Impact of Melt Impregnation on the Color of Wood–Plastic Composites

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ABSTRACT: The aesthetics of wood–plastic composites (WPCs) can affect the acceptance of the products by consumers. This study was aimed at providing a better understanding of how impregnation variables affect color changes, thereby allowing for the development of an optimal process for WPCs. The effects of impregnation parameters and impregnants on the WPC color were investigated in this study via a screening design. Sixteen runs of resolution IV design for seven factors at two levels were conducted. The seven factors were the ratio of maleated polyethylene in the formulations, the ratio of polyethylenes with different molecular weights, four process factors (vacuum, pressure, time, and temperature), and wood species (red maple and aspen). The studied color parameters included the lightness change, chroma change, hue angle change, saturation change, and total color change. All treatments darkened the wood and increased the chroma values and the saturation. Even though all treatments had an impact on the hue angle, the changes were very small. The wood species, impregnants, impregnation time, and temperature played significant roles in the color change and chroma coordinates. However, no parameter dominated the hue angle change and saturation. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2149–2157, 2006

Key words: composites; polyethylene; color; cooperative effects

INTRODUCTION

The shortage of high-quality hardwoods has driven researchers and wood product manufacturers to seek alternative, low quality resources for value-added applications. To achieve this goal, proper technologies, including chemical, thermal, mechanical, and thermomechanical modifications, are needed to improve specific wood quality attributes (e.g., dimensional stability, durability, and mechanical properties) to meet end-use requirements. Chemical modification by the impregnation of common vinyl monomers and *in situ* polymerization generally enhances mechanical properties but hardly improves dimensional stability.[1–7] The thermal modification of wood can improve its dimensional stability but may negatively affect its mechanical properties.[8,9] In this project, a new process was developed to prepare wood–plastic composites (WPCs) through the melt impregnation of a thermoplastic polymer into wood; this was expected to not only enhance the mechanical properties but also improve the dimensional stability.

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WPCs prepared by chemical impregnation exhibit a color change. However, there are no articles dealing with how the impregnation and treatment processes affect the color of the product. In most appearance products, aesthetic appearance is an important attribute. It is necessary to investigate which process variables affect the color.

Even though no studies on the color changes of impregnated wood have been found, there are many reports about color changes due to the thermal treatment of wood.[9–20] Generally, a decrement in the lightness and an increment in the color difference result from heat treatment, especially at high temperatures (240–310°C). The wood species and heat-treatment parameters, such as the pressure, temperature, time, and media, have different impacts on the color change.[11,16–18,20] Bekhta and Niemz[9] investigated the effects of high temperatures on the color change, dimensional stability, and mechanical properties of spruce wood and found that a high temperature had a significant influence on the color change and dimensional stability. A high-temperature treatment induced extensive darkening and reddening of spruce wood. The total color difference can be used as a prediction of wood strength. For example, Okuyama et al.[12] reported that heating green logs lightened the black heartwood of Japanese cedar. Mitsui[17] found that heating irradiated wood enhanced its darkness

TABLE I
Raw Materials

Commercial name	Common name	Properties
Epolene C-18	Maleated polyethylene	Acid number = 1.5–2.5 mg of KOH; softening point = 98–106°C; viscosity = 2400–6000 cps at 150°C,
Epolene C-13	Polyethylene	Weight-average molecular weight = 76,000 g/mol; melt index (190°C) = 200 g at 10 min with 2.16 kg; density = 0.913 g/cm^3
Epolene C-15	Polyethylene	Weight-average molecular weight = 17,000 g/mol; melt index (190°C) = 4200 g at 10 min with 2.16 kg; density = 0.906 g/cm^3
B-215	Antioxidant	Mixture of 67% Irganos 168 and 33% Irganox 1010

and increased its chroma values in comparison with unirradiated wood at high relative humidity.

Oxidative and hydrolytic reactions are mainly considered to be the causes of the production of chromophores during the thermal treatment of wood.[10] Burtin et al.[14,15] reported that steaming walnut sapwood and heartwood led to darkening and reddening of wood tissues and found that the phenolic content and wood color were related. In thermally treated wood, phenolic extractives can contribute to the coloring.[21] Bourgios et al.[13] suggested that color changes by heat treatment were a result of the degradation of hemicellulose in the wood.

Part of a comprehensive study, of which the work reported in this article is also a part, has found that the wood species, molecular weight of polyethylene, impregnation pressure, and impregnation temperature play important roles in polymer retention and hardness.[22] Increasing the impregnation pressure and temperature gives higher polymer retention and hardness; however, increasing the polyethylene molecular weight and switching the wood source from aspen to red maple decrease polymer retention and hardness.

In this study, resolution IV fractional factorial design was applied for melt impregnation as the screening design for seven variables: impregnants *A* and *B* (maleated polyethylene and polyethylenes with different molecular weights, respectively), impregnation parameters *C*–*F* (vacuum, pressure, time, and temperature, respectively), and wood species *G* (listed later in Table II). The focus of this article is color behavior under different treatments, that is, identifying major variables affecting color, quantifying the effects of those variables, and developing an appropriate strategy for future studies.

EXPERIMENTAL

Materials

Wood samples were chosen from defect-free sapwood boards of aspen and red maple supplied by a local wood product company in New Brunswick, Canada. End-matched samples with dimensions of 55 mm × 40 mm × 6–7 mm (longitudinal × tangential × radial) were obtained in a pattern alternating treated samples with control samples.

Maleated polyethylene C-18, polyethylene Epolene C-13, and polyethylene Epolene C-15 were supplied by Eastman Chemical Canada, Inc. (Ontario, Canada), and the antioxidant Irganox B215, a mixture of 67% Irgafos 168 and 33% Irganox 1010, was supplied by Ciba–Geigy Canada, Ltd. (Mississauga, Canada). Detailed information on these chemicals is shown in Table I.

Melt impregnation

The impregnation was performed inside a galvanized 2-gallon pressure tank from DeVilbiss (Glendale Heights, IL). The selected impregnants were premixed

TABLE II
Levels of All Factors

Impregnation variable	Description	Value	
		−1	+1
A	Epolene C-18/(Epolene C-15 + Epolene C-13) (wt %)	0.5	3.5
B	Epolene C-13/(Epolene C-15 + Epolene C-13) (wt %)	0	100
C	Time for applying a vacuum of 30 mmHg (min)	0	30
D	Pressure (kPa)	0	689
E	Time for applying pressure (min)	30	90
F	Vessel temperature (°C)	140	165
G	Wood species	Aspen	Red maple

TABLE III
Screening Design for Melt Impregnation

Run	*A*	*B*	*C*	*D*	*E*	*F*	*G*
1	+1	−1	−1	−1	+1	+1	+1
2	−1	−1	−1	+1	−1	+1	−1
3	+1	+1	+1	+1	+1	+1	−1
4	+1	+1	−1	+1	−1	+1	+1
5	−1	+1	+1	−1	−1	+1	+1
6	+1	+1	+1	−1	+1	−1	+1
7	+1	−1	+1	−1	−1	+1	−1
8	+1	−1	−1	+1	+1	−1	−1
9	+1	−1	+1	+1	−1	−1	+1
10	+1	+1	−1	−1	−1	−1	−1
11	−1	+1	−1	−1	+1	+1	−1
12	−1	+1	−1	+1	+1	−1	+1
13	−1	−1	+1	+1	+1	+1	+1
14	−1	+1	+1	+1	−1	−1	−1
15	−1	−1	+1	−1	+1	−1	−1
16	−1	−1	−1	−1	−1	−1	+1

For the meanings of variables *A*–*G* and values −1 and +1, see Table II.

in the impregnation vessel at a set temperature. The impregnation parameters and the quantities of the materials used are listed in Tables II and III. After impregnation, the samples were removed from the impregnation vessel, and excess polymer was wiped off the sample surface. Ten specimens were used for each treatment. Details of the treatment process are presented in a previous publication.[22]

Measurement of the color

Modern colorimetry is based on the work of the Commission Internationale de l'Eclairage (CIE). CIE developed color scales, and the most popular color system is CIE $L^*a^*b^*$, where L^* describes the lightness and a^* and b^* describe the chromatic coordinates on the green–red and blue–yellow axes, respectively (Fig. 1). Another popular color system is CIE $L^*c^*h^*$, where c^* describes the saturation. The color measurements of all specimens were recorded for the WPC and control sample surfaces with a colorimeter. The sensor head was 10 mm in diameter. The measurements were made with a D65 illuminant and a 2° standard observer. The reflectance percentage was converted into the CIE $L^*a^*b^*$ color system. The hue angle (h^*) and c^* values for another color system (CIE L^*c^*h) were calculated from the CIE $L^*a^*b^*$ color system with eqs. (1) and (2):

$$h^* = \text{arctg}(b^*/a^*) \tag{1}$$

$$c^* = (a^{*2} + b^{*2})^{1/2} \tag{2}$$

The changes in the lightness (ΔL^*), chroma coordinates (Δa^* and Δb^*), hue angle (Δh^*), and saturation (Δc^*) and the total color difference (ΔE^*) were calculated with the following formulas:

$$\Delta L^* = L_t^* - L_c^* \tag{3}$$

$$\Delta a^* = a_t^* - a_c^* \tag{4}$$

$$\Delta b^* = b_t^* - b_c^* \tag{5}$$

$$\Delta h^* = h_t^* - h_c^* \tag{6}$$

$$\Delta c^* = c_t^* - c_c^* \tag{7}$$

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \tag{8}$$

where subscripts t and c denote treated and control specimens, respectively.

Statistical analysis

The analysis of covariance was applied to adjust the mean response for each treatment to eliminate the influence of variability in the wood density or physical properties on the test results. The adjusted response was used for further analyses.

The effect (E) of a variable (x) on the response (Y) was calculated as the difference between the averages resulting from the + and − levels of the variable:[23]

$$E_x = \frac{\sum Y(+)}{n} - \frac{\sum Y(-)}{n} \tag{9}$$

where $\sum Y(+)$ and $\sum Y(-)$ are the sums of the responses when variable x is at its high (+1) and low (−1) levels, respectively, and n is the number of times factor x is at the + or − level.

To determine the significance of the influence of various variables, a half-normal probability plot of the effects was applied. First, the effects were ranked. From the rank, the z value was calculated under the assumption that the estimates came from a normal distribution with a common zero mean. The half-nor-

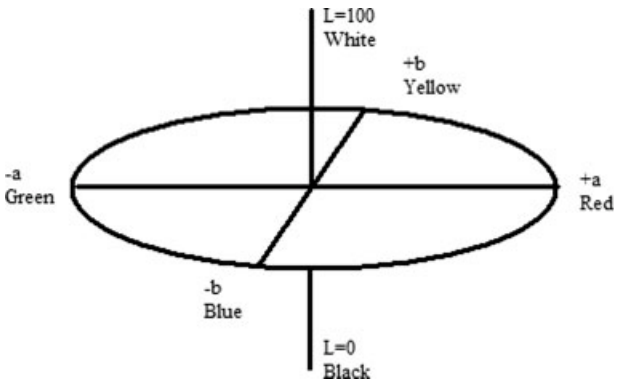

Figure 1 Three-dimensional CIE color space.

mal plot of the effects was prepared with absolute z values on the y axis and effects on the x axis. The effects lying along the line were negligible, whereas those that had significant effects were located off the line. The multinominal linear model of variables with large effects at the coded level (-1 or $+1$) was used for the prediction of each response. After that, a normal probability plot of the residual between the response and the prediction with the aforementioned model was adopted to check if all the points on the plot were reasonably close to a straight line; this determined if the output regression model was reasonable and the assumptions of the analysis were valid.

RESULTS AND DISCUSSION

Effects of the treatments on the wood color

Figure 2 shows that color changes occurred after melt impregnations. All treatments darkened the wood because ΔL^* was negative for all treatments. The results from this study are consistent with those obtained by Burtin et al.[14,15] The greatest reduction in L^* was observed for run 13 (red maple impregnated with a high pressure, high temperature, long impregnation time, and vacuum), which reduced L^* by about 43%. On the other hand, the lowest reduction in L^* (6.7%) was observed for run 10 (aspen impregnated with a low pressure, low temperature, low impregnation time, and vacuum). Different impregnation conditions had different impacts on ΔL^*.

The a^* value increased for all treatments, as shown in Figure 2. The lowest increment was 52.9% for run 2, and the greatest increment was 147.3% for run 11. Figure 2 also shows that the b^* value increased for all treatments. The lowest increment was 37.0% for run 10, and the greatest increment was 102.6% for run 8. All treatments resulted in a reddish-yellow color.

Effects of the variables on ΔL^*

The effects of variables on ΔL^* are shown in Figure 3(a). The significant effects are G, the two-way interaction of B and G (BG), B, E, and F. According to the half-normal plot shown in Figure 3(a), the influences of G, B, E, F, and BG were all significant at the 0.05 probability level. The linear regression model, with a regression coefficient of 0.94, of ΔL^* versus these variables was estimated as follows:

$$\Delta L^* = -13.82 + 2.70B - 1.84E - 2.09F - 4.78G + 2.96BG \quad (10)$$

The values of B, D, F, and G were within the range bounded by the minimum (-1 code value) and maximum ($+1$ code value).

For G, switching from aspen to red maple caused a reduction in L^* from 86.73 to 71.21. The natural lightness difference between red maple and aspen made G the most influential variable in the experiment. Apart from that, aspen is generally composed of 53% cellulose, 31% hemicelluloses, and 16% lig-

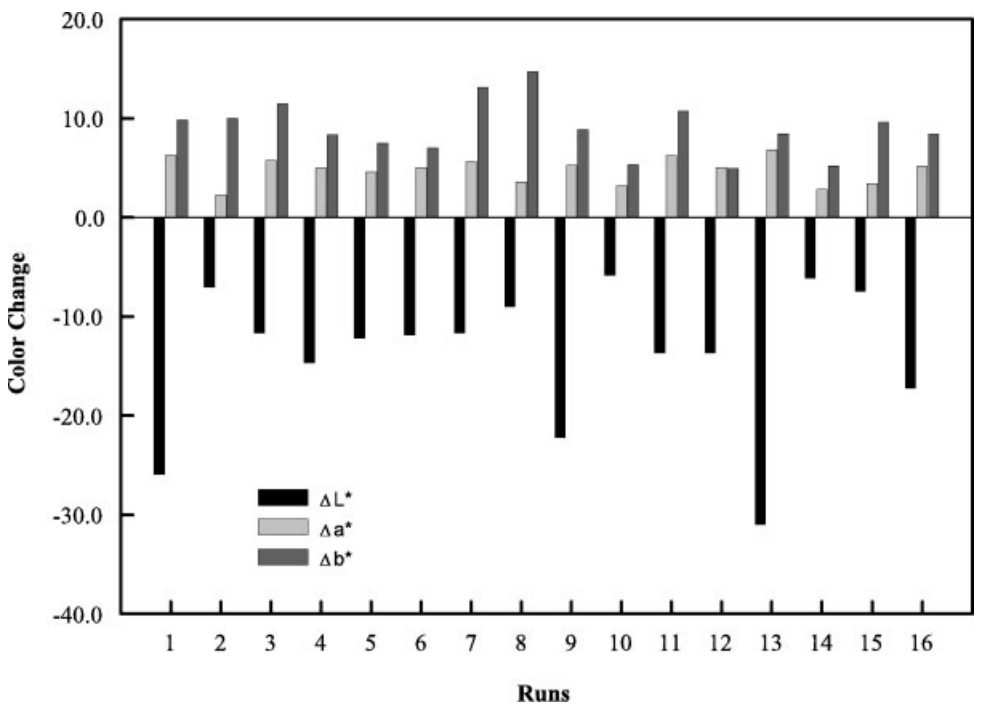

Figure 2 Color changes for different treatments.

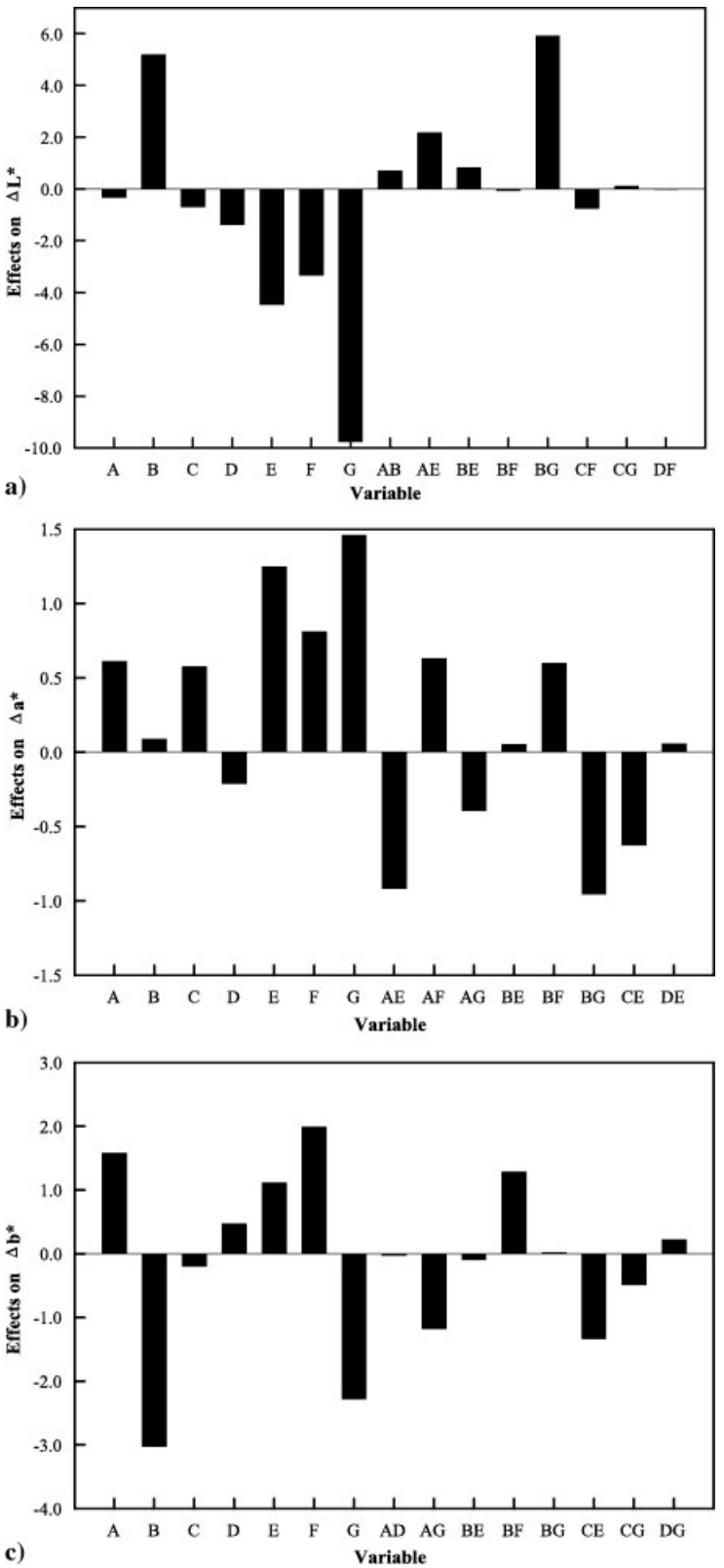

Figure 3 Effects of variables on color changes: (a) ΔL^*, (b) Δa^*, and (c) Δb^*.

nin, and red maple is composed of 41% cellulose, 35% hemicelluloses, and 24% lignin.[24] Higher hemicellulose contents could make it easier to change the color of red maple than that of aspen in a high-temperature environment. This agrees with the study of Bourgios et al.[13]

The L^* measurements for polyethylenes C-15 and C-13 were 58.54 and 55.69, respectively. Under the same impregnation conditions, low-molecular-weight polyethylene achieved higher polymer retention in the wood than the high-molecular-weight polyethylene. The wood was also darker than the untreated wood, even though L^* of high-molecular-weight polyethylene (C-13) is only slightly lower than that of C-15.

BG had a significant effect on lightness. However, it was confounded with several other two-way interactions, such as the two-way interaction of *A* and *D* (*AD*), the two-way interaction of *B* and *D* (*BD*), the two-way interaction of *C* and *D* (*CD*), the two-way interaction of *D* and *G* (*DG*), and the two-way interaction of *E* and *F* (*EF*). If any two variables have no impact on ΔL^*, it is reasonable to assume that their two-way interaction could not contribute to ΔL^*. Therefore, the term *BG* in eq. (4) could be mainly determined by *B* and *G*.

When the impregnation time was increased from 30 to 90 min, this resulted in more oxidation and degradation of the wood constituents, especially lignin and hemicellulose, and also altered the lightness. As Bekhta and Niemz[9] mentioned, the high-temperature thermal treatment of wood has a significant impact on the color. The temperature plays a role similar to that of impregnation time. Lignin and hemicellulose are more likely to be oxidized at a high temperature (165°C) than at a low temperature (145°C). This makes wood treated at 165°C darker than that treated at 145°C. This finding is similar to that observed by Bourgios et al.[13]

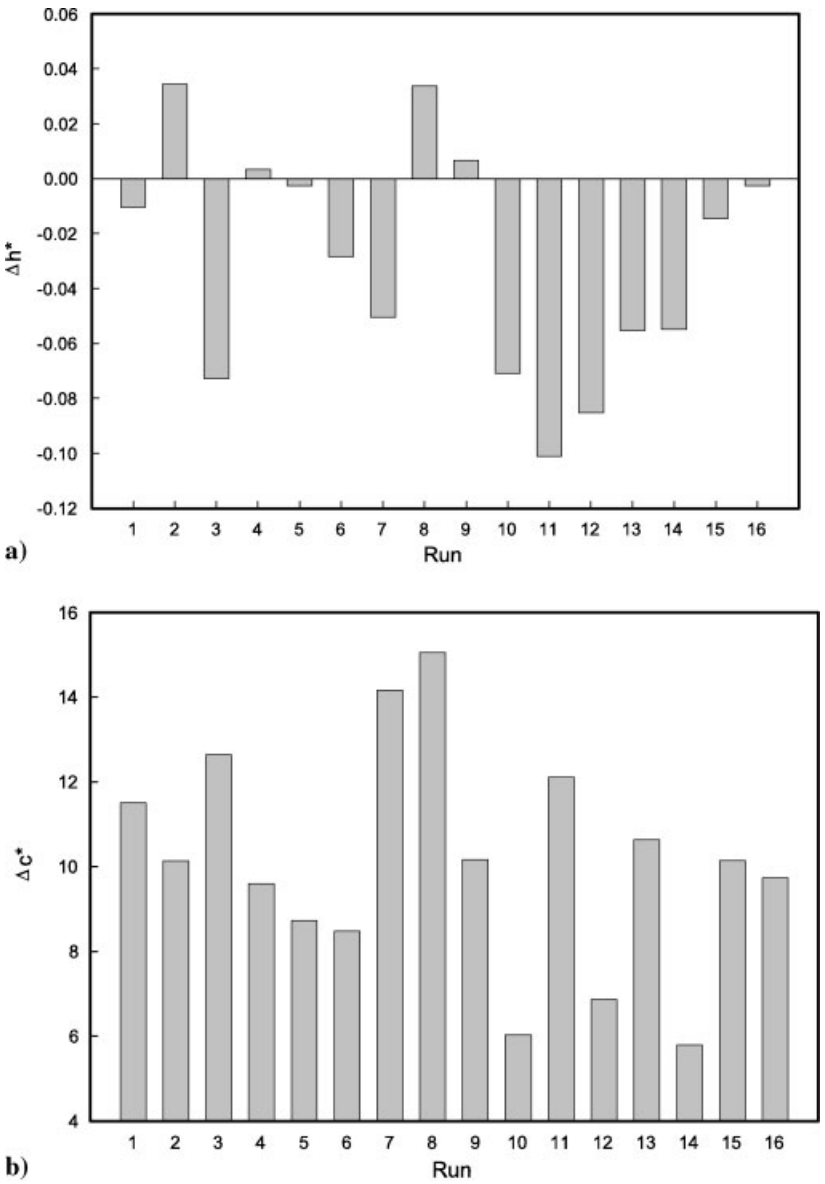

Figure 4 (a) Δh^* and (b) Δc^* for different treatments.

Effects of the variables on Δa^* and Δb^*

The effects of the variables on Δa^* and Δb^* are also depicted in Figure 3(b,c), respectively. With the exception of *B* and *D*, all the variables and their two-way interactions altered Δa^*. Although many variables and their two-way interactions affected Δa^*, few actually dominated this change, even though *G* and *E* had the largest effects on Δa^*. Switching from aspen to red maple and prolonging the impregnation time both increased Δa^* and made the WPC more reddish.

The effects of the variables on Δb^* are presented in Figure 2(c). The most influential variables were different from those that affected Δa^*, and they were *B*, *G*, *F*, and *A*. However, there were no variables significant at the 0.05 level. Increasing the molecular weight of polyethylene and switching the wood species from aspen to red maple reduced b^* and led to a slightly blue appearance, whereas increasing *A* and *F* made the wood more yellowish.

Effects of the treatments on the hue and saturation

Δh^* and Δc^* after the treatments are depicted in Figure 4, which demonstrates that various treatments affected Δh^* and Δc^*. The Δh^* values of all the treatments were small. The largest Δh^* value was 0.10 arc (5.8°) for treatment 11, changing by 7.9%, and the smallest Δh^* was 0.003 arc (0.15°) for treatment 16, changing by 0.25% with respect to untreated wood [Fig. 4(a)]. Figure 4(b) demonstrates that all treatments increased c^*. The largest Δc^* value was 15.04

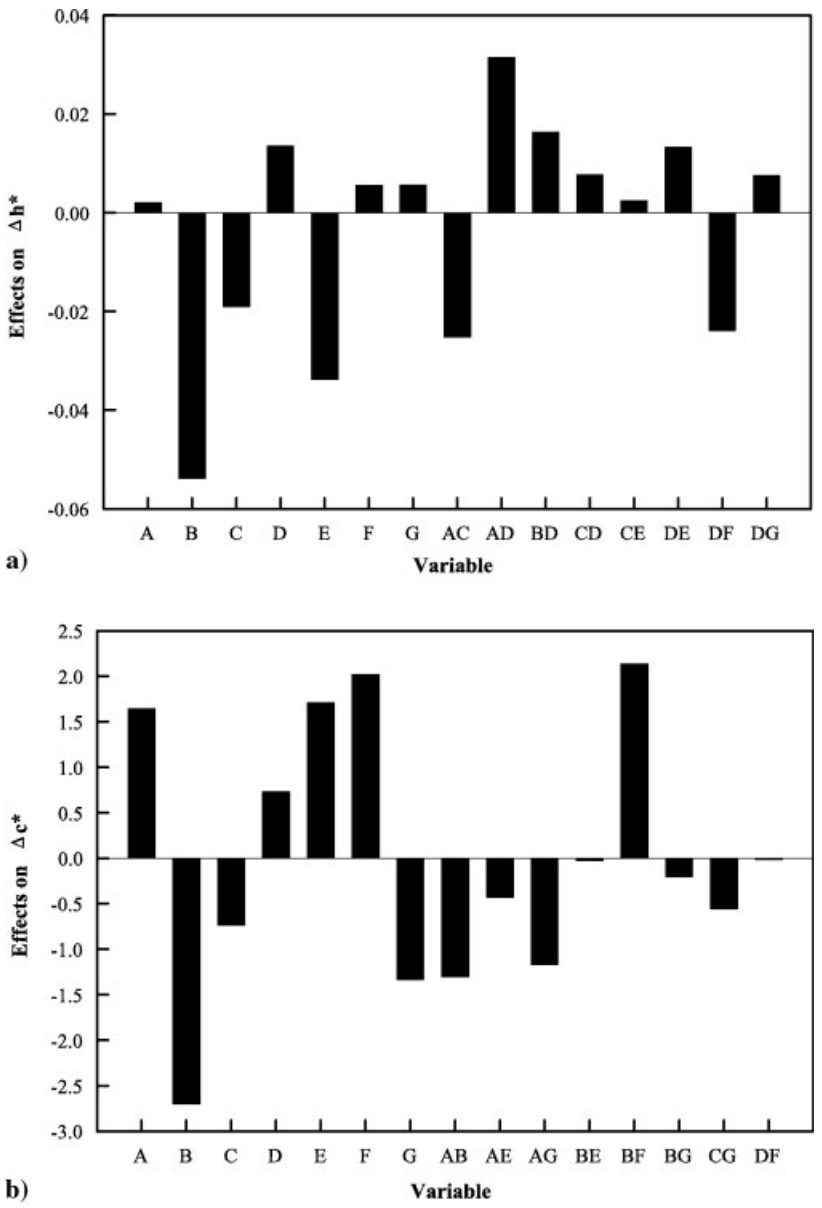

Figure 5 Effects of variables on (a) Δh^* and (b) Δc^*.

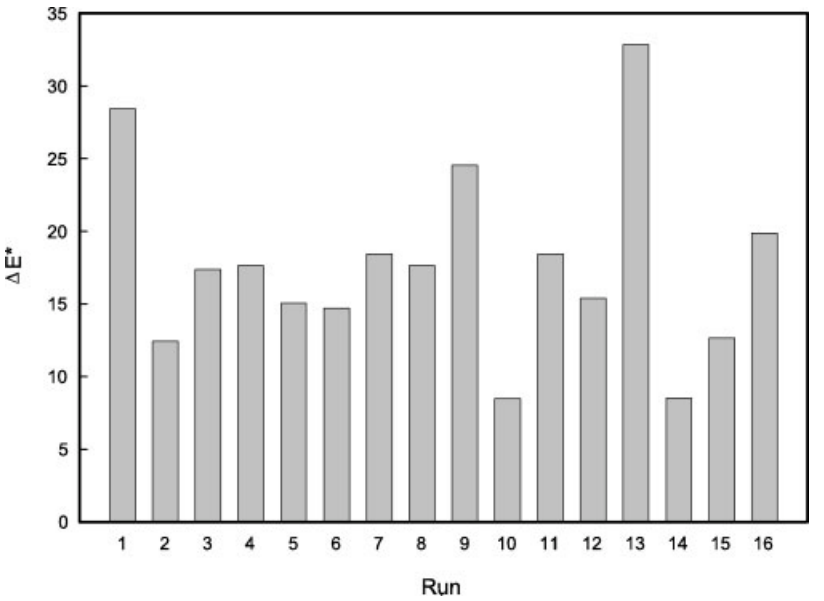

Figure 6 ΔE^* for different runs.

for treatment 8 (100% increase with respect to an untreated sample), and the lowest Δc^* value was 5.78 for treatment 14 (38% increase).

Effects of the variables on Δh^* and Δc^*

The effects of the variables on Δh^* and Δc^* are shown in Figure 5. Among all the variables, including the two-way interactions, the variables displaying the greatest impact on h^* were *B*, *E*, *AD*, the two-way interaction of *A* and *C* (*AC*), and the two-way interaction of *D* and *E* (*DE*). However, none of the variables were significant at the 0.05 level according to the half-normal plot. This indicates that several variables and two-way interactions worked together to determine Δh^*. h^* of lower molecular weight polyethylene (C-15) was 1.41, which was slightly lower than h^* of high-molecular-weight polyethylene (C-13; 1.48), and those of untreated wood species were 1.27 for aspen and 1.03 for red maple. The impregnation of polyethylene into wood altered h^* of the wood. From Figure 5(a), *B* had the largest impact on Δh^* [0.054 (3.08°)], but the value was small.

B had the greatest effects on Δc^*, whereas the two-way interaction of *D* and *F* (*DF*) had the smallest effect. No variables were significant at the 0.05 level

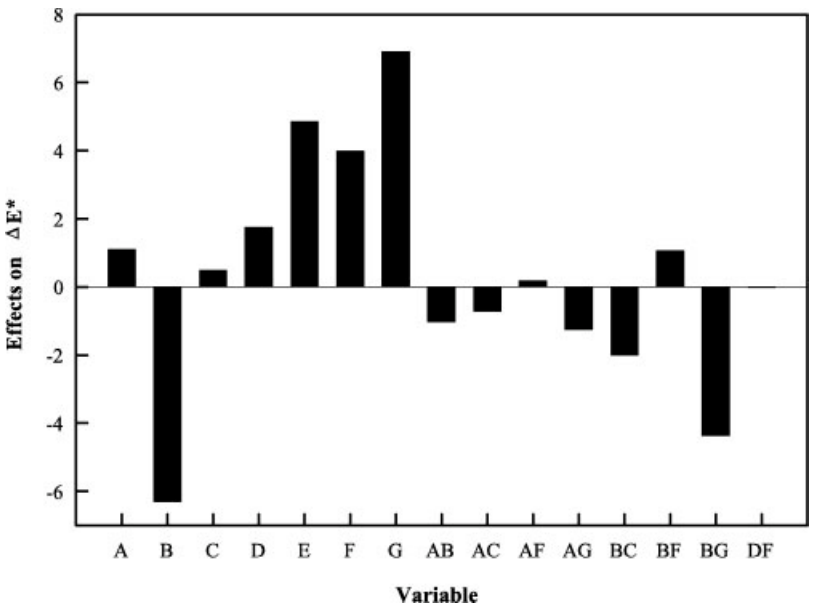

Figure 7 Effects of variables on ΔE^*.

according to the half-normal plot. Nevertheless, *B*, *F*, *E*, *A*, and the two-way interaction of *B* and *F* (*BF*) had the largest contributions to Δc^* [Fig. 5(b)].

Effects of the treatments and variables on ΔE^*

The ΔE^* values of different treatments are shown in Figure 6: treatment 13 gave the largest increment, whereas treatments 10 and 14 provided the smallest increments. This demonstrates that different combinations of impregnation parameters have significant effects on the total color change.

G, *B*, *E*, *F*, and *BG* had significant effects on ΔE^* (Fig. 7).

The linear regression of ΔE^* versus the more influential variables with an R^2 value of 0.91 is shown next:

$$\Delta E^* = 17.62 - 3.23B + 2.14E + 2.31F + 3.38G - 2.18BG \quad (11)$$

where the values of *B*, *E*, *F*, and *G* are within the range bounded by the minimum (−1 code value) and maximum (+1 code value).

Equation (11) shows *G*, *B*, *E*, *F*, and *BG* dominated ΔE^*.

CONCLUSIONS

The experimental design approach applied here enabled us to identify the significant variables of the melt impregnation process for color change, including ΔL^*, Δa^* and Δb^*, Δh^*, Δc^*, and ΔE^*. This work shows that the process parameters (pressure and temperature), impregnants (polyethylenes of different molecular weights), and wood species contributed differently to color changes. All treatments decreased the lightness and darkened the wood. The wood species, impregnant, impregnation time, and impregnation temperature were dominating variables affecting the lightness change. Switching from aspen to red maple, increasing the impregnation time, and increasing the impregnation temperature decreased the lightness, whereas increasing the polyethylene molecular weight resulted in a lighter product.

All treatments increased Δa^* and Δb^*. No variables dominated the chroma change. However, the wood species and impregnation time had the largest effects on Δa^*, and the polyethylene type, wood species, and impregnation temperature had the highest impacts on Δb^*.

The following experimental design could be investigated in future studies: (1) a full factorial design with the few identified significant variables and (2) the use of two or three levels of important factors to determine the optimal process parameters for color changes. This study recommends that the wood species, impregnant polyethylene, impregnation time, and impregnation temperature be considered in future experiments for color-change studies.

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