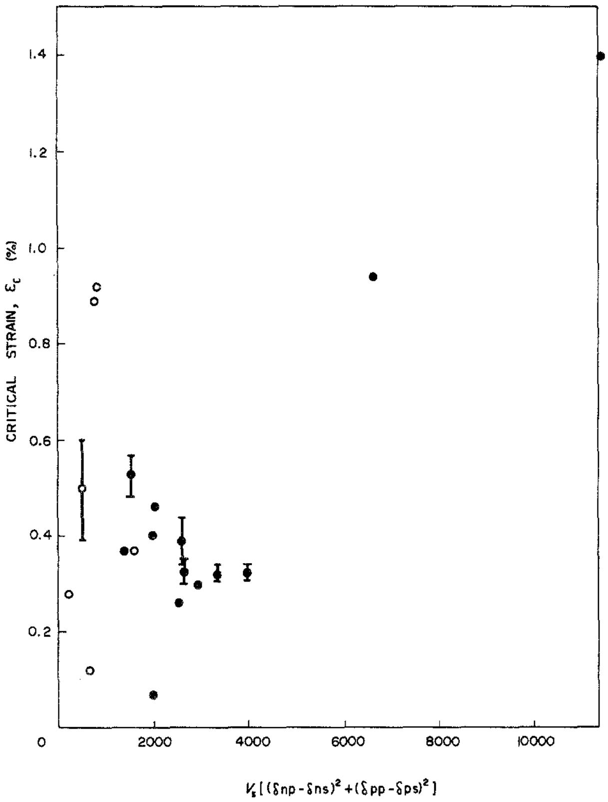

Figure 3 Critical strain (ε_c) against χ_H (Equation 7) for PMMA–alcohols: (●) alcohols, (○) others.

given in Fig. 3. Despite these efforts to include molecular interactions and molar volumes of solvents it seems that from these two figures ε_c still cannot be said to increase with χ_H. There does not seem to be any correlation between ε_c and χ_H.

An attempt to analyse the environmental stress crazing/cracking results in terms of Gent's [3] theory gives the $\bar{\sigma}_c^*$ against χ results in Fig. 4. χ is determined from Equation 12 using ϕ_p and D from Equations 13 and 14. We have assumed $k = 20$, $E = 2.9\,\text{GPa}$, $\bar{\sigma}_c = 70\,\text{MPa}$ and $\bar{\sigma}_c^* = E\varepsilon_c$. The term ϕ_p/m is negligible as it does not affect the solution for χ. It seems that the critical crazing stress $\bar{\sigma}_c^*$ is now directly dependent on, and increases with, the Flory–Huggins semi-empirical interaction parameter χ, although there is some considerable experimental scatter.

3.2.2. PPO, PS, PVC, PSF and PC

Figs. 5 and 6 show the ε_c against χ_H results for the PPO–alkane and PPO–(alcohol, ketone and ester) systems, respectively. Again appropriate equations have been used for χ_H. It is seen here that there is a general correlation between ε_c and χ_H and that ε_c increases with χ_H. However, there is an even better correlation between $\bar{\sigma}_c^*$ and χ for all the liquid environments (except octanol) as shown in Fig. 7.

Similar plots of ε_c against χ_H for the other polymers are given in Figs. 8 to 16. For the PS–alkane and PS–alcohol systems there is no correlation at all between the critical strain (ε_c) and χ_H (see Figs. 8 and 9). The same can be said of the following polymer–solvent systems: PVC–alcohols (Fig. 11), PSF–alkanes and hydrocarbons, PSF–(alcohols and others) (Figs. 12 and 13) and PC–(alcohols, ketones, etc.) (Fig. 16). However, for the PVC–(alkanes and hydrocarbons) (Fig. 10), PC–alkanes and PC–hydrocarbon mixtures [9] (Figs. 14 and 15), there is a general trend that ε_c tends to increase with χ_H.

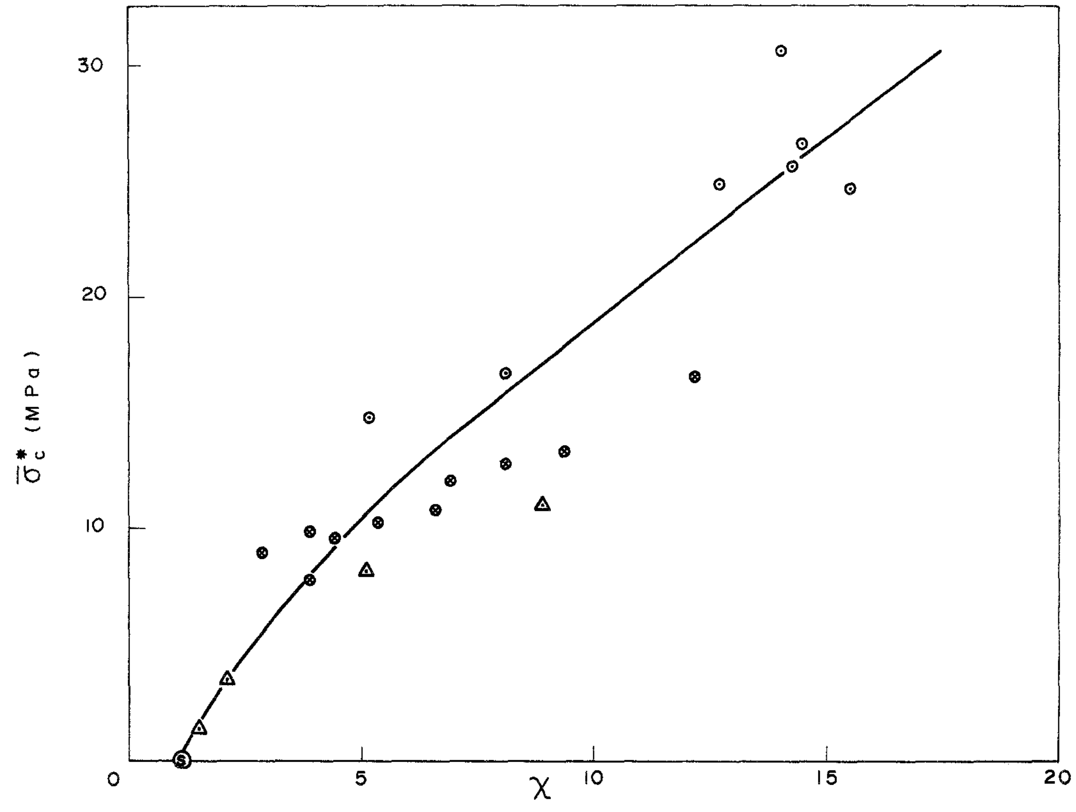

Figure 4 A plot of environmental crazing stress ($\bar{\sigma}_c^*$) against the Flory–Huggins interaction parameter χ (Equation 12) for PMMA. (⊗) Monohydric alcohols, (⊙) zero hydrogen-bonding liquids, (△) all others, (Ⓢ) solvents. $k = 20$, $E = 2.9\,\text{GPa}$, $\bar{\sigma}_c(\text{air}) = 70\,\text{MPa}$.

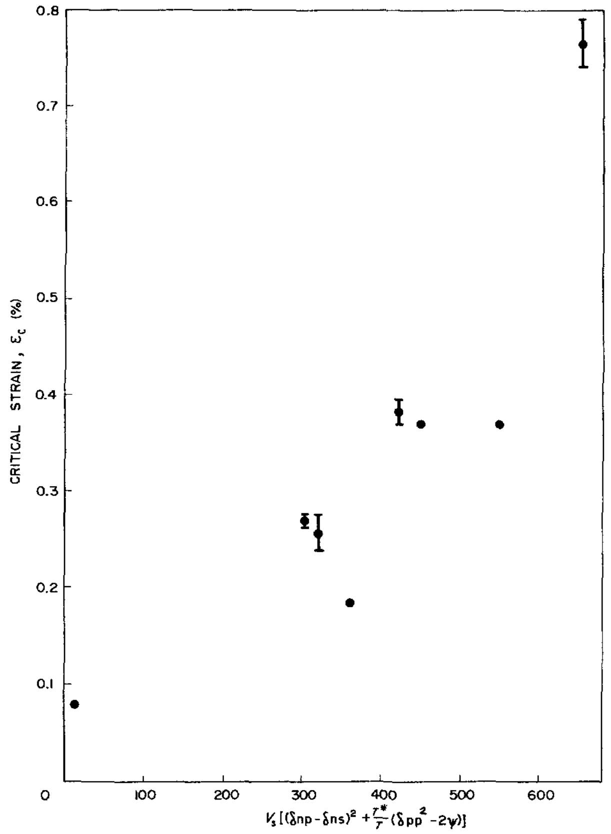

Figure 5 Critical strain (ε_c) against χ_H (Equation 6) for PPO–alkanes.

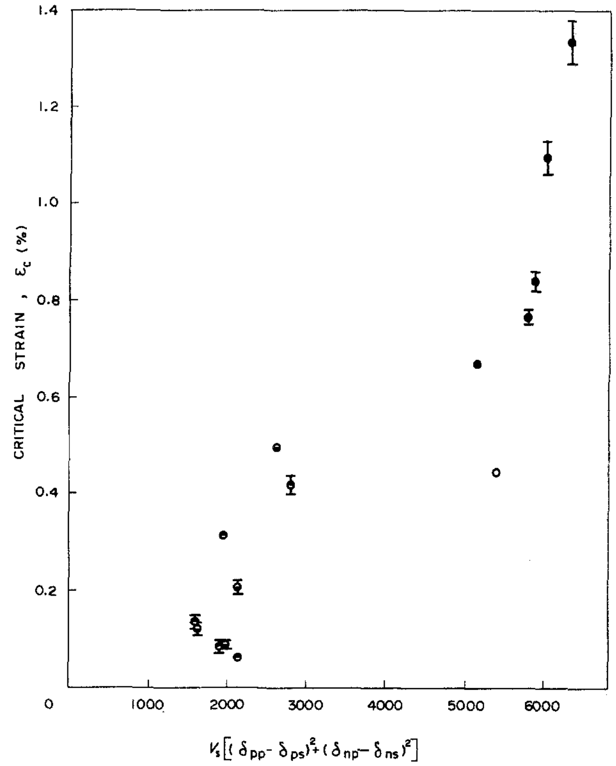

Figure 6 Critical strain (ε_c) against χ_H (Equation 7) for PPO–(alcohols, ketones, esters). (●) Alcohols, (◑) ketones, (◑) esters, (○) others.

Re-analysing all these experimental data according to Gent's theory we obtain Figs. 17 to 21 for the various polymers. In the most general sense, $\bar{\sigma}_c^*$ increases with χ except for the PC–alcohol system in which the correlation between these two parameters is extremely poor (Fig. 20). The PC–(alkane, ether, ester and ketone) systems, on the other hand, have a very good correlation between $\bar{\sigma}_c^*$ and χ (Fig. 21). The values for E, $\bar{\sigma}_c$ (air) and k used in calculating χ are given in the caption to each figure.

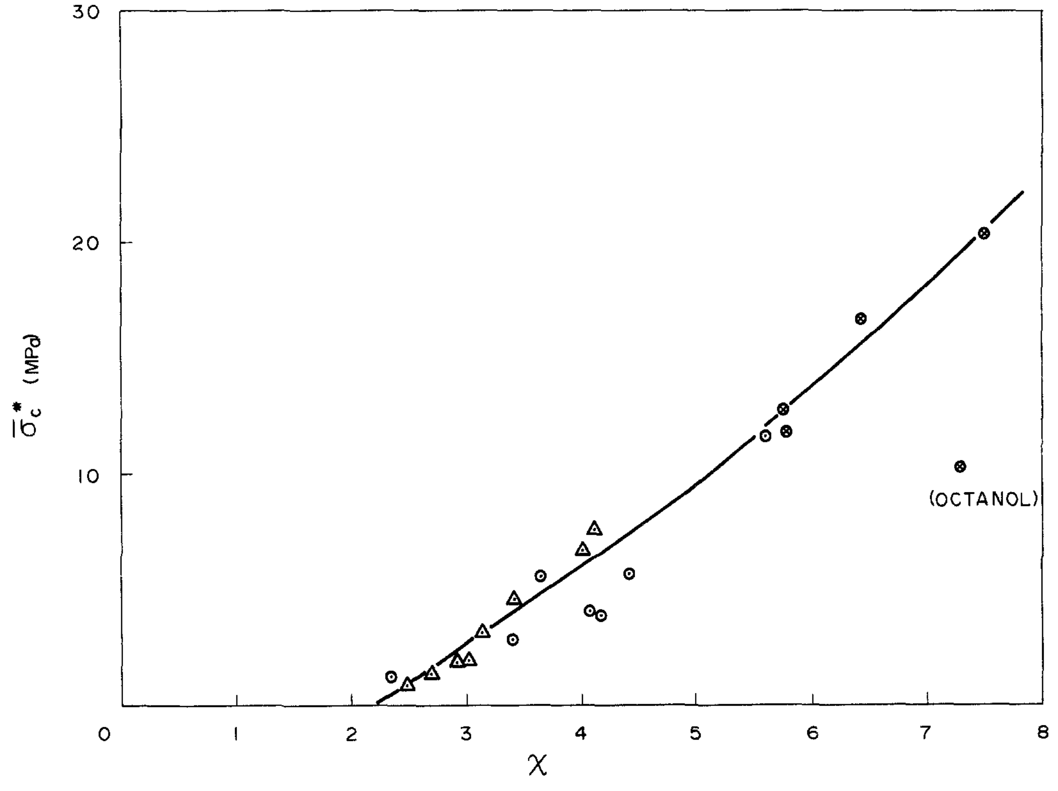

Figure 7 A plot of environmental crazing stress ($\bar{\sigma}_c^*$) against χ (Equation 12) for PPO, poly(2,6-dimethyl-1,4-phenylene oxide). (⊗) Monohydric alcohols, (⊙) zero hydrogen-bonding liquids, (△) ketones and esters.

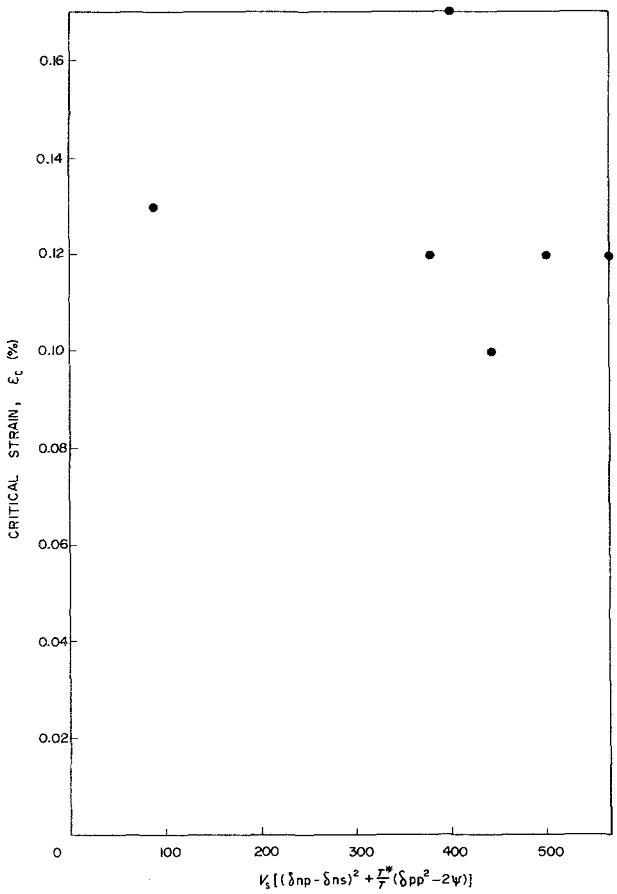

Figure 8 Critical strain (ε_c) against χ_H (Equation 6) for PS–alkanes.

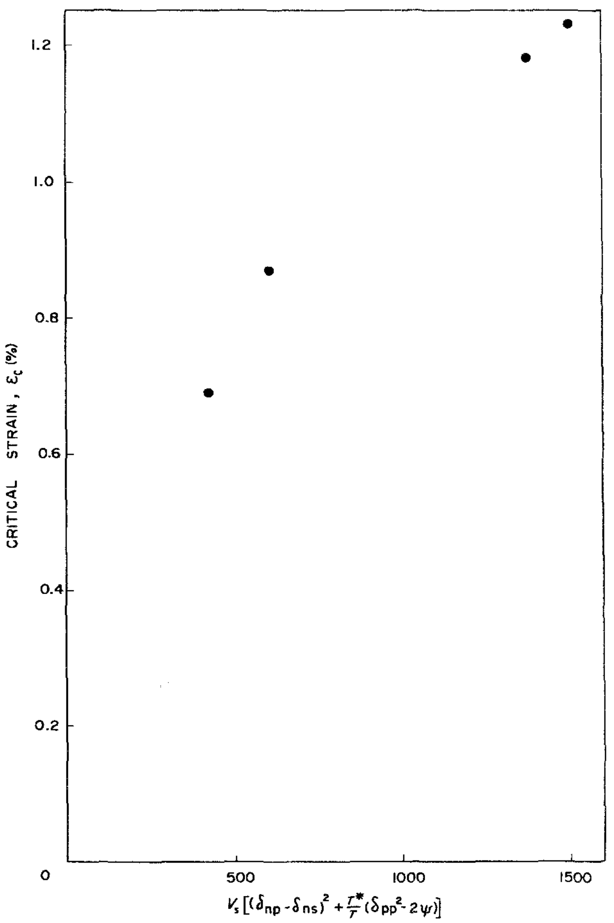

Figure 10 Critical strain (ε_c) against χ_H (Equation 6) for PVC–(alkanes and hydrocarbons).

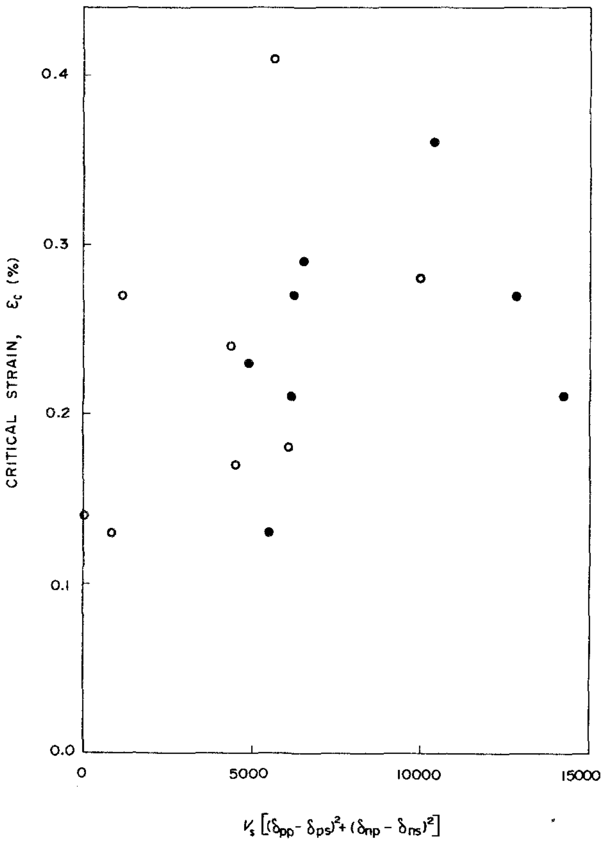

Figure 9 Critical strain (ε_c) against χ_H (Equation 7) for PS–alcohols. (●) Alcohols, (○) others.

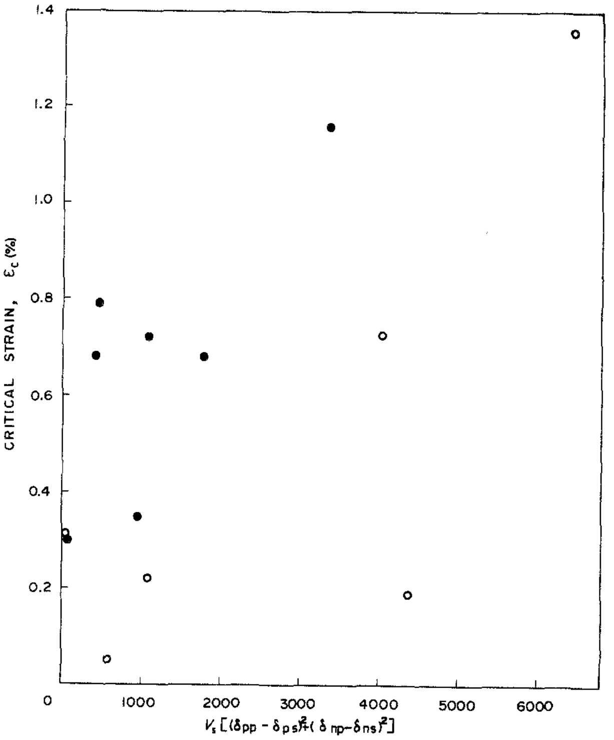

Figure 11 Critical strain (ε_c) against χ_H (Equation 7) for PVC–alcohols. (●) Alcohols, (○) others.

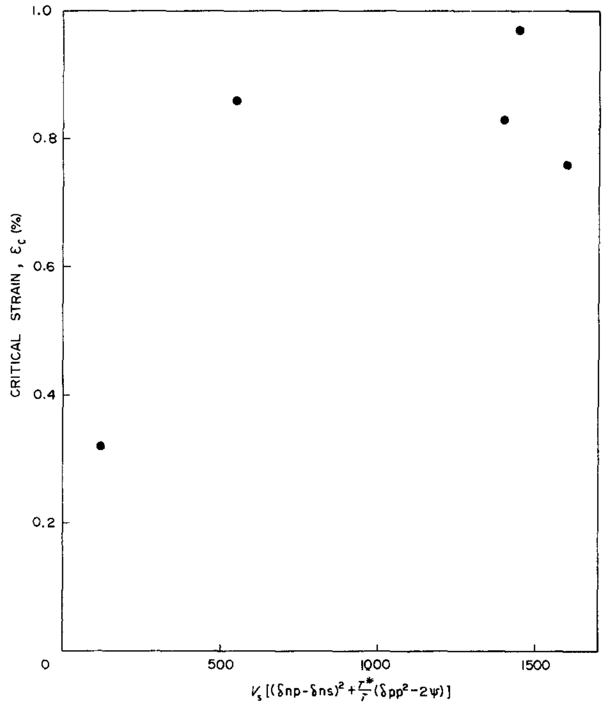

Figure 12 Critical strain (ε_c) against χ_H (Equation 6) for PSF–hydrocarbons (P1700).

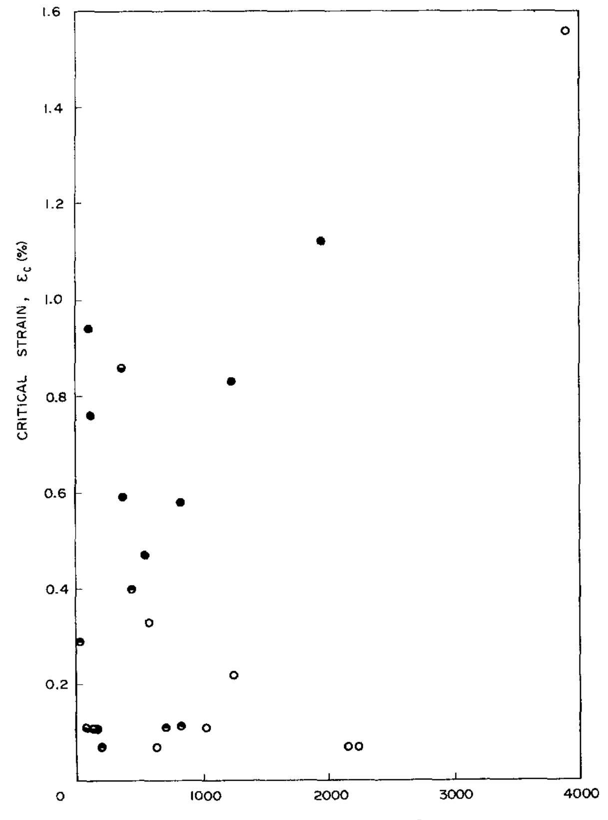

Figure 13 Critical strain (ε_c) against χ_H (Equation 7) for PSF–(alcohols, ketones, esters). PSF = Polysulfone 1700. (●) Alcohols, (◒) ketones, (⊖) esters, (○) others.

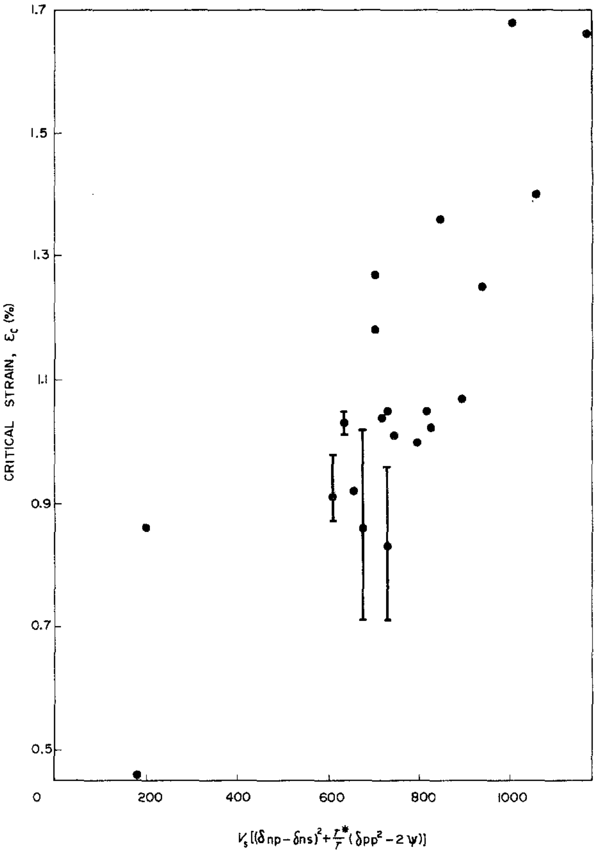

Figure 14 Critical strain (ε_c) against χ_H (Equation 6) for PC–(alkanes and hydrocarbons).

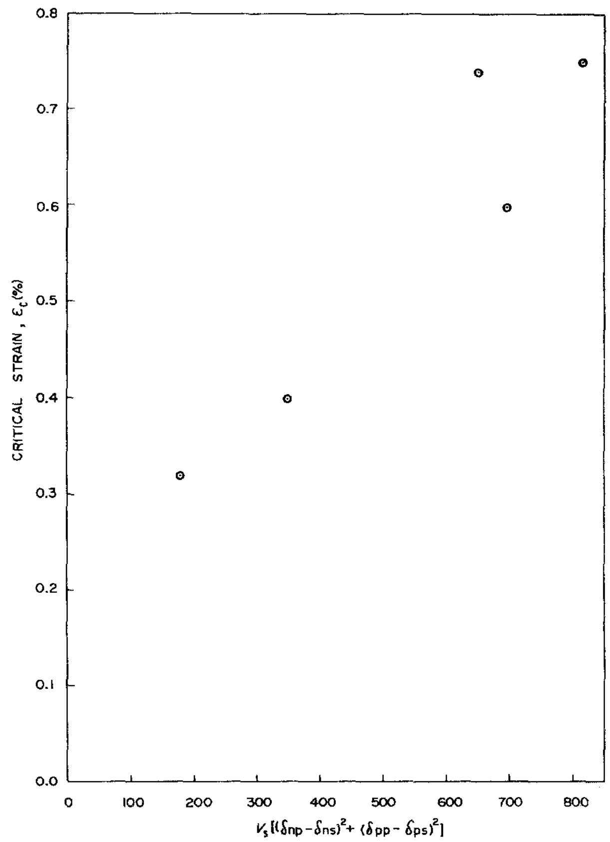

Figure 15 Critical strain (ε_c) against χ_H (Equation 7) for PC–(hydrocarbon mixtures).

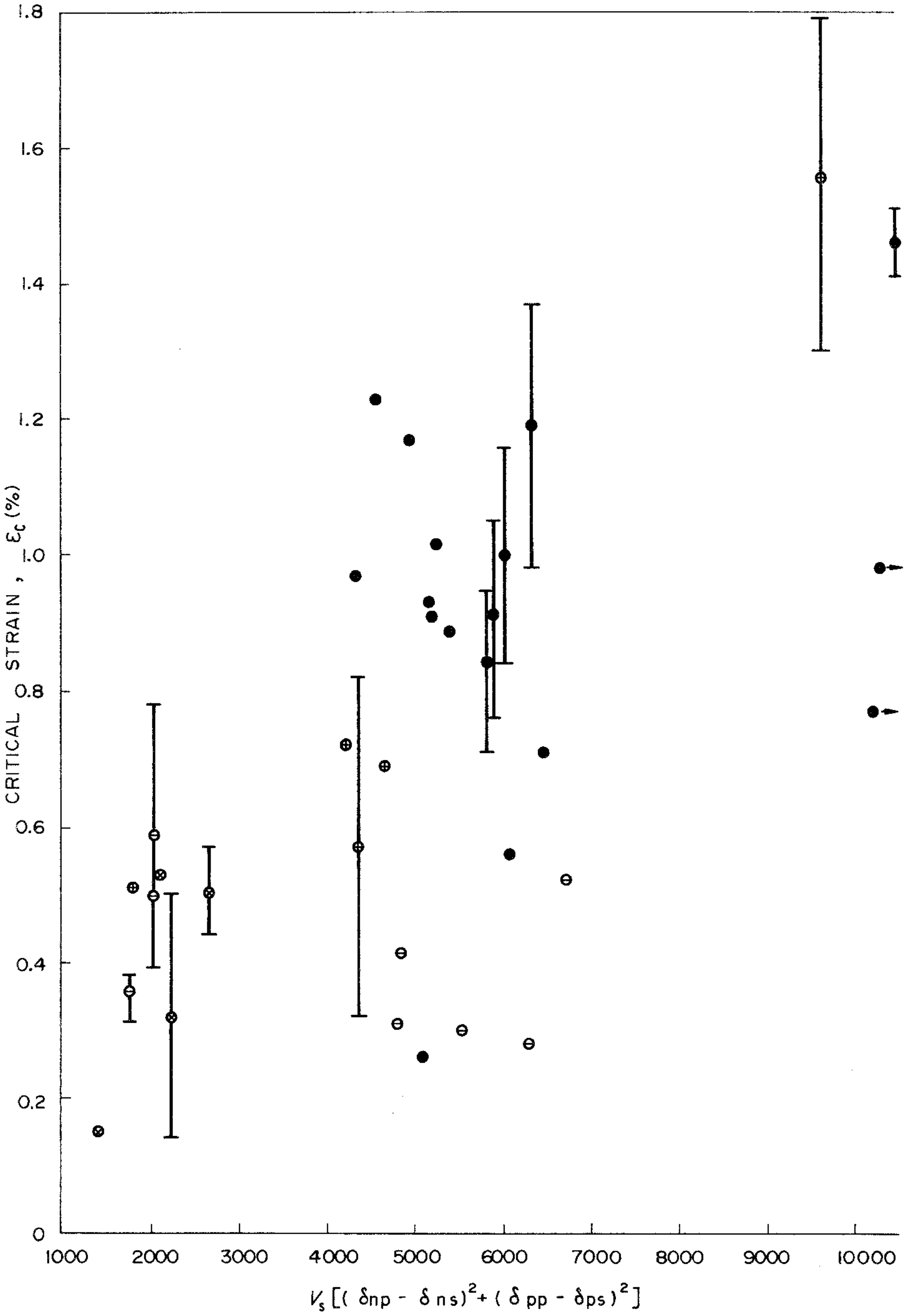

Figure 16 Critical strain (ε_c) against χ_H (Equation 7) for PC–(alcohols, nitrogen compounds, ketones, esters). (●) Alcohols, (⊕) nitrogen compounds, (⊗) ketones, (⊖) esters.

3.3. Discussion and concluding remarks

From the results given in Section 3.2 it has become clear that the use of Hildebrand's solubility parameter or the use of the enthalpic component χ_H of the Flory–Huggins interaction parameter (i.e. Equations 5 to 7) is not always successful in correlating with critical strain (ε_c) results. This finding is disappointing since it was originally thought that χ_H would already have taken care of the effects of the molar volume of the solvent and the various possible molecular interactions between polymer and solvent. PPO seems to be the only polymer that gives good correlation between ε_c and χ_H for all the liquid environments tested. It may also be justified to say that reasonably good correlations are obtainable in all the polymer–(alkane and hydrocarbon) systems with the exception of PS, PSF and PMMA for which there are probably not enough data to make a critical conclusion (see Figs. 2, 8 and 12). For strongly polar and hydrogen-bonding liquids like alcohols, ketones and esters there is virtually no correlation between ε_c and χ_H. A two-dimensional solubility parameter mapping technique in which $V_s(\delta_{pp} - \delta_{ps})^2$ is plotted against $V_s(\delta_{np} - \delta_{ns})^2$ together with superposed critical strain contours may have to be used in these cases. Such a technique has been proven for the PC–(hydrocarbon, alcohol, ester, ketone, ether and nitrogen compound) systems by Jacques and Wyzgoski [9]. Whether this technique will work for other polymers is unknown. Also, its success depends on the appropriate choice of δ_{np} and δ_{pp} for the polymer to give the best fit to the data. For PC they chose $\delta_{np} = 3$ and $\delta_{pp} = 9.5$ [9] which are dramatically different to those values given in Table I.

Gent's theory of environmental stress crazing/cracking has been extensively tested in this work and in general, there is a trend for the crazing stress (σ_c^*)

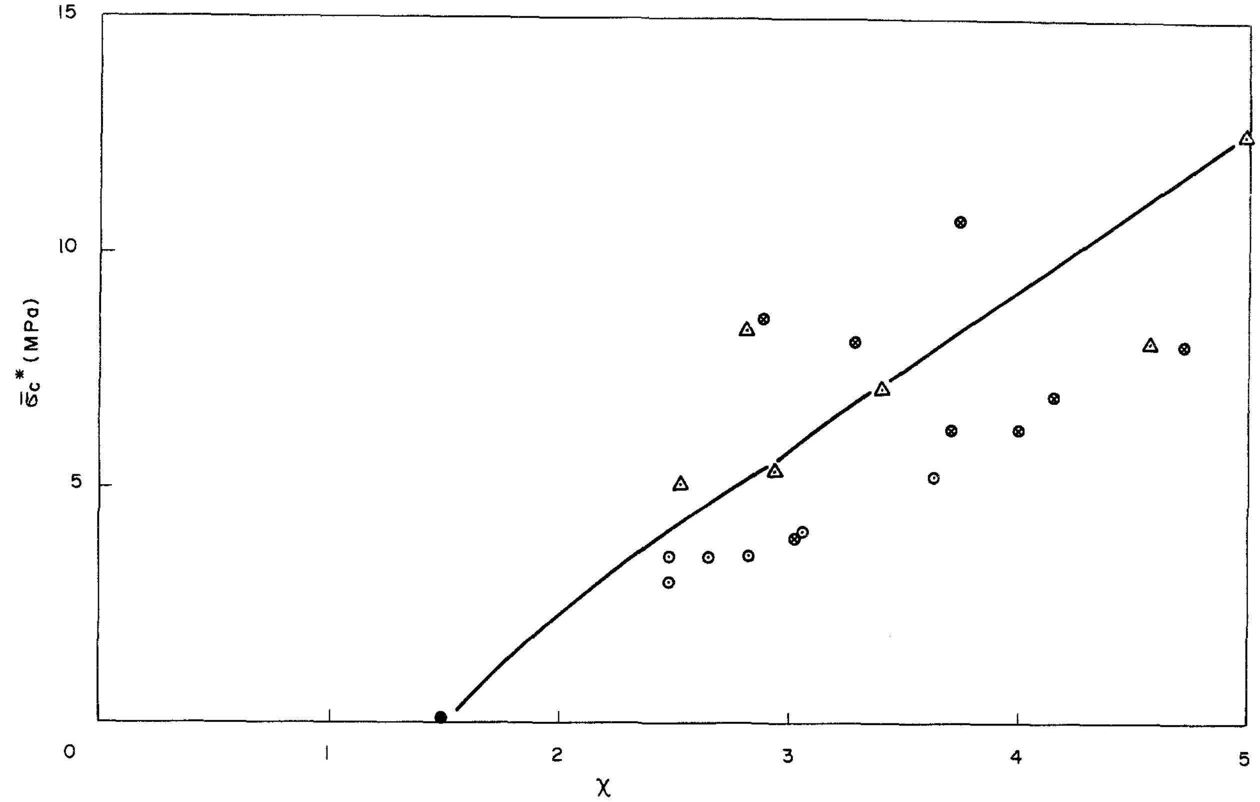

Figure 17 A plot of $\bar{\sigma}_c^*$ against χ (Equation 12) for PS. $E = 3\,\mathrm{GPa}$, $k = 20$, $\bar{\sigma}_c(\mathrm{air}) = 40\,\mathrm{MPa}$. (⊗) Alcohols, (⊙) hydrocarbons with zero hydrogen bonding, (△) ethers and nitrogen compounds, (●) solvents.

to increase with the Flory–Huggins parameter χ obtained from Equation 12. Except for the PPO–(alcohol, alkane, ketone and ester), PC–(alkane, ketone, ester and hydrocarbon) systems the correlation between $\bar{\sigma}_c^*$ and χ for the other polymer–solvent systems is only fair. Nevertheless, these results have given support to the mechanism of environmental stress crazing as proposed by Gent [3] which until now has not been critically assessed. The basic problem remains that χ cannot be determined from empirical solubility parameters such as δ_p, δ_s, δ_{ns}, δ_{np}, etc. because it is stress-dependent as given in Equation 12.

It seems, therefore, that the prediction of ε_c from solubility parameters is still largely problematical.

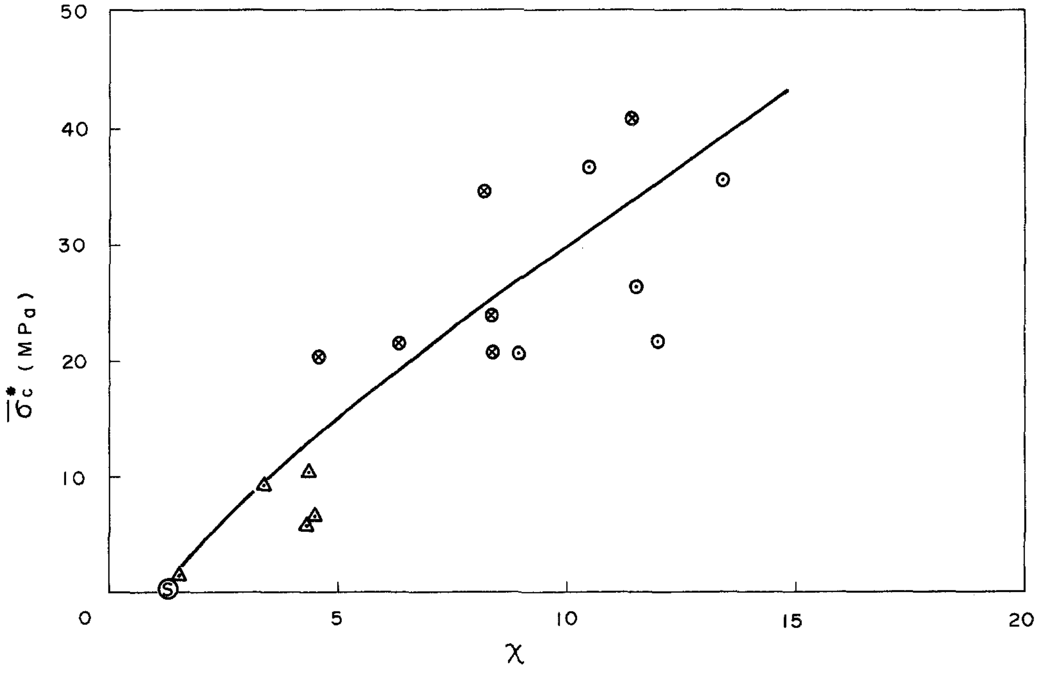

Figure 18 A plot of $\bar{\sigma}_c^*$ against χ (Equation 12) for PVC. $E = 3\,\mathrm{GPa}$, $k = 20$, $\bar{\sigma}_c(\mathrm{air}) = 60\,\mathrm{MPa}$. (⊗) Alcohols, (⊙) zero hydrogen-bonding liquids, (△) all others, (Ⓢ) solvent.

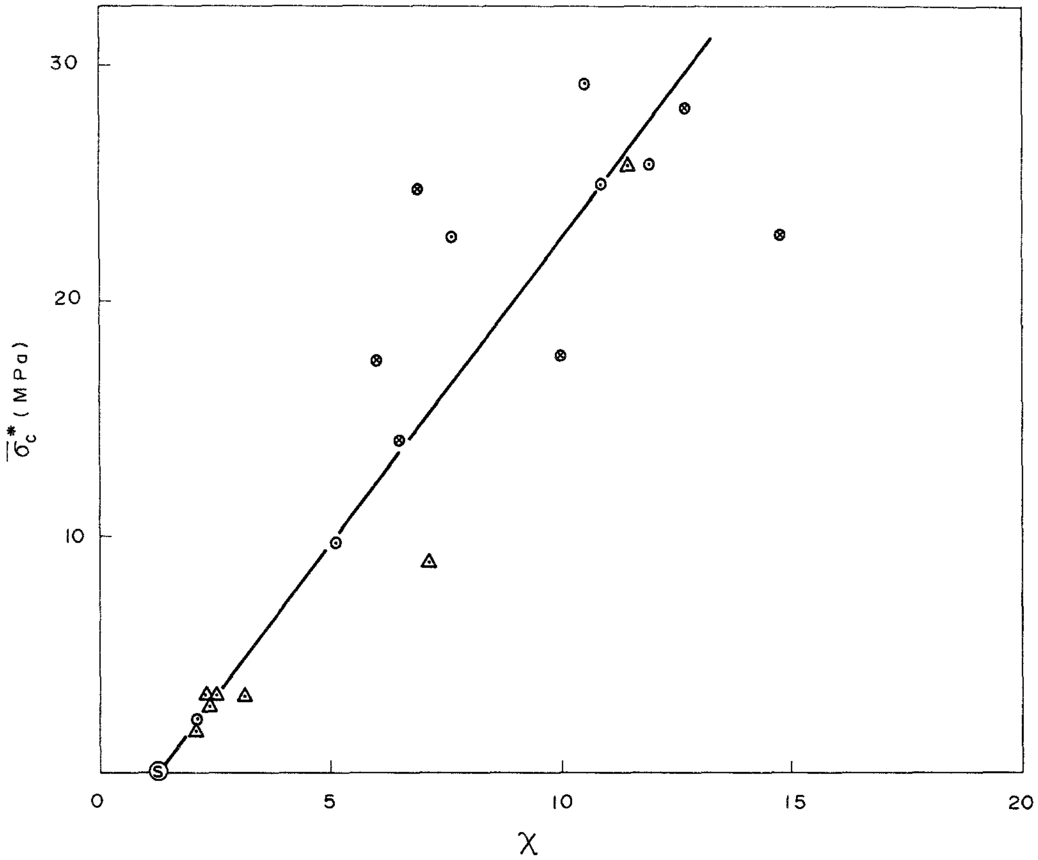

Figure 19 A plot of $\bar{\sigma}_c^*$ against χ (Equation 12) for PSF (polysulfone 1700). E = 3 GPa, $\bar{\sigma}_c$(air) = 75 MPa, k = 20. (⊗) Alcohols, (⊙) zero hydrogen-bonding liquids, (△) esters and ketones, (Ⓢ) solvent.

Except for those polymer–solvent systems that have an established empirical relationship between ε_c with χ_H (such as the polymer–alkane and polymer–hydrocarbon systems) it is not possible to predict *a priori* the critical strain for crazing, given the solubility parameters of the solvent.

Acknowledgements

The author wishes to thank O. F. Yap and N. B. Leete for performing the experimental work on PMMA (Figs. 1 to 3) and for useful discussions during the various stages of this project.

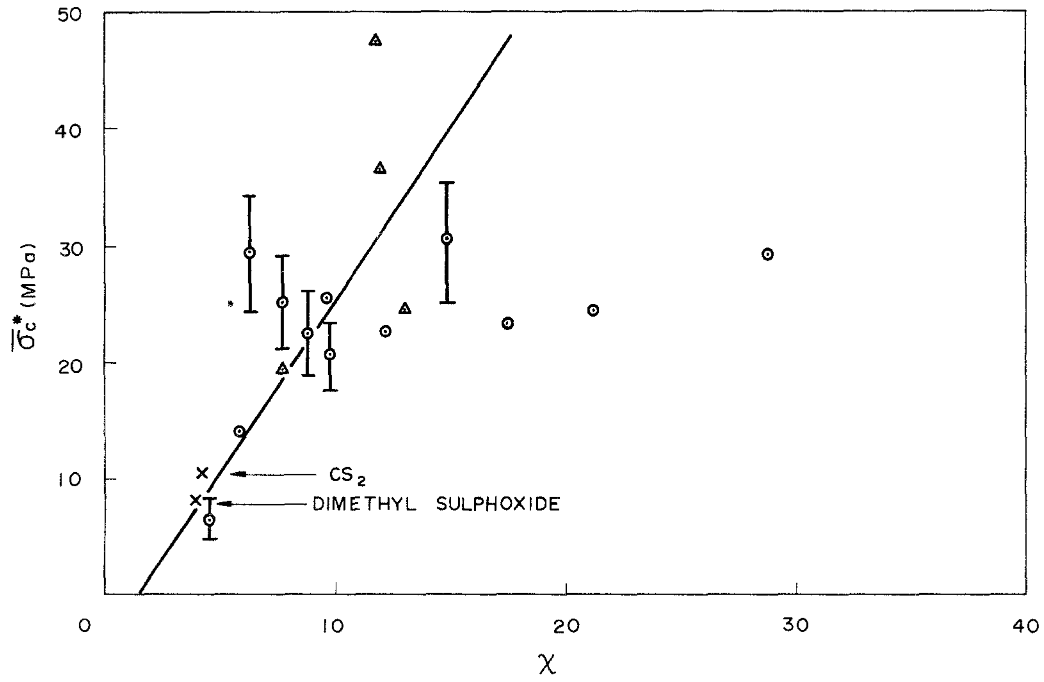

Figure 20 A plot of $\bar{\sigma}_c^*$ against χ (Equation 12) for PC–alcohols. E = 2.5 GPa, $\bar{\sigma}_c$(air) = 90 MPa, k = 20. (⊙) Monohydric alcohols, (△) polyhydric alcohols.

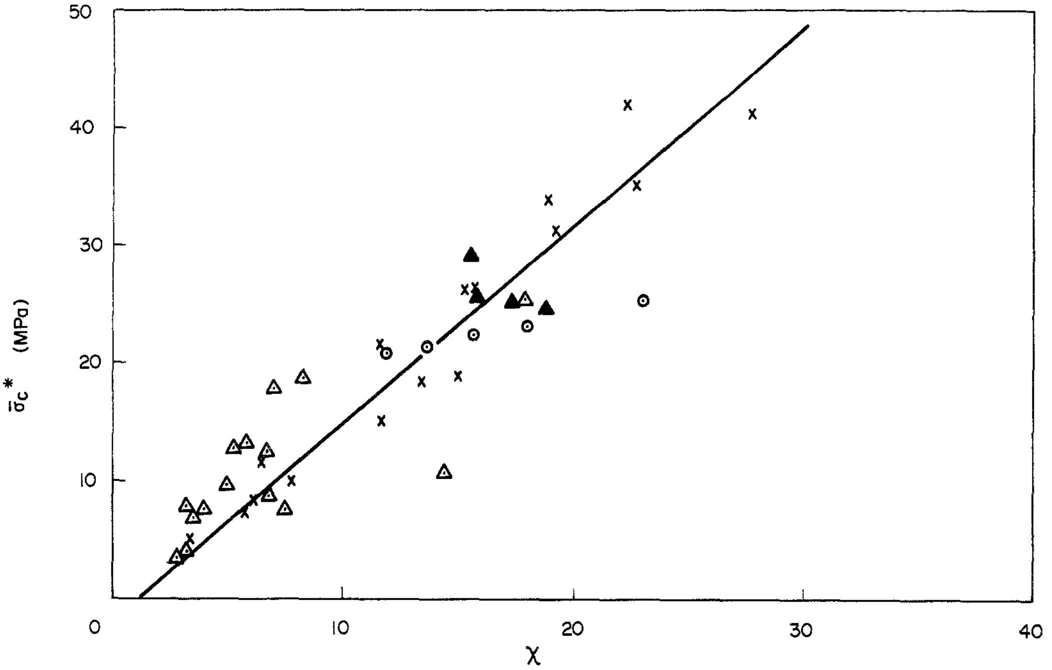

Figure 21 A plot of $\bar{\sigma}_c^*$ against χ (Equation 12) for PC–(alkanes, esters, ethers, ketones). $E = 2.5\,\text{GPa}$, $\bar{\sigma}_c(\text{air}) = 90\,\text{MPa}$, $k = 20$. (△) Ethers, esters and ketones, (⊙) normal alkanes, (▲) 2-methyl alkanes, (⊗) other alkanes and hydrocarbons.

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