Using the Solubility Parameter to Explain Disperse Dye Sorption on Polylactide

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ABSTRACT: The solubility parameters of polylactide (PLA), poly(ethylene terephthalate) (PET), and various disperse dyes calculated according to the group contribution method were used to explain the low sorption of some disperse dyes on PLA but the high sorption of the same dyes on PET. It was found that the dyes with high sorption on PLA tended to have solubility parameters near that of PLA, which has a lower solubility parameter than that of PET. It was also found that the solubility parameter, which was calculated based on cohesive energy and molar volume at 25°C, was more appropriate for explaining dyeings at lower temperature, 100 and 110°C, than those at higher temperature, 130°C. Based on the finding that dyes with solubility parameters near that of PLA tend to have high sorption on PLA, general structures for disperse dye that may have high sorption on PLA were proposed. J Appl Polym Sci 96: 416–422, 2005

Key words: solubility parameter; dyes; polyesters; polylactide; miscibility; PLA

INTRODUCTION

Polylactide (PLA) fiber is relatively new to the textile industry and is dyed with disperse dyes due to its hydrophobic structure. One potential concern with PLA is that only limited disperse dyes have good sorption on PLA at 100 or 110°C.[1–4] The advantage of good dye sorption is the decrease in dye consumption required to obtain a given shade, especially a dark shade. This results in less pollution and a lower cost of dyeing. Good dye sorption indicates that the dye has high affinity for the textile fiber and, therefore, good colorfastness. The tendency of a dye to be sorbed on a fiber partly depends on the mutual solubility of the dye molecules and the fiber, especially for disperse dyeing of polyester. Most people believe that dyeing is the dissolution of disperse dyes in a solid solvent such as polyester.[5] Therefore, the sorption ability of dyes on certain fibers can be predicted according to their solubility parameters, which have been determined for dyes, polymers, and solvents using various methods.[6–19]

The solubility parameter of a chemical characterizes the interactions between its molecules due to dispersion forces, polar forces, and hydrogen bonding. The total solubility can be expressed in terms of these components. Two chemicals tend to be mutually soluble if their solubility parameters are approximately equal. The solubility parameter can be experimentally determined and is the square root of the cohesive energy density.[20,21] The solubility parameters for polymers and small molecules have been estimated to within 10% accuracy by accounting for the contributions of each functional group and each fragment of the parent structure to the cohesive energy and molar volume of the molecule.[20,22] This method is called the group contribution method and is expressed in Eq. (1).

$$\delta = \left(\frac{\Sigma E\mathrm{coh}_i}{\Sigma V\mathrm{m}_i}\right)^{1/2} \tag{1}$$

δ is the solubility parameter of a molecule, $E\mathrm{coh}_i$ is the cohesive energy for the i functional group on the molecule, and $V\mathrm{m}_i$ is its molar volume. Cohesive energy and molar volume data given by Fedors are considered more appropriate for small molecules at 25°C.[22] The cohesive energy and molar volume data given by Van Krevelen et al. are more appropriate for polymers at 25°C.[20]

The method of using the solubility parameter to predict dye sorption has been applied to disperse dyeing on PET fiber with good correlation.[18,23–26] For each study, the solubility parameters were calculated based on data at 25 or 21°C, and the dyeings were performed at relatively low temperatures, 105°C or lower. The close proximity between the temperature

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for the calculations and the dyeing temperature probably accounted for the good agreement between the solubility parameter calculations and the actual dye sorption.

Studies have found in some cases that a disperse dye and polymer are not mutually soluble even if their solubility parameters are nearly equal.[8,28] The polymers tested in each study were PET or nylon 6,6, and various disperse dyes such as azo and anthraquinone dyes were used. The possible causes for the deviation were that the calculated solubility parameters were based on data valid at 21 or 25°C, but the dyeings were performed at relatively high temperatures, 125°C or greater. The predicted solubility in the Biedermann and Datyner study deviated from the actual solubility by 57–107%.[8] In the Gerber study, very few dyes with a solubility parameter within 5% of that of poly(ethylene terephthalate) (PET) had good sorption on PET.[27] The calculations in the study of Bommu et al.[28] were based on data that were less accurate for polymers than for dyes. The dyes that had greater than 70% sorption on PET had solubility parameters within 40% of that of PET, but eight other dyes also had solubility parameters within that range and had sorption of 40–70%.[28]

Past studies also have used the solubility parameter to successfully predict the mutual solubility of other polymers, dyes, and solvents. Good correlation was achieved probably because the solubility parameters were based on data at 25°C, and the actual dyeing conditions were also at relatively low temperatures. In general, dyes with good sorption on a polymer tend to have solubility parameters close to that of the polymer.[10,13–17,29] This method also has been used to explain the solubility of dyes in various solvents and the solubility of carriers in textile fiber.[6,11,30] As a continuation of the studies on using the solubility parameter to predict dye sorption on fiber, the goal of this research was to use the solubility parameter to explain the results of previous studies that measured the percentage sorption of disperse dyes on PLA and PET. Another objective was to use the solubility parameter to predict which existing disperse dyes may have good sorption on PLA and to suggest new disperse dye structures that could have high affinity to PLA. The solubility parameters were estimated using the group contribution method, and the cohesive energy and molar volume values were obtained from Fedors[22] for the dye solubility parameters and from Van Krevelen and Hoftyzer[20] for PLA and PET.

EXPERIMENTAL

Dyeing

Percentage sorption data for disperse dyes on PLA and PET were borrowed from three previous studies, and all dyes with published chemical constitutions in the three references were included and summarized in Figure 1. The dyeing conditions are summarized in Table I.

Solubility parameters

The solubility parameters for PLA and disperse dyes were estimated using the group contribution method according to Eq. (1). For calculating the solubility parameters of the dye molecules, the values of Ecoh and Vm for each functional group at 25°C were obtained from Fedors as shown in Table II. Using these values, the estimation of the cohesive energy and molar volume is accurate to within 10% of experimentally measured values for small molecules.[22] For PLA and PET, the values of *Ecoh* and *Vm* shown in Table III were obtained from reference 20 because they give more accurate estimates of the solubility parameter for polymers.[20] Those values are from calculations of Hayes, Small, Hoy, Hoftyzer, and Van Krevelen. An average solubility parameter was used for PLA and PET since the Ecoh and Vm values from each reference were assumed to have the same accuracy. A sample calculation of the solubility parameter is shown in Table IV for the dye C.I. Disperse Blue 3 shown in Figure 1. Solubility parameters were calculated for all disperse dyes shown in Figures 1 and 2.[31] The group contribution method is an acceptable method for estimating the solubility parameter of solvents and polymers.[22] However, this method gives more reliable values at or near 25°C.[21] The dyeing temperature was not considered in calculating the solubility parameters because values of Ecoh and Vm at those temperatures were not available.

RESULTS AND DISCUSSION

Relationship between solubility parameter and dye sorption

The solubility parameters for PLA and various disperse dye molecules were calculated based on cohesive energy and molar volume data at 25°C and were compared to their percentage sorption on PLA fabric at a temperature of 100 or 110°C. Based on Ecoh and Vm values from various sources, the average solubility parameter of PLA was 20.2 $(J/cm^3)^{0.5}$, and that of PET was 21.7 $(J/cm^3)^{0.5}$ as shown in Table V. Most of the disperse dyes that gave greater than 70% sorption had solubility parameters less than 25.0 $(J/cm^3)^{0.5}$ as shown in Table VI, and these were relatively close to that of PLA. The exception was Yellow 82, which had a solubility parameter of 24.6 $(J/cm^3)^{0.5}$. In contrast, the dyes with sorption on PLA of less than 70% had solubility parameters much greater than that of PLA. This result agrees with previous studies that have

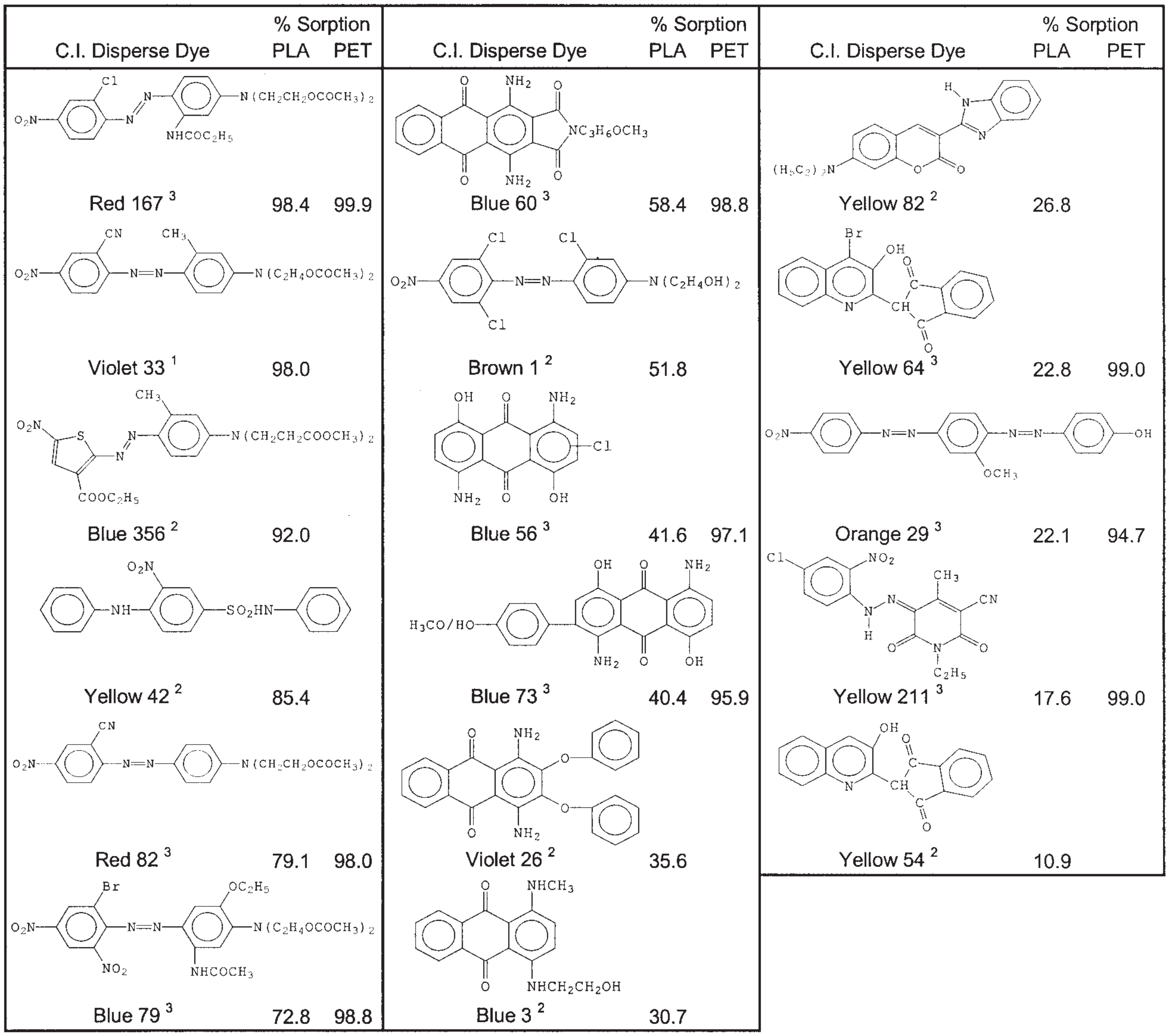

Figure 1 Chemical constitution and percentage sorption of various disperse dyes on PLA and PET.

found that dyes with high sorption on fiber have solubility parameters close to that of the polymer.[18,23–26]

The solubility parameters calculated from data at 25°C were useful for explaining dye sorption at 100 and 110°C. Among the intermolecular forces characterized by the solubility parameter, the forces that are most important for disperse dye sorption onto a polymer are the dispersion forces and the polar forces.[32] The energies due to the dipole-induced dipole forces and the induced dipole-induced dipole forces are independent of temperature, but the energy due to the dipole–dipole interactions changes with temperature.[33] The energy due to hydrogen bonding does not change much within the temperature range studied.[34] Since the intermolecular forces that are most important for disperse dye

TABLE I
Dyeing Conditions Used to Dye PLA and PET

Ref.	Dye conc., % owf	Liquor ratio	Temp for PLA (°C)	Temp for PET (°C)	pH
1	0.72	—	110	—	4–7
2	2	50:1	100	—	5
3	2	15:1	110	130	5

TABLE II
Group Contributions to the Cohesive Energy and Molar Volume Used to Estimate the Solubility Parameter for Dyes[22]

Group	*E*coh (J/mol)	*V*m (cm^3/mol)
–CH3	4707	33.5
–CH2–	4937	16.1
–CH–	3431	−1.0
C	1464	−19.2
–H2C=	4310	28.5
–CH=	4310	13.5
C=	4310	−5.5
HC≡	3849	27.4
–C≡	7071	6.5
Phenyl	31924	71.4
Phenylene (*o, m, p*)	31924	52.4
Phenyl (trisubstituted)	31924	33.4
Phenyl (tetrasubstituted)	31924	14.4
Phenyl (pentasubstituted)	31924	−4.6
Phenyl (hexasubstituted)	31924	−23.6
Ring closure 5 or more atoms	1046	16.0
Ring closure 3 or 4 atoms	3138	18.0
Conjugation in ring for each double bond	1674	−2.2
–COOH	27614	28.5
–CO2–	17991	18.0
–CO–	17364	10.8
–CONH–	33472	9.5
–NH2	12552	19.2
–NH–	8368	4.5
N	4184	−9.0
–N=	11715	5.0
–N=N–	4188	0.0
–CN	25522	24.0
NO2 (aromatic)	15355	32.0
–O–	3347	3.8
–OH	29790	10.0
–OH (disubstituted or on adjacent C atoms)	21840	13.0
S	14142	12.0
–SO–	39140	0.0
–SO4–	28451	31.6
–F	4184	18.0
–Cl	11548	24.0
–Br	15481	30.0
–I	19037	31.5

sorption on PLA do not change much within the temperature range of 25 to 110°C, it is reasonable to use the solubility parameter calculated at 25°C to explain dye sorption at 100 and 110°C. In addition, although these temperatures are above the glass transition temperature of PLA, 58°C, the dye accessible volume of PLA may not increase with temperature to the extent that all of the dyes will have high

TABLE III
Group Contributions to the Cohesive Energy and Molar Volume Used to Estimate the Solubility Parameters for Polymers[20]

	*E*coh (J/mol)				
Group	Hayes	Hoftyzer and Van Krevelen	Small	Hoy	Vm (cm^3/mol)
–CH(CH3)–	7120	10,060	7505	7039	32.7
–CH2–	4150	4190	4498	4399	16.5
p-Phenylene	23,880	25,140	29,507	33,875	61.4
–COO–	14,160	13,410	16,340	18,150	24.6

TABLE IV
Sample Calculation of the Solubility Parameter for C.I. Disperse Blue 3 Using the Group Contribution Method

Group	*E*coh (J/mol)	*V*m (cm^3/mol)
CH3 × 1	4707	33.5
CH2 × 2	9874	32.2
Phenylene (*o, m, p*) × 1	31924	52.4
Phenyl (tetrasubstituted) × 1	31924	14.4
Ring closure 5 or more atoms × 1	1046	16.0
CO × 2	34727	21.6
NH × 2	16736	9.0
OH × 1	29790	10.0
Total	160728	189.1
δ, $(J/cm^3)^{0.5}$	29.2	

sorption on PLA regardless of their solubility parameters.

The disperse dyes that were used to dye PET fiber all had at least 95% sorption, and the solubility parameters of these dyes were as high as 38.8 $(J/cm^3)^{0.5}$, which was much higher than the solubility parameter of PET. Due to the high dyeing temperature, the fiber structure was more open, which provided more accessible dye sites. In the Yang and Huda study,[3] PLA was also dyed at 130°C, and the resulting dye sorption was much higher than at 110°C. However, PLA should not be dyed at temperatures much higher than 110°C due to substantial strength loss for the fiber. The solubility

TABLE V
Estimated Solubility Parameters for PLA and PET Based on Various Sources of Cohesive Energy and Molar Volume Values

Source of *E*coh and *V*m	δ $(J/cm^3)^{0.5}$ PLA	δ $(J/cm^3)^{0.5}$ PET
Hayes	19.3	20.5
Hoftyzer and Van Krevelen	20.2	20.5
Small	20.4	22.3
Hoy	21.0	23.5
Average	20.2	21.7

parameter was less useful for explaining dye sorption on PLA and PET at 130°C than at 110°C possibly because within the temperature range 110 to 130°C, the dye accessible volume in PLA may increase with temperature substantially such that the dyes sorb more readily onto PLA and PET at 130°C than at 110°C.

Among the dyes used in the sorption studies, the dyes with the lowest solubility parameters were azo dyes that had -NHR, $-NR_2$, -CONHR, -OR, -COOR, and $-CH_3$ functional groups present on two aromatic rings bonded to the azo group, and the R groups were $(CH_2)_nCH_3$ or CH_3 as shown in Figure 1. These groups contribute lower cohesive energy and higher molar volume compared to the -OH, $-NO_2$, -CN, $-NH_2$, and halide groups, and at least one of the lower cohesive

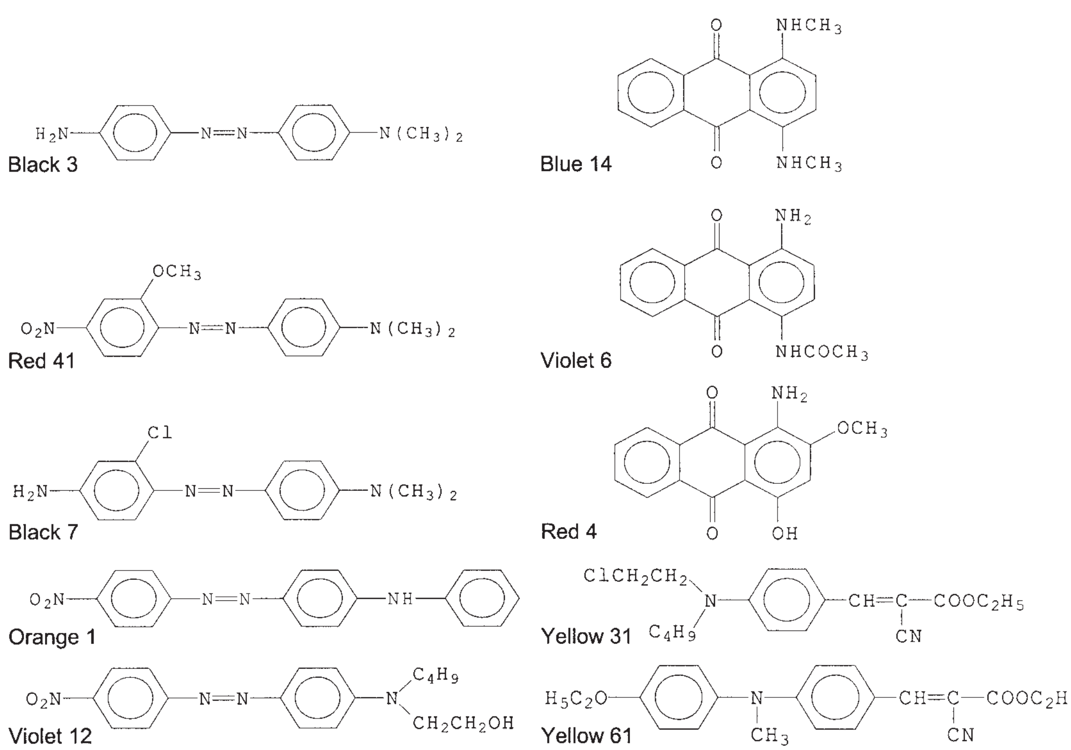

Figure 2 Chemical constitutions for some disperse dyes listed by C.I. name.

energy/higher molar volume groups is present on the molecule for each of the higher cohesive energy/lower molar volume groups. The disperse dyes with the highest solubility parameters are anthraquinone or quinoline dyes, and they also tend to have the higher cohesive energy/lower molar volume groups such as -OH, -NO_2, -CN, -NH_2, and halides as shown in Figure 1.

Solubility parameters of other existing dyes

Since the only disperse dyes with greater than 70% sorption on PLA were the dyes with solubility parameters less than 25.0 $(J/cm^3)^{0.5}$ as discussed above, other dyes with solubility parameters close to that of PLA could be selected to determine whether they may have high sorption on PLA. Examples of azo, anthraquinone, and other dyes and their functional groups are discussed below.

Azo dyes

Some examples of azo dyes with solubility parameters close to that of PLA are C.I. Disperse Black 3, Red 41, Black 7, Orange 1, and Violet 12. Their solubility parameters range from 21.9 to 25.0 $(J/cm^3)^{0.5}$ as shown in Table VII. These are mono-azo dyes with at least one -NR_2, -NHR, or -OR group substituted on the two aromatic rings for each -NH_2, -NO_2, or halide substituted on the rings as well. The R groups are -CH_3, -$(CH_2)_nCH_3$, or a phenyl.

TABLE VI
Percentage Sorption for Various Disperse Dyes on PLA and PET and Their Solubility Parameters

Dye	% Sorption PLA	% Sorption PET	δ $(J/cm^3)^{0.5}$
Red 167	98.4	99.9	24.7
Violet 33	98.0		24.1
Blue 356	92.0		23.4
Yellow 42	85.4		24.9
Red 82	79.1	98.0	24.4
Blue 79	72.8	98.8	24.9
Blue 60	58.4	98.8	29.3
Brown 1	51.8		29.2
Blue 56	41.6	97.1	38.8
Blue 73	40.4	95.9	38.2
Blue 73	40.4	95.9	33.9
Violet 26	35.6		27.7
Blue 3	30.7		29.2
Yellow 82	26.8		24.6
Yellow 64	22.8	99.0	31.3
Orange 29	22.1	94.7	26.9
Yellow 211	17.6	99.0	27.6
Yellow 54	10.9		30.8

TABLE VII
Solubility Parameters for Some Existing Disperse Dyes

Dye	δ $(J/cm^3)^{0.5}$
Black 3	21.9
Red 41	22.3
Black 7	23.7
Orange 1	24.1
Violet 12	24.1
Yellow 31	22.3
Yellow 61	22.9
Blue 14	26.4
Violet 6	30.0
Red 4	31.5

Anthraquinone dyes

The anthraquinone group with no substituents has a solubility parameter of 26.4 $(J/cm^3)^{0.5}$, and most anthraquinone dyes such as C.I. Disperse Blue 14, Violet 6, and Red 4 have solubility parameters at least as high as 26.4 $(J/cm^3)^{0.5}$ as shown in Table VII. Some of these dyes shown in Figure 2 contain the -NHR, -NHCOR, -COR, or -OR groups, but the R group is -CH_3, which is too small to give a solubility parameter below 25.0 $(J/cm^3)^{0.5}$. Also substituted on some of these dyes are the -NH_2, and -OH groups, which give a high solubility parameter.

Other dyes

Other existing disperse dyes such as C.I. Disperse Yellow 31 and Yellow 61 have solubility parameters close to that of PLA as shown in Table VII. These dyes contain the functional groups -NR_2 and -CH = on an aromatic ring as shown in Figure 2. The dyes have at least one -COOR, -OR, -CH_2-, or -CH_3 group for every -CN or halide group.

Summary of disperse dyes with solubility parameters near that of PLA

The disperse dyes with solubility parameters below 25.0 $(J/cm^3)^{0.5}$ are mainly mono-azo dyes bonded to

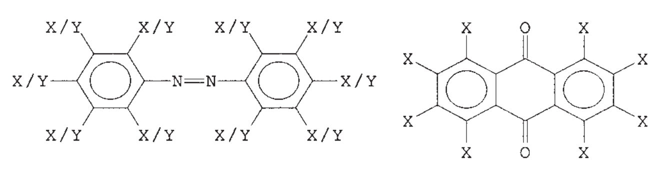

Figure 3 Chemical constitutions for mono-azo and anthraquinone disperse dyes with solubility parameters near that of PLA (*X* is -NHR, -NR_2, -NHCOR, -COR, -OR, -COOR, or a phenyl, *Y* is -NO_2 -NH_2, -OH, -CN, or a halide, *R* is -CH_3, -$(CH_2)_nCH_3$, or a phenyl, and at least one *X* group should be present for each *Y* group present).

two aromatic rings. As shown in Figure 3, at least one X group should be present on the aromatic rings for every Y group present as well. The X groups can be –NHR, $–NR_2$, -NHCOR, -COR, -OR, –COOR, or a phenyl, and the R group can be $-CH_3$, $-(CH_2)_nCH_3$, or a phenyl. The Y groups can be $-NO_2$ $-NH_2$, -OH, -CN, or a halide. Other disperse dyes that can have solubility parameters close to that of PLA are anthraquinone dyes if the only groups substituted on the anthraquinone are the X groups mentioned above and no Y groups as shown in Figure 3. The R groups on the X groups should be $-(CH_2)_4CH_3$ or longer.

Based on the dye sorption studies discussed earlier, all of the disperse dyes with solubility parameters above 25.0 $(J/cm^3)^{0.5}$ had less than 70% sorption on PLA, and therefore dyes with solubility parameters below 25.0 $(J/cm^3)^{0.5}$ should be selected to test whether they have high sorption on PLA.

CONCLUSIONS

The solubility parameter has been shown to be useful for explaining disperse dye sorption on PLA at 100 and 110°C even though the solubility parameters were calculated based on group contributions of cohesive energy and molar volume at 25°C. Among the disperse dyes tested in previous studies, the dyes with greater than 70% sorption had solubility parameters less than 25.0 $(J/cm^3)^{0.5}$, which is close to that of PLA, 20.2 $(J/cm^3)^{0.5}$.

The solubility parameter was less useful for explaining the sorption of disperse dyes on PET and PLA at higher temperatures. At a dyeing temperature of 130°C, most of the disperse dyes had good sorption on PET and PLA, regardless of the proximity of their solubility parameter to that of the polymers.

Disperse dyes with solubility parameters close to that of PLA are mainly azo dyes and other dyes that that contain more -NHR, $-NR_2$, -NHCOR, -COR, -OR, or -COOR groups than $-NO_2$ $-NH_2$, -OH, -CN, and halide groups, and the R groups are $-CH_3$, $-(CH_2)_nCH_3$, or a phenyl. This chemical constitution gives low cohesive energy and high molar volume. Most anthraquinone dyes do not have solubility parameters close to that of PLA, but they can if they contain only the functional groups with an R group, which should be a large $-(CH_2)_nCH_3$ group.

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