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Influence of Cohesive Forces on the Glass Transition Temperatures of Polymers

W. A. LEE and J. H. SEWELL, *Ministry of Technology, Materials Department, Royal Aircraft Establishment, Farnborough, Hants, England*

Synopsis

The relationship between cohesive energy (c.e.) or cohesive energy density (c.e.d.) and the glass transition tenperature (T_g) of polymers has been re-examined on the basis of literature data. For polymers with T_g above 25°C., there is no correlation between published or calculated values of c.e. or c.e.d. and T_g. However, for the rest of the polymers there is a linear relationship between c.e.d. and T_g, and a broad relationship between c.e. and T_g. These results imply that c.e.d. is the regulating, though not the only, factor in determining T_g's up to values of approximately 25°C.

INTRODUCTION

For the glass transition T_g to occur, the thermal energy of a polymer must exceed the barrier opposing long-range molecular motion of the main chain. Strong cohesive forces therefore, are likely to be an important factor in the determination of polymer T_g. Several authors have related cohesive energy (c.e.) or cohesive energy density (c.e.d.) with the T_g of polymers. For example, Boyer[1] stated that T_g increases with increase of c.e.d. and "to date, we are unaware of any evidence to the contrary." Tobolsky[2] reported that polymers of high δ_p (square root of c.e.d.) tend to have high values of T_g. Havlik and Smith,[3] dealing with crosslinked and noncrosslinked diisocyanate-linked elastomers containing substituted urea groups, said that the value for T_g is determined by the cohesive energy density of the polymer and possibly by the stiffness of the chains; increasing the c.e.d. or chain stiffness raises T_g in general agreement with empirical relationships as proposed by Marei[4] and Hayes.[5] These relationships indicate that T_g increases with increasing c.e.d. Fujimoto[6] stated that the glass temperature was proportional to the molar cohesion energy of the polymer, and Uematsu[7] related c.e.d. to T_g for a wide range of polymers, claiming linear relationships. That intermolecular forces are of prime importance in governing the magnitude of T_g was also reported by Bunn,[8] though he also recognized that other factors such as geometry and hindered rotation must play some role.

In this paper, the validity of published c.e. and c.e.d. data and the relationships between these parameters and the T_g of polymers are re-examined

to establish their usefulness in estimating polymer T_g; it is shown that previous views on these relationships need some qualification.

Methods of Obtaining Cohesive Energy Densities

The cohesive energy (c.e.) of a liquid may be defined as the internal latent heat of vaporization

$$E = U_{\text{vap}} + \int_{V=V_{\text{vap}}}^{V=\infty} (\partial U/\partial V)_T dV$$

where E is molar c.e., U is internal energy, and V is volume.

The integral is the correction for the imperfection of the vapor; this correction becomes small when the vapor pressure is low, and then

$$E = L - RT$$

where L is latent heat of vaporization. The c.e. is then equal to the latent heat of vaporization less the mechanical work done in separating the molecules beyond their sphere of interaction.

The cohesive energy density (c.e.d.) may be defined as the latent heat of vaporization per cubic centimeter at constant volume and is equal to E/V, where V is molar volume.

The c.e. or c.e.d. of a liquid may therefore be measured directly by vapor pressure, electrical, or calorimetric methods, but the c.e. or c.e.d. of a polymer cannot be measured directly. Above its T_g, however, a rubber has many of the characteristics of a lightly crosslinked liquid, and the theory of mixing has been applied to the swelling of rubbers by various liquids. For the mixing of liquids, Scatchard[9] and Hildebrand[10] proposed relationship (1):

$$\Delta H_m = v_1 v_2 (\delta_1 - \delta_2)^2 \tag{1}$$

where ΔH_m is the heat of mixing (cal./cc. of mixture), v_1 and v_2 are volume fractions of liquids, and δ_1 and $\delta_2 = (E_1/V_1)^{1/2}$ and $(E_2/V_2)^{1/2}$ for the respective liquids. As E_1/V_1 and E_2/V_2 are the c.e.d.'s of the liquids, δ_1 and δ_2 are the square roots of the c.e.d.'s and are sometimes called solubility parameters.

ΔH_m is always positive, i.e., endothermic, and tends to oppose the process of solution. Thus, when ΔH_m is a minimum, i.e., when $\delta_1 \rightarrow \delta_2$, mixing is most easily facilitated. Therefore, it has been postulated[11] that the liquid which gives rise to the maximum equilibrium swelling at a particular temperature (i.e., tends to dissolve the rubber most easily) has a similar value of δ to that of the rubber. The value of δ must, of course, be corrected for the temperature at which swelling takes place.

Practical details and methods used to calculate c.e.d.'s from swelling of polymers in various liquids are described by several authors.[11–15]

It has also been found[16,17] that the intrinsic viscosity $[\eta]$ of a polymer solution is a Gaussian function of $V^{1/2}(\delta_l - \delta_p)$, where V is molar volume of solvent and the subscripts l and p refer to the liquid and polymer, respec-

tively. The solvent having the same c.e.d. (δ^2_l) as the polymer corresponds to a maximum value of $[\eta]$ by analogy with swelling coefficients. Thus the value of δ_p may be calculated from viscosity measurements on the polymer in a variety of solvents.[17–19]

Small[20] has devised a set of additive constants, called molar-attraction constants, which allow molar c.e.'s, c.e.d.'s and solubility parameters δ of a wide variety of compounds to be calculated from a knowledge of the constituent groups in a molecule. The internal pressure of amorphous polymers has also been related to c.e.d.[21] However, internal pressure measurements cannot be used as an indirect method of obtaining c.e.d.; a single relationship has not been established and would be unlikely to hold for a wide variety of polymers. Other methods used include extrapolation of c.e.d. of aliphatic hydrocarbon liquids against the reciprocal of the number of carbon atoms in the chain to infinite chain length (e.g., polymethylene[22]) and a calculation of c.e.d. from measurements made on solvent interactions with a polymer (e.g., polychlorotrifluoroethylene[23]).

Validity of Cohesive Energy Density Values

Values Obtained by Swelling and Viscosity Techniques. Several authors, including those who have made measurements, have doubted the accuracy and validity of c.e.d. determinations on polymers. The relationship from which calculations from swelling measurements (and, by analogy, viscosity measurements) are made [eq. (1)] and which refers to the mixing of liquids, is subject to several limitations. Scatchard, the proposer of the relationship, assumed that the c.e. behaves as the gravitational energy between point masses, or as electrostatic energy between point charges, and was aware that the accuracy of the assumption needed to be very great if the behavior of mixtures was to be predicted to a good approximation; since his assumption implied[9] homogeneous molecules, it is only approximate. Gee, who applied the analogy of mixing of liquids to the swelling of rubber, stated[11] that eq. (1) could be true only if there were no specific interactions between the two components of the mixture. When both rubber and swelling agents possessed polar groups, such interactions must be general and would lead to deviations from the simple theory. As most synthetic polymers and most solvents contain polar groups, the validity of many estimations from swelling measurements must be in doubt. Mangaraj[15] draws attention to difficulties encountered with systems of different polar character and, pending the solution of the problem, says that no mathematical manipulation is likely to improve the situation. Various authors have commented that the choice of solvents is important in calculating c.e.d.'s from swelling measurements[15,21,24,25] and that strong dipole effects must be avoided. There are often important contributions to swelling properties from non-c.e.d. factors of which there is no *a priori* knowledge for any specific case.[18]

It has been reported[18] that the determination of c.e.d. from swelling measurements is limited to polymers having a T_g below the swelling tem-

perature, because crosslinked polymers having T_g above this temperature have been found to break up during swelling.[17] This may be a factor which puts a practical limitation on swelling measurements, but careful experimentation to remove stress concentrations arising in the polymer on swelling may overcome this objection.[26]

The Scatchard-Hildebrand relationship [eq. (1)] is strictly correct only if $(\partial\delta_p/\partial T) = (\partial\delta_l/\partial T)$, but an examination of $(\partial\delta/\partial T)$ for different liquids shows that this is quite unlikely. The error introduced, however, may be small.

The analogy between a lightly crosslinked rubber and a liquid, on which the whole concept is based, is only an approximation. Bristow[27] points out differences between the thermodynamic behavior of polymer solutions and solutions of low molecular weight compounds. Swelling phenomena might therefore exhibit differences in thermodynamic behavior from the mixing of liquids which would invalidate use of eq. (1). Bristow[27] also states that the c.e.d. concept is applicable only to some liquid–liquid mixtures and its universal applicability to polymer–liquid systems is improbable.

Summing up, it appears that the calculation of c.e.d.'s from swelling measurements and from viscosity readings is very approximate for all but a few selected polymers.

Calculated Cohesive Energy Density Values. Small's molar-attraction constants[20] give the best values over a wide range of compounds but can be improved for a restricted field[22] and are thus semiquantitative.

Experimental Conditions for Cohesive Energy Density Measurements on Rubbers

Despite the many objections to the c.e.d. concept as applied to polymer–liquid interactions, it is claimed[11] that the swelling of a rubber by a given liquid may be roughly predicted. However, swelling measurements on rubbers must conform to the following conditions.

(*1*) The swelling must be allowed to reach as close to equilibrium as practicable. It has been found[13] that some solvents swell rubbers more slowly than others; however, the solvent which causes rapid swelling may not cause maximum swelling over a long time.

(*2*) Sufficient liquid must be used to swell any one rubber to prevent ambiguity or approximation concerning the maximum of the curve of swelling against δ_l. The value of c.e.d. is obtained from $(\delta_l)^2$ so that considerable error is introduced if δ_l is only approximate. Unfortunately an accurate value of δ_l is often difficult to achieve.

(*3*) The rubber should be undiluted, subject to the requirements of additives for crosslinking, as results[11] show that a different liquid causes maximum swelling of natural rubber when loaded with carbon black compared with the unloaded vulcanizate. Neoprene GN shows the same effect when filled with whiting.

The value of δ_l for the liquid must be accurately obtainable for the temperature of swelling, which involves knowledge of the latent heat of evaporation at this temperature.

Viscosity measurements also require that the value of δ_l be known at the temperature of measurement and that sufficient liquids must be used for measurements.

Results of Cohesive Energy and Cohesive Energy Density Measurements

Results of c.e. and c.e.d. measurements are given in Table I together with some calculated values.

The c.e. figures are derived from the corresponding c.e.d. values by multiplying the c.e.d. by the molar volume (molecular weight of repeating unit/density of polymer). The density of the polymer can vary with degree of crystallinity, molecular weight, additives, etc.; the density of the particular polymer used for determining c.e.d. was usually not stated, so that it was taken as that most frequently quoted in the literature. Errors in c.e. arising from errors in density are unlikely to be very large, but they make c.e. values rather less reliable than c.e.d values. The T_g values, carefully selected from a wide range of published data, are considered to be the most probable.[28]

Discussion of Results

Where more than one value for c.e. or c.e.d. is given for a particular polymer the difference between the highest and lowest values is usually only a few per cent (see Table I). Natural rubber shows quite a good correlation between several results. In a few cases, the calculated value differs appreciably from the experimental results, as in the case of polystyrene and, to a lesser extent, polyethyl acrylate. It has been noted[25] that the c.e.d.'s of poly(methyl methacrylate), poly(methyl acrylate), poly(ethyl acrylate), and poly(butyl acrylate) are 15–20% higher than those of the corresponding model compounds (methyl isobutyrate, methyl propionate, ethyl propionate, and *n*-butyl propionate, respectively). This has been attributed to an increase of density on polymerization, the corresponding decrease in intermolecular distance causing increased cohesion. However, it is worth restating that swelling measurements can be very approximate if polymers have T_g's above the swelling temperature;[18] thus, for example, it will be seen from Table I that the data from swelling measurement on poly(methyl methacrylate) may be unreliable. The swelling result on poly(butyl acrylate) may also be erroneous; the sample broke up during measurement making it difficult to estimate the degree of swelling accurately.[29]

Although all the measurements were not made at the same temperature, correction of the results to a single temperature, say, 25°C., would not significantly alter the conclusions which are drawn.

TABLE I

Cohesive Energies, Cohesive Energy Densities and Glass Transition Temperatures T_g of Various Polymers

No.	Polymer	Cohesive energy, cal.	Cohesive energy density, cal./cc.	Temp., °C.	Method of estimation	Ref. for c.e.d.	T_g, °K.
1	Natural rubber	4972	66.4	25	Calculation	20	201
		4765	63.7	20	Swelling	11	
		5413	69.7	24	Swelling	13	
		4907	65.6	25	Swelling	12	
2	Polyacrylonitrile	7280	162.6	25	Calculation	20	378
3	Polybutadiene	4089	70.2	25	Calculation	20	165 (*cis*); 225 (*trans*)
		4155	71.4	24	Swelling	13	
4	Polychloroprenes						
	Neoprene GN	4698	88.0	25	Calculation	20	228 (*trans*)
	Neoprene GN	3578	67	20	Swelling	11	
	Neoprene GN	4569	85.6	24	Swelling	13	
	Neoprene WRT	3950	74.0	25	Swelling	12	
5	Polyethylene	1077	65.6	25	Calculation	20	148
		950	62.4	20	Swelling	14	
6	Polymethylene	1074	65.6	25	Calculation	20	155
		1146	70 ± 1	20	Calculation	22	
7	Poly(ethylene terephthalate)	16521	114.5	25	Calculation	20	342
8	Polyisobutylene	3604	59.3	25	Calculation	20	200
	Butyl rubber	3699	60.8	25	Swelling	12	
9	Polymethacrylonitrile	7105	114.5	25	Calculation	20	393

10	Poly(methyl methacrylate)	7197	85.6	25	Calculation	20	378
		6935	82.5	25	Viscosity	18	
		7511	89.3	20	Swelling	25	
		7432	88.4	35	Viscosity	31	
11	Polystyrene	8172	83.2	25	Calculation	20	373
		7198	73.3	25	Viscosity	18	
		7368	75 ± 2	25	Viscosity	19	
12	Polytetrafluoroethylene	930	38.4	25	Calculation	20	160; 400
13	Poly(vinyl acetate)	6439	88.4	25	Calculation	20	301
14	Poly(vinyl chloride)	4116	91.2	25	Calculation	20	354
		4083	90.8	25	Viscosity	18	
15	Poly(methyl acrylate)	7263	103.0	20	Swelling	25	279
		7192	102.0	35	Viscosity	29	
16	Poly(ethyl acrylate)	7934	94.1	25	Calculation	29	249
			88.4	20	Swelling	25	
			87.4	35	Viscosity	29	
17	Poly(propyl acrylate)	8562	81.0	25	Calculation	29	225
			81.0	35	Viscosity	29	
18	Poly(butyl acrylate)	10156	81.9	20	Swelling	25	218
		9603	77.4	35	Viscosity	29	
19	Poly(vinylidene chloride)	5174	85.4	25	Calculation	20	254
20	Poly(propylene oxide)	3409	58.7	25	Calculation	20	198
21	Poly(butadiene monoxide)	[a]	83	22	Swelling	30	198
22	Poly(ethyl methacrylate)	[a]	83.7	35	Viscosity	31	330
23	Poly(butyl methacrylate)	[a]	81	35	Viscosity	31	249
24	Poly(isobutyl methacrylate)	[a]	74.8	35	Viscosity	31	326

[a] Density not available for calculation.

Relationship between Cohesive Energy, Cohesive Energy Density, and T_g of Polymers

It is worth while reexamining the claims of other authors concerning the relationships between cohesive forces and T_g, based on similar published data, in order to show to what extent trends in T_g can be estimated.

The variation of c.e. with T_g is shown in Figure 1 and the variation of c.e.d. with T_g in Figure 2 for a wide variety of polymers.

The c.e. value for poly(ethylene terephthalate) is not shown on Figure 1 and the c.e.d. value for polyacrylonitrile is not shown in Figure 2, as their insertion would involve considerable lengthening of the abscissae.

Both graphs show that T_g tends to increase broadly with increase in c.e. and c.e.d., but it has not been possible to form a direct relationship as the scatter of points is too great, although the c.e.d. values appear to show a

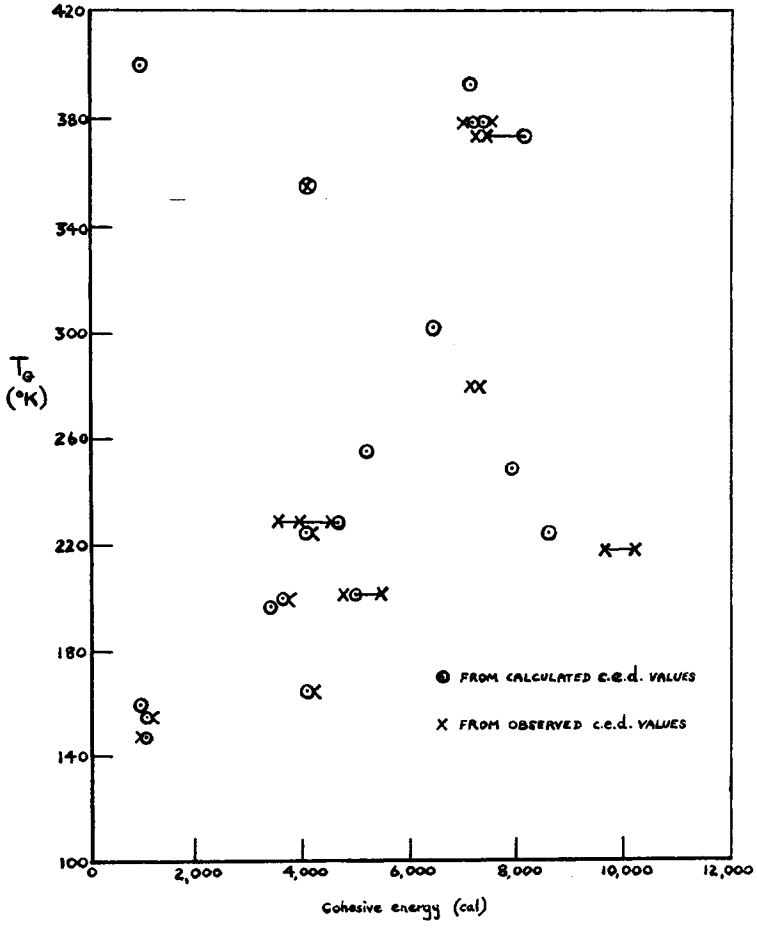

Fig. 1. Variation of glass transition temperature with cohesive energy for various polymers.

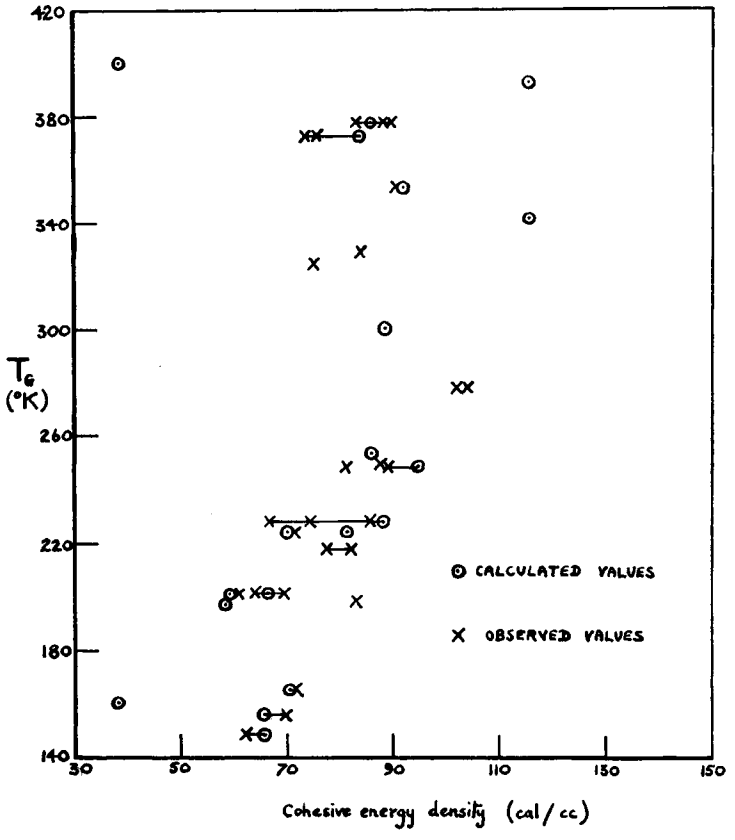

Fig. 2. Variation of glass transition temperature with cohesive energy density for various polymers.

more definite trend than do the c.e. values. There are, however, several instances where a particular polymer has a higher T_g yet significantly lower c.e. or c.e.d. than another polymer, so that only the broadest generalization is possible. The error of trying to compute T_g from c.e.d. data increases with increase in T_g, assuming a general trend in the points.

It is interesting to note that of the two reported transitions in polytetrafluoroethylene at 160 and 400°K., the value at 400°K. is so far from the main bulk of points on Figures 1 and 2 as to make it likely that the most significant transition is in fact at 160°K.

Consideration of the structures of polymers 4 (*trans*), 10, and 16 (see Table I) suggests that steric hindrance is high for poly(methyl methacrylate), while in Neoprene GN and poly(ethyl acrylate) the side groups are quite free to rotate about the main chain. Thus, as these polymers have approximately the same c.e.d., these steric factors may override c.e.d. considerations. A similar conclusion can be drawn from polymers 11 (observed value), 4 (*trans*, observed value), 3 (*trans*), 3 (*cis*), 1, and 6 (observed value).

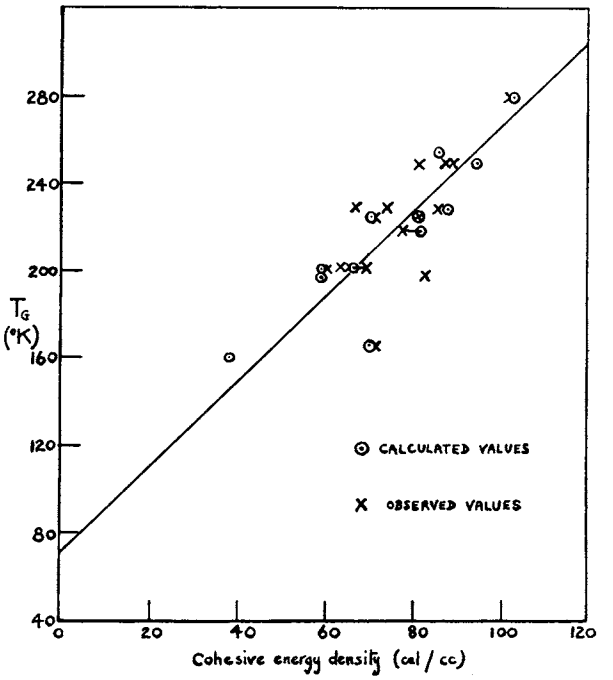

Fig. 3. Variation of glass transition temperature with cohesive energy density for rubbers.

Considering only those polymers which are above their T_g at the temperature of c.e.d. measurement, linear relationship between c.e.d. and T_g is shown in Figure 3, provided that the polymer is not too crystalline.

Polymethylene and polyethylene, which always possess a high degree of crystallinity, are excluded. The values for poly(butadiene monoxide) and *cis*-polybutadiene are exceptions to the general conformity, but the observed and calculated values of c.e.d. for polybutadiene when related to the T_g of the *trans* isomer only show good correlation.

The relationship is of the form

$$T_g = K(E/V) + C$$

where K and C are constants and equal the slope and intercept, respectively, of Figure 3.

$K = 2°$ cc./cal. and $C = 70°$K., and the deviation of measured T_g values from the mean given by this equation is $\pm 20°$C. (excluding polybutadiene monoxide and *cis*-polybutadiene).

The presence of the intercept C, suggests that, although c.e.d. is a regulating factor in determining the T_g of these polymers, other independent factor(s) are also important. The possibility that the barrier opposing internal rotation is the dominant factor governing the T_g's of these polymers, but that its magnitude is regulated to a great extent by cohesive forces, is a concept which is in accord with the above results.

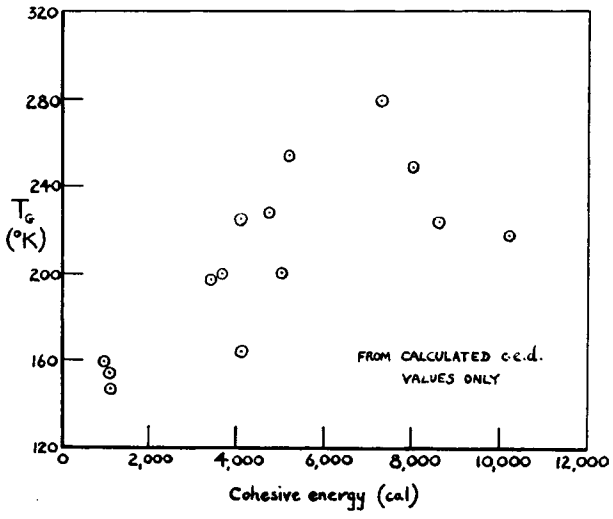

Fig. 4. Variation of glass transition temperature with cohesive energy for rubbers.

The fact that a relationship is found only for polymers with T_g below the temperature of c.e.d. measurement supports the view that the c.e.d. concept is of limited applicability[27] and that swelling measurements in particular may be applicable only to rubbers above their T_g.[17,18] However, as previously mentioned, careful experimentation may overcome this limitation.[26]

There is also a broad correlation between c.e. and T_g for polymers with T_g below the temperature of c.e.d. measurement. Figure 4 shows that in general the T_g of such rubbers increases with increase in c.e., although there are several exceptions to this rule.

This relationship between c.e. and T_g is much less close than that of c.e.d. versus T_g shown in Figure 3. For purposes of graphical clarity, only calculated values of c.e. are shown in Figure 4.

The comparatively good correlation between c.e.d. and T_g for polymers having a T_g below 298°K. may mean that the c.e.d. is a more important parameter in determining T_g than is c.e., or it may just be a reflection of the inaccuracy of the estimation of c.e.

Conclusions

There are many doubts regarding the validity of the basic assumptions involved in applying the cohesive energy (c.e.) concept to polymer–liquid interactions and the extension of the theory of mixing to such interactions. In addition, there are several conditions which must be observed when making practical estimations of cohesive energy density (c.e.d.) which are not always followed. A fairly high scatter of results is found therefore when data from different measurements on the same polymer are compared and it is necessary to be very discriminating in the selection of data.

Calculated c.e. and c.e.d. values are derived from molar-attraction constants, which in turn are estimated from published vapor-pressure and heat of vaporization values obtained from measurements on liquids. This approach may not be valid for polymers in the glassy state.

For polymers having T_g above the temperature of estimation of c.e.d. (ca. 298°K.) there is no good correlation between the published or calculated c.e. or c.e.d. values and T_g, although very broadly an increase in c.e.d. is accompanied by an increase in T_g. This lack of good correlation is not unexpected in view of the possible objections to the validity of measurements in this range. However, for nearly all polymers examined with T_g below the temperature of c.e.d. measurement there is a direct correlation of T_g with c.e.d. which is accurate to ±20°C. Although there is a broad correlation between c.e. and T_g for such polymers, there is a much greater error in predicting T_g from c.e. values than from c.e.d. values. This implies that, for polymers with T_g below 298°K., the most important factor regulating T_g is c.e.d. The broad contention of other workers that T_g of polymers increase with increase in c.e. or c.e.d. should therefore be qualified in accordance with the above observations.

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References

1. R. F. Boyer, *Rubber Rev.*, **36**, No. 5, 1361 (1963).
2. A. V. Tobolsky, *Properties and Structure of Polymers*, Wiley, New York, 1960, p. 67.
3. A. J. Havlik and T. L. Smith, *J. Polymer Sci. A*, **2**, 539 (1964).
4. A. I. Marei, *Kauchuk i Rezina*, **19**, 2, (1960); *Soviet Rubber Technol.*, **19**, 1 (1960).
5. R. A. Hayes, *J. Appl. Polymer Sci.*, **5**, 318 (1961).
6. K. Fujimoto, *Kobunshi Kagaku*, **17**, 39 (1961).
7. Y. Uematsu, *Forestry Sci. Lab. Bull. Japan*, **12**, 101 (December 3, 1962).
8. C. W. Bunn, *J. Appl. Phys.*, **25**, 820 (1954).
9. G. Scatchard, *Chem. Rev.*, **8**, 321 (1931).
10. J. H. Hildebrand, *Solubility of Nonelectrolytes*, 3rd ed., Reinhold, New York, 1950.
11. G. Gee, *Trans. Inst. Rubber Ind.*, **18**, 266 (1943).
12. G. M. Bristow and W. F. Watson, *Trans. Faraday Soc.*, **54**, 1731 (1958).
13. R. L. Scott and M. Magat, *J. Polymer Sci.*, **4**, 555 (1949).
14. R. B. Richards, *Trans. Faraday Soc.*, **42**, 20 (1946).
15. D. Mangaraj, *Makromol. Chem.*, **65**, 29 (1963).
16. G. Gee, *Ann. Rept. Chem. Soc. (London)*, **1942**, 7.
17. D. Mangaraj, S. K. Bhatnagar, and S. B. Rath, *Makromol. Chem.*, **67**, 75 (1963).
18. G. M. Bristow and W. F. Watson, *Trans. Faraday Soc.*, **54**, 1742 (1958).
19. J. H. S. Green, *Nature*, **183**, 818 (1959).
20. P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).
21. G. Allen, G. Gee, D. Mangaraj, D. Sims, and G. J. Wilson, *Polymer*, **1**, 467 (1961).
22. G. Allen, G. Gee, and G. J. Wilson, *Polymer*, **1**, 456 (1960).
23. A. M. Bueche, *J. Am. Chem. Soc.*, **74**, 65 (1952).
24. G. Gee, *Proc. Chem. Soc.*, **1957**, 111.
25. D. Mangaraj, S. Patra, and S. Rashid, *Makromol. Chem.*, **65**, 39 (1963).

26. G. Allen, private communication.
27. G. M. Bristow, *The Chemistry and Physics of Rubber-like Substances*, L. Bateman, Ed., Maclaren, London, 1963, p. 137.
28. W. A. Lee and G. J. Knight, unpublished work.
29. D. Mangaraj, S. Patra, and S. B. Rath, *Makromol. Chem.*, **67**, 84 (1963).
30. G. Allen and H. G. Crossley, *Polymer*, **5**, 553 (1964).
31. D. Mangaraj, S. Patra, and P. C. Roy, *Makromol. Chem.*, **81**, 173 (1965).

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