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Application of the Kwei equation to the glass transition of dye solute–polymer blends

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Abstract

The effect of a number of dyes on the glass transition temperatures of a variety of polymers has been investigated. The glass transition temperatures of each dye–polymer blend were compared to the Kwei equation to obtain Kwei *q* parameters. It was demonstrated that the *q* parameter correlated to dye–polymer interaction independent of the variation in dye structure and polymer composition. The highest *q* parameters were obtained as the solubility parameters of dye and polymer approached equality corresponding to the maximum dye–polymer affinity. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Dye; Solute; Polymer

1. Introduction

In previous work [1,2] the effects of solute–polymer affinity on the glass transition temperature of solute–polymer blends were investigated using four different dye molecules in a range of polymers. Glass transitions were usually higher than expected when compared to the Fox equation and this enhancement in *Tg* was correlated with dye–polymer affinity using solubility parameter differences between dye and polymer as a predictive tool. Averaging polar and hydrogen bonding solubility parameters produced a good correlation between the elevation of *Tg* and enhanced dye–polymer affinity, suggesting that these longer range forces were more important in controlling *Tg*. The variation of *Tg* with polymer solubility parameter only was found to be excellent producing a dumb-bell shape giving a maximum *Tg* at a certain solubility parameter. The solubility parameter producing the maximum *Tg* was assumed to be the point of maximum dye–polymer affinity, i.e. dye solubility parameter equal to polymer at maximum *Tg*. This value was different to that calculated for the dye from group contributions, suggesting that the latter is subject to error. Dye–polymer solubility parameter differences were recalculated and the repeated correlation of *Tg* with dye–polymer affinity was found to be excellent.

It is well known that copolymers or polymer blends can give rise to glass transition temperatures significantly higher than expected, resulting from intermolecular interactions. Examples include poly(vinylidene chloride-co-(meth)-acrylates) [3], poly(vinylidene chloride-co-acrylonitrile) [4], poly(*N*-vinyl pyrrolidone-co-acrylic acid) [5], blends of poly(4-vinyl pyridine) with poly(4-hydroxystyrene) [6], blends of poly(acrylic acid) with poly(vinyl methyl ether) [7] and blends of poly(*N*-ethylcarbazol methyl methacrylate) with poly(dinitrobenzoyloxy ethyl methacrylate) [8–10]. In all of these systems the *Tg* is elevated as a result of relatively strong interactions between electron donating and electron accepting functional groups on separate components. The glass transitions of polymer–polymer blends have been reported extensively and there are a number of equations relating the glass transition of a polymer blend to its composition. These equations include those of Fox [11], Kelly–Bueche [12], Couchman–Karasz [13], Gordon–Taylor [14] and Kwei [15]. The latter includes a factor which accounts for the increase in *Tg* resulting from interactions between the two components. Although usually applied to polymer–polymer blends, these expressions and principles can also be applied to copolymers and solute–polymer blends. It is the purpose of this paper to build on our previous work on dye–polymer blends and use the Kwei equation to correlate the glass transition temperatures.

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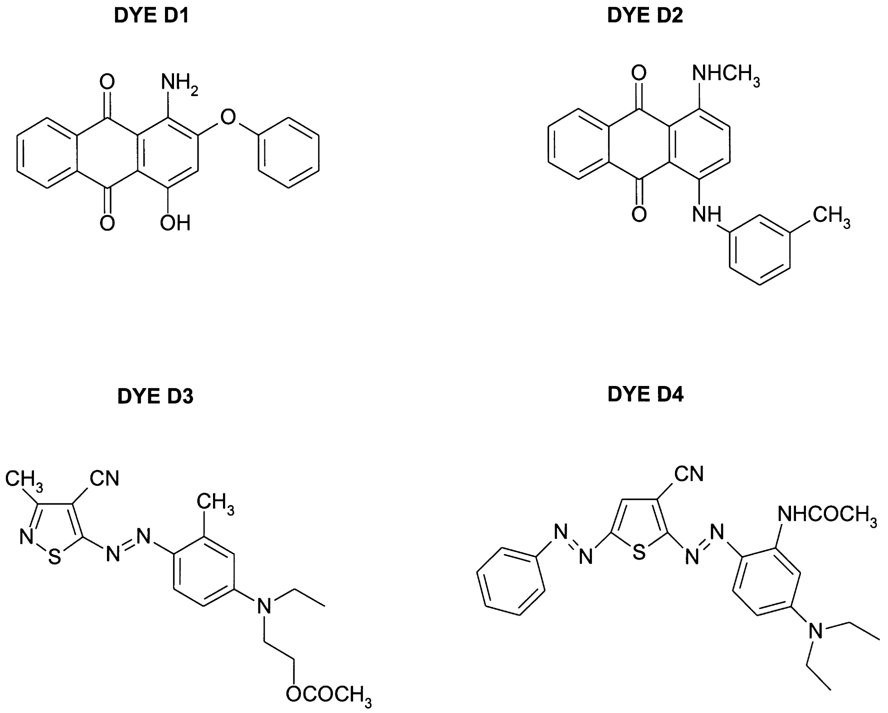

Fig. 1. Structures of the various dye molecules studied.

2. Method

2.1. Materials

The dye molecules studied in this work were used as supplied by Zeneca Specialties and their structures are illustrated in Fig. 1. The various polymers investigated are listed in Table 1 and these were used as obtained from the various suppliers without further purification. The polymers were deliberately chosen to be amorphous in order to simplify the analysis of results, with a variety of functional groups and glass transition temperatures.

2.2. Formation of dye–polymer blends

Dyes and polymers were dissolved in tetrahydrofuran (THF) solvent according to the following mixtures (all w/w%):

D1 anthraquinone magenta	dye 6.5%/polymer 5.9%/THF 91.0%
D2 anthraquinone cyan	dye 4.5%/polymer 4.5%/THF 91.0%
D3 isothiazole magenta	dye 3.0%/polymer 6.0%/THF 91.0%
D4 disazothiophene cyan	dye 2.25%/polymer 4.50%/THF 93.25%

Surface coatings of these homogeneous mixtures were formed on polyester substrates as described previously [1,2]. It should be noted that the transformation from dye and polymer in solution to dye–polymer solid state under these conditions is very rapid ($\ll 1$ s with residual THF $<$ 0.05 μg cm^{-2}). This is thought to produce a solid solution of dye in polymer with the dye being dispersed at a molecular level in the polymer matrix, thereby interacting with polymer chains and affecting the solid state properties. All films were assessed using optical microscopy prior to evaluation, to establish that no undissolved dye particles or crystals were present.

2.3. *Determination of Tg* of dye–polymer blend coatings

A Perkin–Elmer DSC-4 instrument was used to characterise transitions in the dyecoat layers studied, using Indium standard for calibration and a heating rate of 20°C/min. The experimental method is described in detail elsewhere [1,2]. Polymer *Tg* values are given in Table 1 whereas the *Tg* of the dye–polymer blends is summarised in Table 2.

3. Results and discussion

3.1. Solubility parameters as a guide for dye–polymer affinity

Hansen [16,17] proposed an extension of the original Hildebrand theory to polar and hydrogen bonding forces [18], assuming that cohesive energy is made up of a linear combination of contributions from non-polar/dispersion forces, polar interactions and hydrogen bonding interactions

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (1)$$

where δ is the global solubility parameter and δ_d, δ_p and δ_h are the solubility parameters resulting from dispersion, polar

Table 1
Polymers used to create dye–polymer blends

Polymer type	Supplier	*Tg* (°C)	Abbreviation
Phenoxy	Union Carbide	78.5	PHEN
Poly(vinyl chloride)	Polysciences	82.5	PVC
Poly(vinyl butyral)	Sekisui Chemical	85.0	PVB
Poly(vinyl formal)	Monsanto	86.5	PVF
Ethyl cellulose	Hercules	93.0	EC
Poly(vinyl aceto acetal)	Sekisui Chemical	96.0	PVAA
Chlorinated poly(vinyl chloride)	Zeneca Resins	99.0	CPVC
Polycarbonate	Dow Chemical	100.0	PC
Polyester	Dynamit Nobel	100.0	PEST
Poly(styrene-co-acrylonitrile)	Polysciences	103.0	SAN
Polystyrene	Polysciences	104.5	PS
Poly(para hydroxy styrene)	Maruzen Petrochemical	145.0	PPHS

and hydrogen bonding forces, respectively. The previous work [1,2] on the correlation of *Tg* with dye–polymer affinity illustrated that polar and hydrogen bonding forces controlled the increase in T_g resulting from enhanced dye–polymer affinity. Best results were obtained by ignoring dispersion forces and combing the polar and hydrogen bonding components as one parameter (δ_{ph}), i.e.

$$\delta_{ph}^2 = \delta_p^2 + \delta_h^2 \tag{2}$$

where δ_p and δ_h are defined by the equations

$$\delta_p = \frac{\sqrt{\left(\sum F_{pi}^2\right)}}{V} \tag{3}$$

$$\delta_h = \sqrt{\left(\frac{\sum E_{hi}}{V}\right)} \tag{4}$$

F_{pi} and E_{hi} are the group contributions for polar and hydrogen bonding forces, respectively. δ_{ph} for polymers were calculated from group contributions for the polymer average repeating units, using the values compiled by Van Krevelen [19]. These calculated polymer solubility parameters are illustrated in Table 3. The dye solubility parameters in Table 3 are those values determined experimentally since group contributions are not available for all of the dye structures producing errors in calculated values. As detailed in previous work [1,2], the dye solubility parameters were determined from the maximum of the relationship between T_g and polymer solubility parameter δ_{ph}.

3.2. Comparison of dye–polymer blend Tg with the Kwei equation

The Kwei equation [15] is given by the expression

$$T_g = w_1 Tg_1 + w_2 Tg_2 + q w_1 w_2 \tag{5}$$

where T_g is the glass transition temperature of the blend; Tg_1 is the glass transition temperature of component 1; Tg_2 is the glass transition temperature of component 2; w_1 is the weight fraction of component 1; w_2 is the weight fraction of component 2; q is a measure of the interaction between the two components 1 and 2.

The *Tg* of the blend and the *Tg* of the polymer were those glass transition temperatures determined experimentally via DSC. The dye *Tg* was obtained as previously described [1,2] using the Fox equation (which neglects intermolecular forces) applied to the dye–EC polymer systems as a

Table 2
Glass transition temperatures of dye–polymer blends [1,2]

Polymer	D1–polymer blend *Tg*/°C	D2–polymer blend *Tg*/°C	D3–polymer blend *Tg*/°C	D4–polymer blend *Tg*/°C
PHEN	61.0	–	46.0	–
PVC	60.0	–	41.5	–
PVB	–	61.0	–	88.5
PVF	67.0	65.5	47.5	91.5
EC	48.5	38.0	26.5	85.0
PVAA	65.0	72.0	52.0	98.0
CPVC	63.5	65.5	53.5	97.0
PC	61.5	–	45.5	–
PEST	61.0	–	45.0	–
SAN	63.5	64.0	54.0	97.0
PS	52.5	55.0	34.0	95.0
PPHS	–	80.0	–	122.0

Table 3
Solubility parameters of dyes and polymers [1,2]

Material	δ_p (J cm^{-3})$^{1/2}$	δ_h (J cm^{-3})$^{1/2}$	δ_{ph} (J cm^{-3})$^{1/2}$
Dye D1			10.8[a]
Dye D2			11.0[a]
Dye D3			10.6[a]
Dye D4			10.9[a]
PHEN	3.03	10.11	10.55
PVC	12.17	2.97	12.53
PVB	4.51	10.42	11.35
PVF	5.83	9.37	11.04
PVAA	5.36	10.47	11.76
CPVC	9.17	3.40	9.78
PC	3.01	6.80	7.44
PEST	3.04	7.78	8.35
SAN	7.74	4.18	8.80
PS	1.12	0.00	1.12
PPHS	5.09	14.11	15.00

[a] Determined experimentally rather than by group contributions.

Table 4
Thermal properties of dyes [1,22]

Dye type	*Tg* (°C)
D1	17
D2	−3
D3	−55
D4 [1]	70

reference point. EC produced the lowest *Tg* values suggesting that the dye–polymer interactions were weakest for this particular combination. The dye *Tg* values are given in Table 4. This was shown to be a reliable method since, for dye D4, the *Tg* value determined in this way correlated very well with the experimentally determined value obtained via DSC on amorphous dye D4. The latter was prepared by heating a dye sample above its melting point followed by supercooling into its glassy state. The *Tg* values for dye–polymer blend, polymer and dye were fed into Eq. (5) in addition to the blend compositions to obtain q values for each dye–polymer combination. These are summarised in Table 5.

In their paper, Kwei states that q is a measure of interaction between two components with the term qw_1w_2 proportional to the number of interactions existent in the mixture. Our previous papers on the effect of intermolecular forces on the glass transition temperature of solute–polymer blends did not utilise the Kwei equation but demonstrated that increased dye–polymer affinity (indicated by a closer match in dye/polymer solubility parameters) led to an enhancement in *Tg*. In this work, we attempt to correlate q in the Kwei equation with the difference in solubility parameters between the two components. The relationships between q and dye–polymer solubility parameter differences are illustrated in Figs. 2, 3, 4 and 5 for dyes D1, D2, D3 and D4, respectively. In all cases, the q value is low when the solubility parameter differences are large corresponding to low dye–polymer affinity. The parameter q increases substantially as the solubility parameters become more closely matched when dye–polymer affinity is high. These figures demonstrate that for dye–polymer blends, the q parameter in the Kwei equation does correlate with the strength of dye–polymer interaction. These trends are independent of the significant variation in dye structure (four different types) and polymer composition (11 different types), i.e. independent of the wide variety in functional groups present and differences in the conformations of dyes and polymers.

Our results agree with the work of Kanig [20] on mixtures of polymer and plasticiser. He predicted that a good plasticiser is a poor solvent and that low affinity between plasticiser and polymer would result in efficient plasticisation and low *Tg*. Conversely, a poor plasticiser is a good solvent and high affinity between plasticiser and polymer results in higher *Tg*. Our results also agree with the examples cited earlier for copolymers or polymer blends where intermolecular interactions lead to increases in *Tg* [3–8]. However, in plasticisation studies on poly(ethylene terephthalate) and polyacrylonitrile using low molecular weight solvents,

Table 5
q parameters from the Kwei equation for the various dye–polymer blends

Polymer	q values			
type	D1 blends	D2 blends	D3 blends	D4 blends
PHEN	59.1	–	52.3	–
PVC	47.5	–	19.8	–
PVB	–	80.0	–	38.2
PVF	67.9	95.0	34.8	47.4
EC	–	–	–	–
PVAA	41.8	102.0	26.4	47.9
CPVC	30.0	70.0	24.1	34.2
PC	20.1	–	−15.2	–
PEST	18.0	–	−17.4	–
SAN	22.4	56.0	14.2	22.1
PS	−24.7	17.0	−80.8	8.5
PPHS	–	36.0	–	7.9

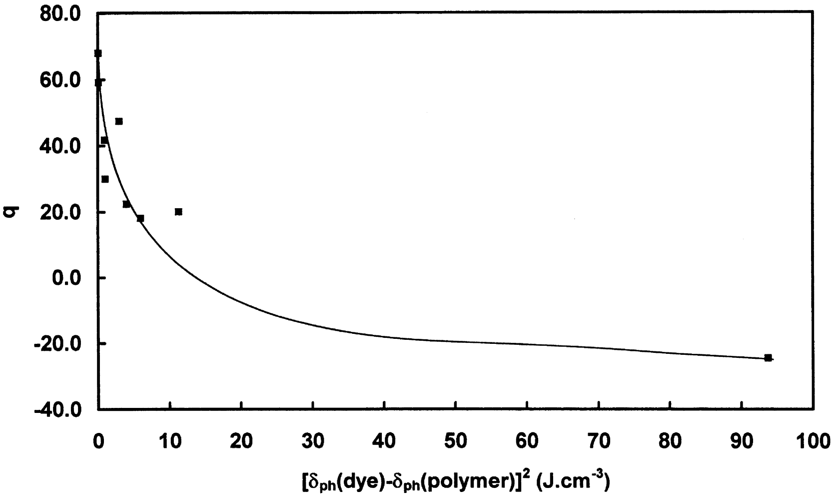

Fig. 2. The relationship between the Kwei q parameter and dye–polymer affinity for dye D1–polymer blends.

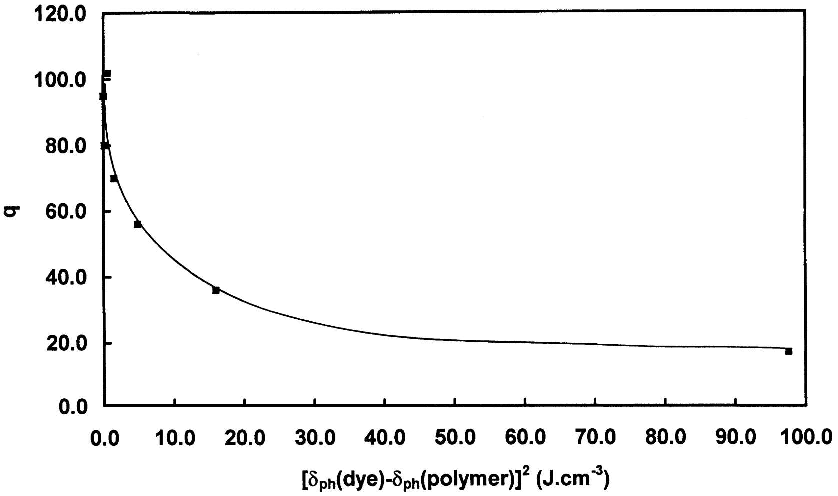

Fig. 3. The relationship between the Kwei q parameter and dye–polymer affinity for dye D2–polymer blends.

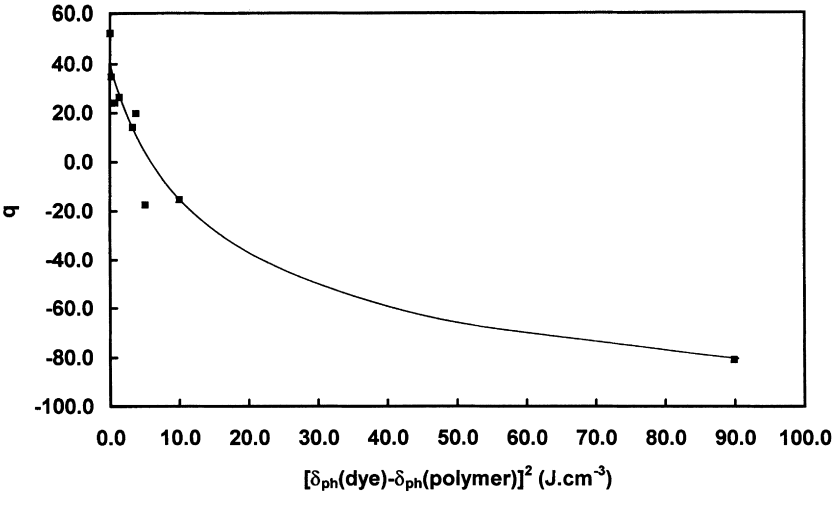

Fig. 4. The relationship between the Kwei q parameter and dye–polymer affinity for dye D3–polymer blends.

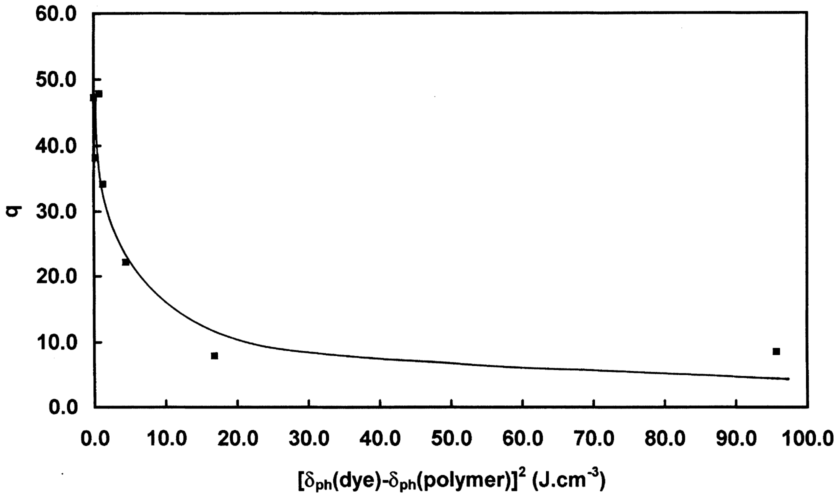

Fig. 5. The relationship between the Kwei q parameter and dye–polymer affinity for dye D4–polymer blends.

Ingamells and Yanumet [21,22] showed that matching solubility parameters and solute–polymer affinity was found to increase plasticisation and decrease the *Tg*; this is completely opposite to the trend displayed in our work reported here. The results for PET and PAN may be confused since the materials studied were semi-crystalline polymers and the effects of plasticiser on the disruption of crystallinity was not studied. Additionally, the solvents were required to diffuse into polymer films before measurements of *Tg* were made. In studies on polymer–polymer blends of poly(ethylene glycol) with cellulosic polymers, Sakellariou et al. found that only small depressions in *Tg* occur when one of the components phase separates [23,24]. Therefore, *apparently* ineffective plasticisation (i.e. relatively high *Tg*) can be obtained from blends where solute–polymer interactions are low due to phase separation resulting from the incompatibility of components. It is important to emphasise that intimate contact between solute and polymer is necessary to correctly elucidate mechanisms of interaction and the method used in our work should be highlighted. The combination of solute and polymer in a mutually good solvent followed by the kinetically rapid removal of a volatile solvent encourages molecular mixing between solute and polymer in the solid state, irrespective of solute–polymer affinity. It is believed that such a situation will lead to a more accurate description of the effects of intermolecular forces on *Tg* and supports the work of Kanig [20].

4. Conclusions

The glass transition temperatures of various dye–polymer blends have been determined and used to obtain Kwei equation q parameters for each individual dye–polymer blend. For a given dye solute, the increase in the q parameter was found to correlate well with enhanced dye–polymer affinity, with the highest q parameters being obtained as the solubility parameters of dye and polymer approached equality. This study confirms that the q parameter is a measure of the strength of intermolecular force between two components and demonstrates that the Kwei equation can be applied to a variety of solute–polymer blends.

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