

Polymer Stain Resistance: Prediction Versus Experiment

Sebastien Narses, Faten Sadaka, Claire-Hélène Brachais, Jean-Pierre Couvercelle

Institute of Molecular Chemistry of the University of Burgundy ICMUB, UMR-CNRS 6302, EMMD, 9 Allée Alain Savary, BP 47870—21078 Dijon, France

Correspondence to: C.-H. Brachais (E-mail: brachais@u-bourgogne.fr)

ABSTRACT: The coloration of different polymer films (from commodity and packaging films to performance films) by contact with various food coloring substances was evaluated. For this purpose, both solubility parameters as a prediction tool, and immersion experiments for time range between 24 and 1000 h were established. The two predicting tools are the Hoy and Hoftzyer-Van Krevelen (HVK) methods. For PE and PP, HVK's method is preferred for predicting coloration. Neither of the HVK's and Hoy's methods was able to establish a coloration prediction for PET while both methods could predict the staining of PEEK. The coloration of partially and fully fluorinated polymers is well predicted by the Hoy's method. The behavior of PP/PA and PP/PA/PP multilayer films was also studied. Crystallinity degree of polymers, temperature and concentration of coloring molecules are also important parameters, which are not taken into account in solubility theories. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2891–2904, 2013

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INTRODUCTION

Over the last few years, the use of polymeric materials continues to increase especially in the domain of materials in contact with food. Plastic materials are used in packaging, cooking, cleaning, sterilization, transportation of all types of food.¹ Many properties such as low cost, processability, variability in composition, shape and size, mechanical and barrier properties make their use attractive. Several families are being used as materials for packaging food including polyolefin, polyesters, polystyrene and multilayer polymer films. Although more than 30 types of polymers are used as packaging materials, polyolefin and polyesters are the most common. The most important polyolefin grades used for food packaging are low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polypropylene (PP).² These materials have specific temperature ranges for which the integrity of the food package is maintained. Among the polyester family, polyethylene terephthalate (PET) is the grade that exhibits the largest application range for food packaging. Polyamide (PA) plays also an important role as a food packaging material and in cooking items.³ Polyetheretherketone (PEEK) is used in heat exchangers for food processing.⁴ Multilayer films are also used for food contact applications^{5–7} to combine the interesting properties of each polymer employed, like mechanical or barrier properties.

The safety of consumers has to be ensured when the food is in contact with the materials. These materials must preserve their mechanical properties, as well as their aesthetic appearance even

after exposure to food substances in the cooking atmosphere and in service use. One of the most important conditions for food contact applications is the stain resistance of plastics.

In general, food contains numerous colored substances. Food colors can be divided into three categories: natural colors,⁸ nature-identical colors⁹ and synthetic colors.⁹

- Natural colors are organic colorants extracted from natural edible sources recognized food preparation methods; for example, Curcumin (Food Additives Number: E100) and Chlorophyll (E140).
- Natural identical colors are colorants identical to colorants found in nature but manufactured by chemical synthesis; for example, β -carotene (E160a(I)) and Astaxanthin (E161j).
- Synthetic colors are produced by chemical synthesis and cannot be found in nature; for example, Patent Blue V (E131) and Indigo dye (E132).

Usually, natural colorants are the most common in food. However they present a large diversity and variety of compounds and it is therefore difficult to study the behavior of all of them in an exhaustive way. In the literature, many studies exist about the loss of food flavor through plastic packaging^{10–16} by permeation and sorption processes. Most of these studies involve the quality alteration of food during storage (see Sajilata et al.¹⁷ and Nielsen et al.¹⁸ for reviews). However, to our knowledge no study has ever investigated the sorption of colorant molecules into thermoplastic materials and/or their prediction.

Permanent coloration of the packaging by food results from chemical sorption of the colorant into the polymer matrix. The extent of this absorption is influenced by the properties of the polymer, the chemical structure of colorant molecules, and also by temperature conditions.

The loss of food flavor (including colorants) through plastic packaging occurs by (1) permeation and (2) sorption processes. The permeability coefficient (expressed in $\text{kg cm}^{-1} \text{cm}^{-2} \text{s Pa}^{-1}$) can be calculated by the relationship (1) between the diffusion coefficient and the solubility coefficient of the molecules in the polymer:

$$P = D.S \quad (1)$$

Equation (1) is applicable when D is independent of permeant concentration (C) and S follows Henry's law. Indeed S follows Henry's law when the concentration of the permeant in the membrane is directly proportional to the applied pressure:

$$P = \frac{C}{S} \quad (2)$$

The loss of volatile low molecular mass organic compounds from food into polymeric packaging materials is essentially based on a sorption mechanism. Sorption, also called scalping, describes the take-up of molecules contained in the product contents by the package material. The permeant is generally a major constituent of the desirable flavor quality.

The solubility explains how much the colorants can potentially be contained in the polymers whereas the concentration of colorants between inside and outside of the polymer is the driving force in sorption process or migration or diffusion.

To predict the coloration of polymers by coloring molecules, the solubility parameters were thus tested in this work. They also can be used for the estimation of various physicochemical parameters like the surface free energy and surface tension,¹⁹ the adhesion capacity,²⁰ the miscibility of different species,^{21,22} the permeation properties,^{13,23,24} for solvent selection and reformulation for coatings²⁵ as well as for prediction of chemical resistance,²⁶ and environmental stress cracking in polymers.²⁷

The three-dimensional Hansen solubility parameters (HSPs) of a polymer provide detailed information on the thermodynamic properties of the molecule and can provide information on the behavior of a polymer versus a solvent. On the basis of these parameters the molecular interactions with colorant substances could be estimated.

This article discusses the coloration resistance of different polymer films (from commodity and packaging films to performance films) by contact with different coloring substances. Monolayer polymeric films are used in this study, as well as multilayer polymeric materials used in packaging food industry. The first part of this work concerns the calculation of solubility parameters for coloring molecules and polymers leading to the expected absorption of the coloring molecules by polymers. The second part concerns the experimental results allowing the evaluation of the coloration resistance of polymer films after con-

tact with colorants for several exposure times. Two different methods of group contribution calculation were compared and discussed toward experimental results.

MATERIALS AND METHODS

Materials

Polychlorotrifluoroethylene film (PCTFE, Aclar UltRx 3000, 76 μm) was kindly supplied by Honeywell (Leuven, Belgium). Polyetheretherketone film (PEEK, Aptiv 1000, 25 μm) was kindly supplied by Victrex (Lancashire, UK). Fluorinated ethylene-propylene (Norton FEP FG, 125 μm), Ethylene-chlorotrifluoroethylene (Norton ECTFE, 25 μm), ethylene-tetrafluoroethylene (Norton ETFE, 125 μm), Perfluoroalkoxy (Norton PFA, 25 μm) films were kindly supplied by Saint-Gobain Performance Plastics (Rochdale Lancashire, UK). Metallocene Low Density Polyethylene film (PE, 310E, 50 μm) was purchased from DOW France (La Plaine St Denis, France). Polypropylene pellets (PP, Borclear RB707CF) were purchased from Borealis A/S (Kongens Lyngby, Denmark), and transformed into films (thickness = 50 μm) by compression at 175°C during 5 min. Polyethylene terephthalate film (PET, from an oven roasting bag) was purchased in a supermarket. Polypropylene/polyamide6 (PP/PA6, Combitherm Flex 150 PP, 115 μm) and polypropylene/polyamide6/polypropylene (PP/PA6/PP, HG 300 PP, 110 μm) multilayer films were kindly supplied by WIPAK SAS (Bousbecque, France). Structural and physical properties of polymers are given in Table I.

Ketchup, tomato concentrate, curry sauce, and blueberry jam were purchased from a supermarket. Exberry extract, elderberry extract, Paprika oleoresin and β -carotene suspension were kindly supplied by Frutarom France (Dijon, France). Curcumin (95%) from Tumeric rhizome, was purchased from Alfa Aesar (Karlsruhe, Germany). Standard vegetable oil, composed of complementary oils (grape seed oil, colza oil, sunflower oil with high oleic acid content) was purchased from a supermarket. Structural and physical properties of coloring substances are given in Table II. Pure ethanol was purchased from Sigma-Aldrich Chemical (Steinheim, Germany).



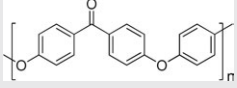
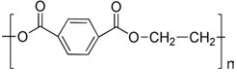


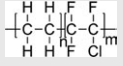
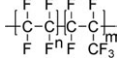
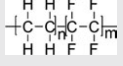
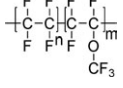
Testing Procedure

Before testing, polymer thicknesses were verified with a high precision digital micrometer. Samples of polymers were cut in squared shapes of $2 \times 2 \text{ cm}^2$. Ketchup, curry sauce, tomato concentrate, and blueberry jam were used without any dilution. Exberry, elderberry and β -carotene suspension were dissolved in water 1 : 100 (v/v). Paprika oleoresin was dissolved in the vegetable oil 1 : 100 (v/v). About 25 mL of colored substance was introduced in a 35 mL vial. Polymer film was plunged into the substance, and the vial was closed with a screw cap equipped with a Teflon® seal.

The vial was placed in a ventilated oven at 60°C. At $t = 24, 170,$ and 340 h, polymer samples were removed from the vials, washed with soapy water and thoroughly wiped with paper tissue to remove any substance excess, and their color was measured. Then the samples were put back into the vials, and the vials were replaced in the oven (until the last measurement at $t = 1000$ h).

For multilayer film, the sample was cut in a square shape of $4 \times 4 \text{ cm}^2$. The substance was poured in the vial. Then the sample was put on the rim of the vial, the latter being closed with the end cap, encircling tightly the sample. The closed vial was then

Table I. Structural and Physical Properties of Polymers

Polymer	Abbrev.	Repeating unit	Thickness (μm)	T_m (°C)	X_c (measured by DSC)	T_g (°C)
Polyethylene	PE		50	112	37%	-100
Polypropylene	PP		50	144	39%	-15
Poly-Ether-Ether-Ketone	PEEK		25	340	31%	155
Polyethylene terephthalate	PET		12	253	53%	77
Polyamide 6	PA6		Depends of the multilayer film	219	50% ²⁸	47-57 ²⁸
Poly(chlorotrifluoroethylene)	PCTFE		76	210	39%	107
Poly(ethylene-co-chlorotrifluoroethylene)	ECTFE		25	240	-	146
Poly(fluorinated ethylene-co-fluorinatedpropylene)	FEP		25	270 ^b	-	97
Poly(ethylene-co-tetrafluoroethylene)	ETFE		25	267	-	115
Poly(tetrafluoroethylene-co-perfluoromethylvinylether)	PFA		25	310	-	105

turned upside down and then placed in an oven at 60°C. The measurement was performed only after 1 week. Cleaning procedure of the sample is the same as described above. Multilayer samples were tested twice: one for each side of the film.

Determination of Coloration Resistance

Color of tested samples was determined with a Konica Minolta CR400 colorimeter. Because the majority of the samples are transparent or translucent, all the measurements were done on the calibration plate ($Y = 93.8$, $x = 0.3156$, $y = 0.3319$ under a D_{65} daylight simulating illuminant). Measurements were recorded three times for each sample in the L , a , b color space.

The coloration resistance of a given sample is determined by the parameter ΔE :

$$\Delta E = \sqrt{(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2} \text{ (in arbitrary unit)} \quad (3)$$

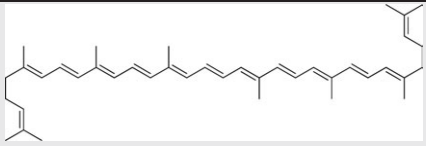
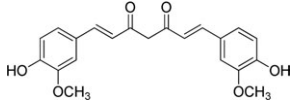
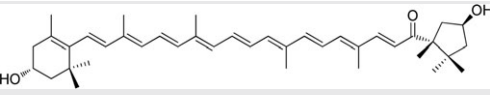
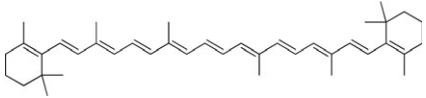
The precision on calculation of ΔE is ± 0.24 .

With L_1 , a_1 , b_1 and L_2 , a_2 , b_2 the values in the L , a , b color space of a virgin sample and a tested sample, respectively. It is generally considered that no color difference can be seen when $\Delta E < 5$.^{29,30}

Thermal Properties

Differential scanning calorimeter (DSC) was carried out with a DSC Q1000 thermal analyzer. The instrument was calibrated using indium standard. Measurements were performed under nitrogen, with a sample mass of 10 ± 3 mg, heated with a

Table II. Structural and Physical Properties of Coloring Substances

Name		Molecular structure	Formula	M (g mol ⁻¹)	Density	Molar volume (mL mol ⁻¹)
Lycopene	Ketchup, Tomato concentrate		C ₄₀ H ₅₆	536	0.89	602.25
Curcumin	Sauce curry		C ₂₁ H ₂₀ O ₆	368	1.351	272.39
Capsanthin	paprika oleoresin		C ₄₀ H ₅₆ O ₃	584.87	1.012	577.93
β-carotene			C ₄₀ H ₅₆	536.87	1	536.87

heating rate of 20°C min⁻¹ from -80 to 50°C above the melting point for semicrystalline polymers and 50°C above the glass transition for amorphous polymers.

Prediction of Coloration Resistance

The concept of solubility parameter (δ or δ_t) was first introduced by Hildebrand and Scott,³¹ who proposed that materials with similar δ values are miscible. They identified a correlation between the cohesive energy density (CED) and mutual solubility. For a small molecule, the solubility parameter δ was defined as the square root of the CED (CED being the energy of vaporization per molar volume).

$$\delta = (\text{CED})^{1/2} = \left(\frac{\Delta E}{V_m} \right)^{1/2} \quad (4)$$

The cohesive energy used to estimate the CED, and consequently the solubility parameter, is the energy of all intermolecular interactions in a mole, thus the energy needed to break all interactions during vaporization of the liquid.

As defined by Hildebrand and Scott, the solubility parameter is often not sufficient to provide a good evaluation of mutual solubility. Thus, Hansen developed a new concept involving three dimensional parameters (or Hansen solubility parameters, HSP).³² According to this concept, the Hildebrand solubility parameter of a compound can be divided into three parameters related to dispersion forces δ_d , polar interactions δ_p , and hydrogen bonding δ_h .^{32,33}

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (5)$$

As the evaluation of solubility parameter by direct measurement of CED is not possible for all chemicals (except for small vaporiz-

able molecules like solvents) empirical methods exist to estimate the solubility parameter of higher molecules. The sets of group constants attributed to each chemical function and provided by Hoy and Hoftzyer-Van Krevelen (HVK) seem to be the most widely used and comprehensive lists.^{34,35}

Method of Hoftzyer and Van Krevelen (HVK)

The HVK group contribution method is traditionally used to calculate the HSP for solvents but can also be applied to polymers on the basis of their repetitive chemical unit formula (the polymer chain length does not need to be known).^{34,36} The solubility parameter components may be predicted from group contributions using the following equation:

$$\delta_d = \frac{\sum F_{di}}{V_m} \quad \delta_p = \sqrt{\frac{\sum F_{pi}^2}{V_m}} \quad \delta_h = \sqrt{\frac{\sum F_{hi}}{V_m}} \quad (6)$$

where F_d is the dispersion component of the molar attraction constant, F_p is the polarity component, and F_h is the hydrogen bonding energy. According to HVK, the polar component is further reduced, if two identical polar groups are present in a symmetrical position. To take this effect into account, the value of δ_p must be multiplied by a symmetry factor. For example, the symmetry factor is 0.5 for one plane of symmetry as in PTFE.

Method of Hoy (HOY)

The Hoy's method is an alternative technique to calculate HSP but is more complex than HVK's method. The system of equation to be used contains four additive molar functions and auxiliary equations which all lead to the final expression of δ_t and its components (δ_d , δ_p , and δ_h).³⁴ Detailed equations are presented in

Table III. The Equations of Hoy's System (1985)³⁴

Formulae	Low-molecular weight liquids (solvents)	Amorphous polymers
Additive molar functions	$F_t = \sum N_i F_{t,i}$ $F_p = \sum N_i F_{p,i}$ $V = \sum N_i V_i$ $\Delta_t = \sum N_i \Delta_{t,i}$	$F_t = \sum N_i F_{t,i}$ $F_p = \sum N_i F_{p,i}$ $V = \sum N_i V_i$ $\Delta_t^{(p)} = \sum N_i \Delta_{t,i}^{(p)}$
Auxiliary equations	$\log \alpha = 3.39 \left(\frac{T_b}{T_{cr}} \right) - 0.1585 - \log V$ $T_b = \text{boiling point}; T_{cr} = \text{critical temperature}$ $\left(\frac{T_b}{T_{cr}} \right) = 0.567 + \Delta_t - (\Delta_t)^2$ (Lydersen equation)	$\alpha^{(p)} = \frac{777 \Delta_t^{(p)}}{V}$ $\bar{n} = \frac{0.5}{\Delta_t^{(p)}}$
Expressions for δ_t and δ components	$\delta_t = \frac{F_t + B}{V}$ $B = 277$ $\delta_p = \delta_t \left(\frac{1}{\alpha} \frac{F_p}{F_t + B} \right)^{1/2}$ $\delta_h = \delta_t \left(\frac{\alpha - 1}{\alpha} \right)^{1/2}$ $\delta_d = (\delta_t^2 - \delta_p^2 - \delta_h^2)^{1/2}$	$\delta_t = \frac{F_t + B/\bar{n}}{V}$ $\delta_p = \delta_t \left(\frac{1}{\alpha} \frac{F_p}{F_t + B} \right)^{1/2}$ $\delta_h = \delta_t \left(\frac{\alpha^{(p)} - 1}{\alpha^{(p)}} \right)^{1/2}$ $\delta_d = (\delta_t^2 - \delta_p^2 - \delta_h^2)^{1/2}$

F_t is the total molar attraction function and F_p is the polar component; V is the molar volume of the solvent molecule or the structural unit of the polymer. ΔT is the Lydersen correction for nonideality, used in the auxiliary equations. α is the molecular aggregation number, describing the association of the molecules; \bar{n} is the number of repeating units per effective chain segment of the polymer.

Table III. For coloring molecules, the equations for low-molecular weight liquids were employed. Hansen solubility parameters of polymers and coloring molecules have been calculated by the two different algorithmic methods and the gap between the δ_t values are given in Table IV. The evaluation was applied to all the compounds used in our work except for the anthocyanins family (contained in blueberry jam and exberry and elderberry extracts). Indeed, up to 600 different molecules in the family of anthocyanins have been reported.^{37,38} They are all based on the same basic core structure, the flavylium ion, and they are known to be responsible for the purple, blue, and red colors found in many flowers, fruits and vegetables (Table V). As the three products used in this study (Blueberry Jam, "Elderberry," "Exberry") contain many different anthocyanins, the prediction of polymers coloration resistance to these products is not possible.

According to Van Krevelen,³⁵ averaging δ_t results obtained from the two methods (HVK and Hoy) can be regarded as representative of the solubility parameter values of a molecule. In this study, the results of δ_t calculated with both methods for the colorants and the five first polymers presented (PE, PP, PET, PEEK, PA6) are of the same order of accuracy ($\pm 15\%$). However, for other polymers and molecules studied, δ_t values can show a major difference between the two methods. A clear example is FEP, for which δ_t values calculated using HVK's method is 15.91 while Hoy's method gives a value four times higher (68.73). The gap between the values of δ_t is so high that averaging would be unnatural. Furthermore, when considering each Hansen parameters, the δ_{db} , δ_p and δ_h values are often totally different even for polymers or molecule presenting a similar δ_t . An example is β -carotene, for which δ_h values calculated by HVK and HOY methods are 0.00 and 10.88, respectively, and δ_p values are 0.00 and 7.98, respectively. For this reason, in this study the Van Krevelen statement mentioned earlier was not applied and the three Hansen parameters calculated from both methods were considered and compared without any averaging.

The evaluation of compatibility (miscibility) of two organic materials A and B is calculated⁴⁶ as:

$$\overline{\Delta\delta} = \sqrt{(\delta_{pol} - \delta_{mol})_d^2 + (\delta_{pol} - \delta_{mol})_p^2 + (\delta_{pol} - \delta_{mol})_h^2} \quad (7)$$

A good solubility is typically reached when $\Delta\delta$ is below 5 J^{1/2}/cm^{3/2}. Applied to coloring molecules, it can be assessed that a low coloration resistance should occur for these low values. The smaller the value, the better the solubility of the colorant into the polymer, and thus the lower the coloration resistance of the material. The results of $\Delta\delta$ calculations are given in Table VI.

Concerning the prediction of the polymer coloration resistance, a high ΔE value measured, thus a low coloration resistance, should correspond to a low $\Delta\delta$ value calculated, and inversely. There is sometimes a remarkable difference between $\Delta\delta$ values calculated from both methods. For example, according to HVK method PE will be colored by β -carotene, however according to Hoy's method this is very unlikely to occur. In the next part of this work, measured colorations and predictions will be discussed by family of polymers towards the following coloration criteria:

- when ΔE is below 5, the coloration resistance is high, and the staining is imperceptible for human eye.
- when ΔE is between 5 and 15, a weak coloration can slightly be perceived.
- when ΔE is above 15, the coloration resistance is low.

It was also checked that none of the polymers studied were colored by an eventual thermal degradation (yellowing or browning) even after 1000 h at 60°C.

RESULTS AND DISCUSSION

Polyolefins

Polyethylene (PE) and polypropylene (PP) are the most widely used plastics in food packaging. These materials were studied

Table IV. Solubility Parameters Components Calculated According to HVK and HOY Methods

	Method	δ_d	δ_p	δ_h	δ_t	δ_t gap values
Lycopene	HVK	15.67	0.00	0.00	15.67	2.63
	HOY	10.76	7.11	12.97	18.30	
Curcumin	HVK	18.76	5.20	13.55	23.28	0.47
	HOY	14.35	12.18	11.82	22.23	
Capsanthin	HVK	16.51	1.81	8.52	18.67	0.69
	HOY	21.53	16.15	24.02	19.36	
β -carotene	HVK	17.55	0.00	0.00	17.55	0.07
	HOY	11.34	7.98	10.88	17.62	
PE	HVK	17.72	0.00	0.00	17.72	0.29
	HOY	18.01	0.00	0.46	18.01	
PP	HVK	16.45	0.00	0.00	16.45	0.24
	HOY	15.91	0.00	5.06	16.69	
PET	HVK	19.00	5.15	10.14	22.15	1.01
	HOY	15.98	12.83	11.99	23.74	
PEEK	HVK	19.71	4.47	6.06	21.10	2.75
	HOY	18.30	10.58	13.01	24.82	
PA6	HVK	18.65	8.25	7.25	21.65	2.60
	HOY	17.39	12.71	11.14	24.25	
FEP	HVK	15.91	0.00	0.00	15.91	52.82
	HOY	52.78	15.81	41.10	68.73	
PFA	HVK	15.76	3.23	4.92	16.83	50.45
	HOY	50.58	17.21	40.88	67.28	
ETFE	HVK	16.96	0.00	0.00	16.96	31.73
	HOY	39.84	10.53	13.56	43.38	
ECTFE	HVK	17.56	6.39	2.16	18.81	21.97
	HOY	31.38	12.86	22.66	40.78	
PCTFE	HVK	17.57	9.96	2.69	20.38	32.16
	HOY	37.08	16.61	33.12	52.42	

$\delta_{h,d,p,t}$ unit is $J^{1/2}/cm^{3/2}$.

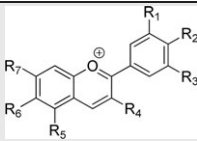
despite their low resistance to coloration,⁴⁷ Indeed the identification of their behavior in presence of coloring molecules allows the establishment of a basis for comparison with more technical polymers. PE and PP both have a combination of properties including flexibility, strength, lightness, stability, moisture and chemical resistance, easy processability, and are well suited for recycling and reuse.⁴⁸

Figure 1 shows the ΔE values measured for PP in contact with the coloring substances up to 1000h (PE shows exactly the same behavior). These polymers had very low coloration resistance when they were in contact with β -carotene (maximum ΔE values for PE and PP were 96.9 and 83.9, respectively). A low coloration resistance was identified when polyolefins were in contact with lycopene from both tomato concentrate and ketchup. ΔE values remained low when PE and PP were in contact with capsanthin from paprika oleoresin and curcumin from curry sauce. Concerning anthocyanins, ΔE values were very low when polyolefins were in contact with the three substances studied (Blueberry Jam, Eldeberry and Exberry).

Lycopene and β -carotene, for which polyolefins have a low coloration resistance, present apolar structures (Table I) as well as PE and PP (Table II). These molecular similarities facilitate the sorption of coloring molecules into the polymer matrix, following the general rule "like dissolves like." Furthermore, the β -carotene solution presents the highest concentration in coloring molecule compared to other substances. This can explain the very low coloration resistance observed for the two polyolefins. Moreover, Caner describes in a recent review⁴⁹ that the substance composition in which the coloring molecule is dissolved plays an important role. For example, polar molecules in fatty foods are expected to move to polar packaging materials such as nylons. Reversely, as in the β -carotene solution studied, the apolar molecule is emulsified in an aqueous continuous phase, the β -carotene molecules can easily be scalped by the apolar polyolefins.

A decrease in ΔE values is observed in presence of this molecule after 340 h of test. The decline observed in the polyolefins coloration after 340 h is due to its thermal degradation under

Table V. Chemical Structures of Principal Anthocyanin and Their Plant Sources³⁸

Anthocyanin	Chemical structure	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	Main color	Plant sources
Apigeninidin		—H	—OH	—H	—H	—OH	—H	—OH	Orange	Ephedra frustillata, Soybean
Aurantidin		—H	—OH	—H	—OH	—OH	—OH	—OH	Orange	Balsaminaceae, in cultivars from genus <i>Alstroemeria</i> ³⁹
Cyanidin		—OH	—OH	—H	—OH	—OH	—H	—OH	Bluish-red	Apple, blackberry, elderberry, peach, pear, fig, cherry, onion, gooseberry, red cabbage, rhubarb
Delphinidin		—OH	—OH	—OH	—OH	—OH	—H	—OH	Magenta	Passion fruit, eggplant, green bean, pomegranate
Europinidin		—OCH ₃	—OH	—OH	—OH	—OCH ₃	—H	—OH	Purple, blue	Plumbago, <i>Ceratostigma</i> ⁴⁰
Hirsutidin		—OCH ₃	—OH	—OCH ₃	—OH	—OH	—H	—OCH ₃	Bluish-red	<i>Catharanthus roseus</i> ⁴¹
Luteolinidin		—OH	—OH	—H	—H	—OH	—H	—OH	Orange	<i>Sorghum bicolor</i> ⁴²
Pelargonidin		—H	—OH	—H	—OH	—OH	—H	—OH	Orange, salmon	Strawberry, banana, red radish, potato
Malvidin		—OCH ₃	—OH	—OCH ₃	—OH	—OH	—H	—OH	Purple	Primula,
Peonidin		—OCH ₃	—OH	—H	—OH	—OH	—H	—OH	Magenta	Peony ⁴³
Petunidin		—OH	—OH	—OCH ₃	—OH	—OH	—H	—OH	Purple	Petunia ⁴⁴
Pulchellidin		—OH	—OH	—OH	—OH	—OCH ₃	—H	—OH	Bluish-red	<i>Plumbago pulchella</i> ⁴⁵
Rosinidin		—OCH ₃	—OH	—H	—OH	—OH	—H	—OCH ₃	Red	<i>Catharanthus roseus</i> , <i>Primula rosea</i>

operating conditions. Indeed, at the end of the experiment the β -carotene emulsion turned from an intense orange color to pale yellow. These results are in accordance with a recent study⁵⁰ showing the stability of β -carotene emulsions when exposed to a temperature of 55°C for 15 days.

The low coloration resistance of PE and PP to lycopene contained in tomato concentrate and ketchup also shows the importance of concentration. Indeed, ketchup and tomato concentrate share the same main coloring molecule and thus the same solubility parameters, however a difference in coloration is observed. This is attributable to the difference in lycopene concentration in these substances.

The coloration resistance of polyolefins to curcumin and capsanthin was high ($\Delta E < 8$). This can be explained by the presence of methoxy and/or hydroxyl groups in their formulas making these molecules polar, in contrary to polyolefins. The rule “like dissolve like” is not verified and thus coloration resistance is high. Likewise, PE and PP show a high coloration resistance to anthocyanins. The difference in molecular formulas between polyolefins and these molecules is obvious and could explain the limited sorption of anthocyanins by polyolefins.

Concerning the predictions for PE (Table VI), on one hand, $\Delta\delta$ values are low for β -carotene/PE and lycopene/PE systems calculated with HVK’s method (0.17 and 2.05, respectively) meaning an expected low coloration resistance of PE. On the other

hand, $\Delta\delta$ values obtained with Hoy’s method are high (16.64 and 18.26, respectively) meaning that a high coloration resistance is expected. As experiments reveal a low coloration resistance of PE for these two molecules, HVK’s method is preferred for predicting coloration. $\Delta\delta$ values calculated for curcumin/PE and capsanthin/PE systems are well above 5 for both methods meaning a high coloration resistance of PE expected. As PE shows a high coloration resistance when tested in presence of these two molecules, both methods can be stated as accurate. However, based on the calculations for β -carotene and lycopene, it can be assessed that HVK method fits best with experimental results than Hoy’s method. This finding is confirmed by the results obtained for PP.

Polyester and Polyketone

In opposition to standard commodity polymers such as polyolefins, PEEK and PET were studied to illustrate the engineering and high performance polymers family. PEEK is known for exhibiting superb chemical resistance, toughness, rigidity, thermal stability, radiation resistance, and very low flammability. This polymer can be processed readily by injection molding, spinning, cold forming, and extrusion.⁵¹ Until now, PEEK was not used in food packaging because of its expensive price comparatively to other polymers. However, this polymer has some special properties which make its use possible, especially its high thermal resistance.

Table VI. $\overline{\Delta\delta}$ Values (in $J^{1/2}/cm^{3/2}$) for Polymer/Molecule Systems Studied

	Method	Lycopene	Curcumin	Capsanthin	β -carotene
PE	HVK	2.05	13.84	8.79	0.17
	HOY	18.26	17.37	30.55	16.64
PP	HVK	0.78	13.99	8.71	1.10
	Hoy	13.86	14.74	27.43	12.61
PEEK	HVK	8.55	7.78	4.83	7.83
	Hoy	10.21	7.91	10.70	10.23
PET	HVK	11.85	4.26	4.47	11.46
	Hoy	9.34	0.89	16.68	7.60
PCTFE	HVK	10.49	13.17	10.08	10.32
	Hoy	35.37	31.69	15.66	35.59
ECTFE	HVK	7.00	12.06	7.91	6.75
	Hoy	24.79	20.28	9.21	24.56
ETFE	HVK	2.33	13.82	8.84	0.45
	Hoy	34.63	30.15	18.57	34.38
FEP	HVK	0.24	14.09	8.73	1.64
	Hoy	52.27	48.52	33.23	52.46
PFA	HVK	5.89	9.16	3.94	6.15
	Hoy	50.57	46.77	31.19	50.77
PA6	HVK	11.38	8.46	6.90	11.04
	Hoy	10.69	2.69	16.05	9.01

Polyesters, such as polybutadiene terephthalate (PBT) and polyethylene naphthalate (PEN) are widely used in technical materials for example in electrical applications. Polyethylene terephthalate (PET) is the most commonly used polyester in food packaging. These materials show a significant heat resistance compare to commodity polymers and, when oriented, exhibit a very high mechanical strength.⁵² PET can tolerate high temperatures, such as in boil-in-bag pouches,⁵³ and recently in oven bags or oven-proof trays.⁵⁴ Moreover, due to its semi-crystalline structure, this polymer shows attractive barrier properties, especially towards odors and flavors.⁵⁵ In addition, due to its physico-chemical properties, such as rigidity and glass-like transparency, as well significant chemical inertness, PET is widely used in

food packaging applications, beverages and drinking water domains being typical examples.

As shown in Figure 2, whatever the nature of the coloring molecule, PEEK shows high coloration resistance. Indeed, ΔE values never exceed 5 except for PEEK films exposed to β -carotene for which maximum ΔE value is 12.9. As for polyolefins, this behavior can also be explained by the high β -carotene concentration in the substance studied.

However, the low sorption of the other molecules can be explained by the PEEK structure. This polymer exhibits a high crystalline rate ($X_c \approx 31\%$) as well as a high T_g detected around 155°C . At the temperature of the coloring test (60°C),

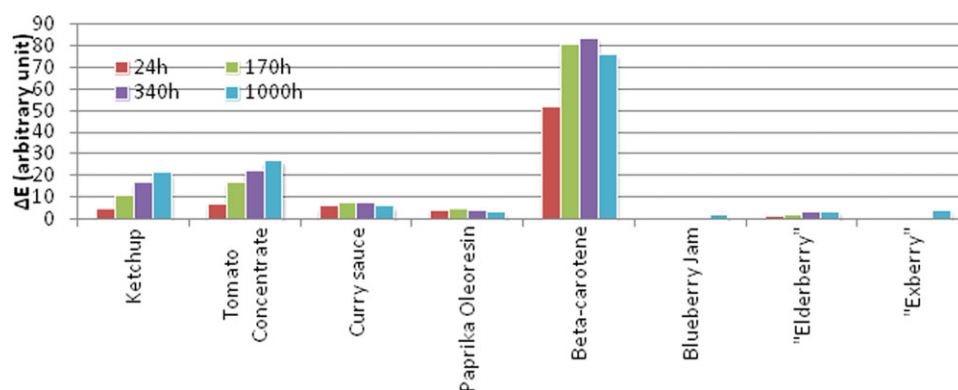


Figure 1. ΔE values measured for PP in contact with studied substances at 60°C . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

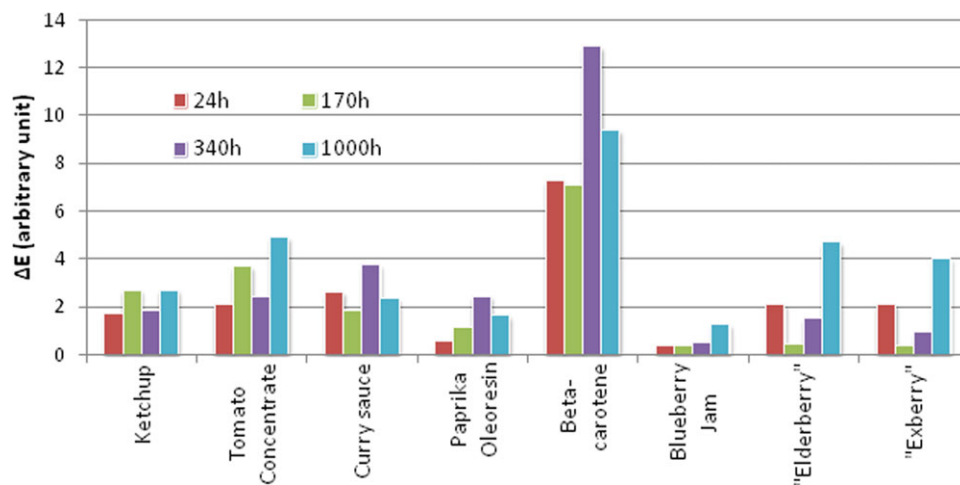


Figure 2. ΔE values for PEEK in contact with selected substances at 60°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

amorphous areas of PEEK exhibit a high stiffness. The combination of these structural properties makes the PEEK matrix very resistant to the sorption of colored molecules at this temperature.

Concerning the predictions of PEEK coloration obtained from HVK's method, the $\Delta\delta$ values are just around or above 5 for all cases (Table VI), meaning that a high coloration resistance of the polymer is expected. Furthermore, the predictions obtained by Hoy's method are in accordance with those obtained by HVK's method since $\Delta\delta$ values are above 5 for all molecule/PEEK systems studied. The experimental results are thus in accordance with the high $\Delta\delta$ values calculated by both methods.

As for PEEK, PET shows a high coloration resistance to all coloring substances, as stated in Figure 3. ΔE values exceed 5 only when PET is in contact with β -carotene (as previously, because of the high concentration of this molecule), curcumin from curry sauce and anthocyanins from Elderberry. Chemical structure of curcumin (Table I) and PET (Table II) are very close which can explain the weak resistance to coloration observed.

However, the chain rigidity of PET at testing temperature ($T_g \approx 77^\circ\text{C}$) associated with the high degree of crystallinity (53%) of the polymer, avoids an intense sorption of the various coloring molecules. Concerning Elderberry, because the exact nature of the molecules present in the substance is not known, the results cannot be fully explained. All the anthocyanins have an aromatic radical structure completed by polar groups. This structure is similar to PET and therefore can explain the sorption of anthocyanins in the PET matrix. However, it is quite difficult to explain why Elderberry induces a lower coloration resistance than other substances also containing anthocyanins.

The calculation by Hoy's method (Table VI) predicts a good compatibility between PET and curcumin since $\Delta\delta$ value is equal to 0.89. This is in accordance with their structural similarities. However, such a low value of $\Delta\delta$, should foretell a very low coloration resistance which is not experimentally observed. Given the calculated values from Table VI obtained for curcumin and other molecules (lycopene, β -carotene and capsanthin), none of the HVK's and Hoy's methods is able to establish a coloration prediction for PET.

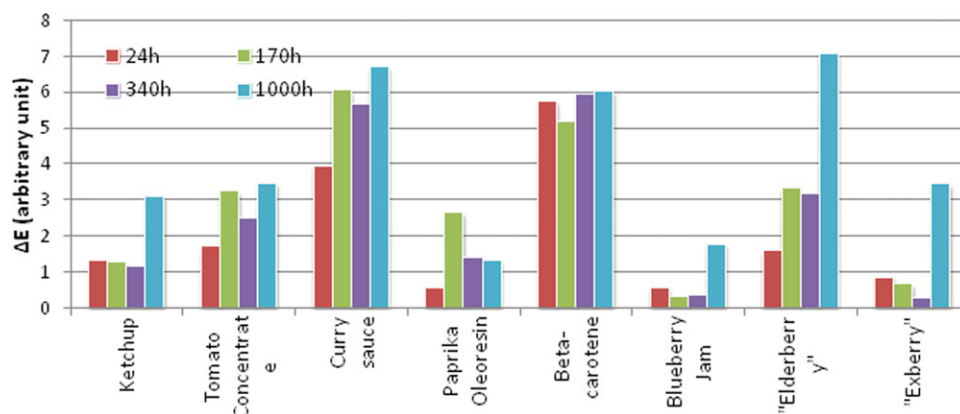


Figure 3. ΔE values for PET in contact with substances containing identified molecules at 60°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

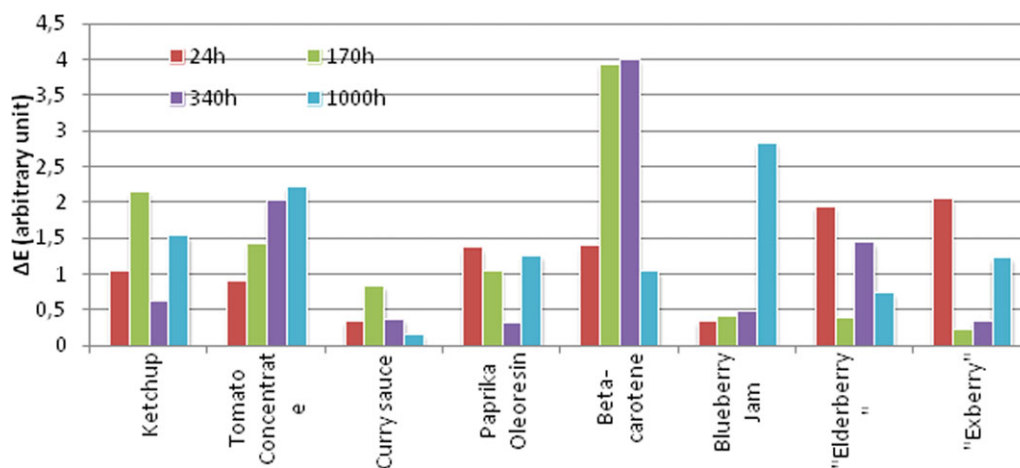


Figure 4. ΔE values for PCTFE in contact with substances containing identified molecules at 60°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Partially Fluorinated Polymers

Fluorinated polymers represent the most versatile and important group of thermoplastics which are involved in many areas of technology as in the chemical process industries such as piping and pumps in harsh environments,⁵⁶ or lining in tubes when steel and iron are corroded by the chemical products.⁵⁷ The strong C—F bonds are responsible for their ability to crystallize as well as for their increased thermal and chemical stability. Among this family, PCTFE is a material showing high performance barrier properties for the pharmaceutical and medical markets. ECTFE is a copolymer exhibiting useful properties for a wide range of temperatures, from cryogenic temperatures up to 180°C, while ETFE offers resistance to chemicals and weathering, low flammability and stress-crack resistance. Concerning the structure of the repetition units, ECTFE is an alternated 1 : 1 copolymer of Ethylene and chlorotrifluoroethylene,⁵⁷ the latter being the monomer used for manufacturing PCTFE. ETFE can be considered equivalent to a poly(vinylidene fluoride) that has a head to head, tail to tail structure.

Values reported in Figure 4 demonstrate that PCTFE films are color resistant, whatever the chemical nature and concentration of coloring substances. Indeed ΔE values are always below 5, even for highly concentrated molecules such as β -carotene. As PEEK, PCTFE exhibits a high glass transition temperature ($T_g \approx 128^\circ\text{C}$) and a high degree of crystallinity ($X_c \approx 39\%$) which both prevent coloration of the films at 60°C. Furthermore, the presence of fluorine atoms in the structure of PCTFE makes this polymer inert and also very repellent to chemicals, including coloring molecules.

Calculated $\Delta\delta$ values are high for both methods of coloring predictions. As an example, the $\Delta\delta$ values obtained for the lycopene/PCTFE system are 10.5 and 35.4 for HVK and Hoy's method, respectively.

ECTFE and ETFE films show exactly the same behavior as PCTFE films. ΔE values always remain below 5. As for PCTFE, the chemical and temperature resistance of these materials is attributed to the presence of fluorine atoms in their constitu-

tional base units. However, these two fluorinated copolymers also contain an ethylene pattern in their repeating unit. The presence of the latter in the repeating unit does not seem to increase sorption of coloring molecules as observed for PE homopolymer films.

The $\Delta\delta$ values calculated for both ECTFE and ETFE are generally slightly lower than the ones calculated for PCTFE. However, these values are still high enough, especially those obtained from the Hoy's method, to predict that coloration of partially fluorinated materials will not occur.

Fully Fluorinated Polymers

FEP and PFA general properties are quite similar to those of the partially fluorinated polymers group. These fully fluorinated polymers are translucent, flexible, and chemically inert, and offer many of the performance properties of PTFE, with the advantage of being able to provide thermoformed and heat-sealed products. FEP and PFA withstands temperatures up to 200°C and may be sterilized by all chemical and thermal known methods.⁵⁶ PFA exhibit particular good heat resistance from -200°C up to near 260°C.

FEP and PFA showed exceptional coloration resistance of all coloring substances (Figure 5). All ΔE values are below 5 for the various coloring substances studied. Furthermore, these values were even lower than the ΔE values obtain for partially fluorinated polymers. The saturation of the polymer chain by fluorine atoms (no hydrogen or chlorine atoms in the repeating unit) provides to these polymers exceptional stability and chemical resistance.

Concerning coloration prediction of these polymers, $\Delta\delta$ values calculated with HVKs method are low and incoherent comparing to the experimental observations, whereas calculation by Hoy's method leads to very high $\Delta\delta$ values, in agreement with the very high coloration resistance observed.

Regarding fully fluorinated and partially fluorinated polymers, Hoy's method should thus be preferred for predicting coloration of fluorinated polymers.

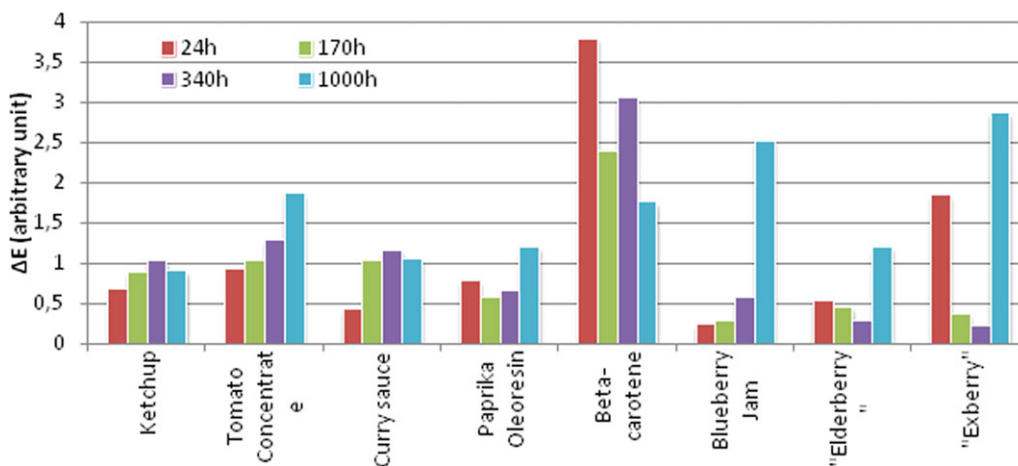


Figure 5. ΔE values for FEP in contact with substances containing identified molecules at 60°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Multilayer Films

In the field of packaging, plastic materials can be manufactured either as a single film or as a combination of different polymer layers. Combining materials results in the addition of properties from each individual material and often reduces the total amount of material required.⁴⁸ Two kinds of multilayer films, currently in use for food packaging at ambient or lower temperatures, are presented in this work. The first one is a bilayer film composed of PP and PA6. The second is composed of a PA6 layer sandwiched between two layers of PP.

As plotted in Figure 6, whatever the coloring substance used for the experiment, the ΔE values for the PP/PA6 bilayer film are far above 5, except in the case of paprika oleoresin showing a very low coloration resistance. In the presence of lycopene (from ketchup and tomato concentrate) and β -carotene, the low coloration resistance observed can be explained by the affinity of the PP layer toward these two molecules. Indeed, PP homopolymer is very sensitive to coloration by lycopene and β -carotene as stated before (Figure 1). In the presence of curcumin from curry sauce, as PP shows high coloration resistance to this

molecule (Figure 1), the low coloration resistance of the multilayer film is attributed to the PA6 layer. This interpretation is based on the polar character of curcumin and PA6. Indeed, both contain highly polar groups such as hydroxyl groups for curcumin, and amide function ($-\text{CONH}-$) for PA6. Furthermore, the T_g of PA6 is situated at about 40°C.⁵⁸ The PA6 layer exhibits a rubber-like state and the sorption of curcumin is increased. The PP/PA6 multilayer film also shows a low coloration resistance in presence of the three substances containing anthocyanins. As PP is resistant to coloration by these substances (Figure 1), the PA6 layer of the bilayer film seems to be responsible for the coloration by anthocyanins.

As this experimental procedure does not reveal which of the layers is affected by the coloration a new procedure of testing with only one side of the film in contact with the substance was developed.

ΔE values measured for the PP/PA6 film reveal that the PA6 layer shows a lower coloration resistance than PP for all the coloring molecules studied (Table VII), except for paprika

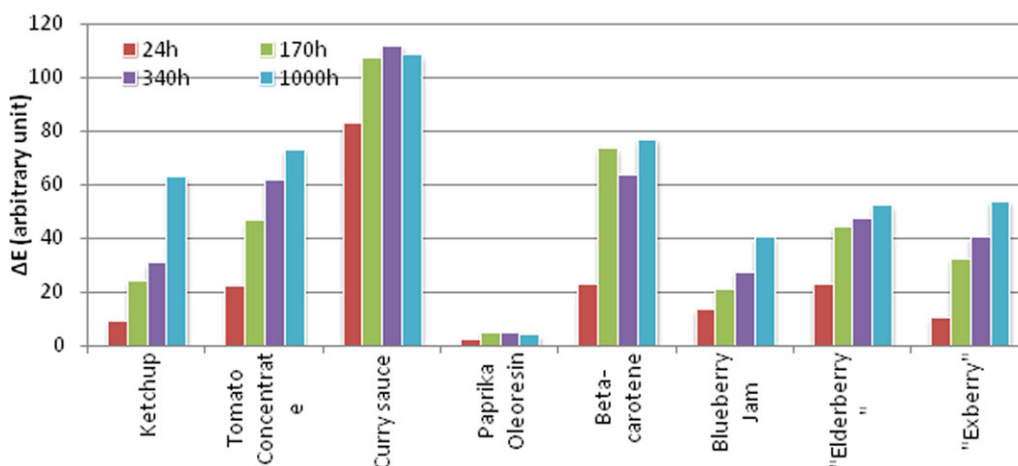


Figure 6. ΔE values for PP/PA6 multilayer film in immersed contact with selected substances at 60°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table VII. Comparison of ΔE Values for Multilayer Films when Immersed and when in Contact on One Side Only (PP/PA6 and PP/PA6/PP)

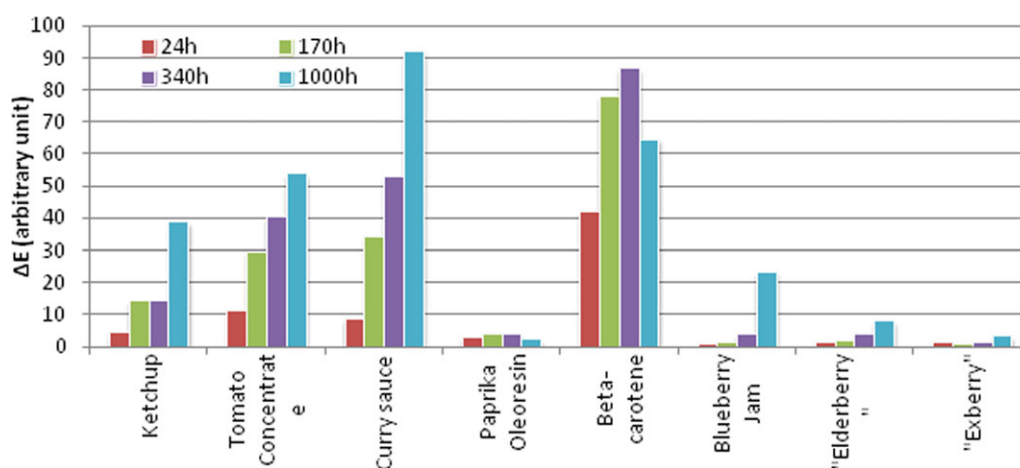
Colorant	PP/PA6			PP/PA6/PP		
	Sample immersed in the coloring substance	PP layer in contact with the coloring substance	PA6 layer in contact with the coloring substance	Sample immersed in the coloring substance	Substance in contact with side 1 (PP)	Substance in contact with side 2 (PP)
Ketchup	23,7	8,3	19,1	14,3	6,2	6,4
Tomato concentrate	46,2	12,0	33,9	29,5	13,4	14,8
Curry Sauce	107,1	15,5	101,7	34,3	8,2	15,9
Paprika Oleoresin	4,9	2,8	1,9	3,8	2,9	2,7
β -carotene	73,5	40,1	53,6	78,0	56,9	48,4
Blueberry Jam	21,2	2,8	14,1	1,5	1,1	1,0
Elderberry	44,2	2,1	34,3	1,9	1,7	1,0
Exberry	32,5	2,8	27,7	1,0	0,4	1,2

oleoresin. When PA6 was in contact with curcumin from curry sauce and anthocyanins, coloration resistance was much lower than when the substances were in contact with PP. These observations confirm the assessments exposed above. For β -carotene, coloration resistance is low for both layers because of the high concentration of this molecule in the test substance. Coloration resistance to lycopene from ketchup and tomato concentrate is lower for the PA6 layer than for the PP layer. This can be explained by the test temperature above T_g , increasing the sorption of this molecule into the polymer matrix. Both layers have a very high coloration resistance to capsanthin from paprika oleoresin. The test with anthocyanins shows PA6 has a much lower coloration resistance to this family of molecules than PP, as assessed previously.

Concerning the prediction of the coloration, the $\Delta\delta$ values concerning PP were already detailed previously. For PA6 both HVK and Hoy's methods predict that lycopene and β -carotene have no affinity for PA6. However the testing temperature above T_g can explain the high ΔE values measured. The other $\Delta\delta$ values calculated with Hoy's method are coherent with the behavior of the PA6 layer.

The general behavior of the PP/PA6/PP multilayer film is very close to the behavior of the bilayer PP/PA6 film. However, the slight differences observed can be explained by the composition of this film. Indeed, the PA6 layer is sandwiched between two layers of PP, acting as protective layers against coloring molecules. As a result, coloration resistance to paprika oleoresin is very high, and very low in presence of β -carotene and lycopene from ketchup and tomato concentrate because of the high sensitivity of the PP layer to these molecules. However, in presence of curcumin, coloration resistance is higher than the one observed in Figure 7, and reveal the "protective" effect of the external PP layers which retards the migration of the coloring molecules into the PA6 layer. However, as the film was cut during preparation, PA6 shows a few zone directly in contact with the substances. This can explain the low coloration resistance observed despite the two external PP layers. Concerning the anthocyanins, The PA6 layer is more resistant to their coloration because of the PP layers. The film is less resistant to coloration by blueberry jam than other anthocyanins.

When tested with the second protocol, the ΔE values for both sides are in the same range as those measured when the PP side

**Figure 7.** ΔE values for PP/PA6/PP multilayer film in immersed contact with selected substances at 60°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the previous bilayer film was in contact with the substances (Table VII). Coloration resistance is higher than the one obtained with the first protocol (immersion test). Indeed, the PA6 layer is not directly exposed to the coloring molecules since cut sides are not in contact with the substances. When comparing to results obtained for the PP/PA6 film, the protective effect of the external PP layers is obvious, especially in the presence of anthocyanins or curcumin.

The addition of the second PP layer does not modify the $\Delta\delta$ values, thus the discussion concerning the prediction of the coloration for the multilayer PP/PA/PP film is the same as the discussion concerning PP coloration.

CONCLUSION

Empirical methods such as group contribution methods are generally used for predicting the solubility of a polymer in a solvent. This study shows that they can successfully be applied to predict the coloration of polymers in presence of alimentary substances containing coloring molecules. HVK's method should be preferred for polyolefins and Hoy's method for other polymeric materials. However, in both methods, a few important parameters are not taken into account. Temperature plays an important role since no polymer with a T_g above the testing temperature was colored in this study. Crystallinity rate and concentration of the coloring molecule in the substance have also to be considered. Indeed, differences are observed in ΔE values between ketchup and tomato concentrate, related to lycopene concentration. Concerning the coloration resistance of polymers, polyolefins show a low coloration resistance. PEEK shows low coloration resistance to β -carotene and PET exhibits a high coloration resistance to all molecules. It is noticeable that soaking a polymer in a very high concentration of a low soluble colorant could possibly cause a higher coloration level than using a high soluble colorant at very low concentration.

Partially and fully fluorinated polymers (PCTFE, ECTFE, ETFE) have a very high coloration resistance. Multilayer films present a very low coloration resistance to all molecules, mainly because of the low coloration resistance of the PA6 layer. Their PP layer can protect the PA6 layer, making the PP/PA6/PP film show a higher coloration resistance to some molecules.

Although the Hoy's and the HVK's methods seem to be useful tools for predicting the sorption of coloring molecules in thermoplastic materials, it is also clear from this work that it is necessary to investigate experimentally the coloration resistance of the materials when exposed to food.

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