PROGRESS
IN COLOR, COLORANTS AND COATINGS

available online @ www.pccc.icrc.ac.ir
Prog. Color Colorants Coat. 8 (2015), 219-235

Ministry of Science, Research and Technology
Institute for Color Science and Technology

Characterizing films of polyethylene blends: An application of colorimetric parameters measurements

M. Mohammadi[1], A. A. Yousefi*[2] and M. Ehsani[3]

[1] Assistant Professor, Department of Polymer Engineering, Faculty of Engineering, Qom University of Technology, P. O. Box: 37195-1519, Qom, Iran.

[2] Professor, Department of Plastics Engineering, Faculty of Polymer Processing, Iran Polymer and Petrochemical Institute, P.O. Box: 14965-115, Tehran, Iran.

[3] Associate Professor, Department of Plastics Engineering, Faculty of Polymer Processing, Iran Polymer and Petrochemical Institute, P.O. Box: 14965-115, Tehran, Iran.

ARTICLE INFO

Article history:
Received: 02-02-2015
Final Revised: 05-06-2015
Accepted: 28-06-2015
Available online: 28-06-2015

Keywords:
Optical properties
Polyethylene blend
CIELAB color coordinates
spectrophotometry

ABSTRACT

This study reports an application of instrumental color measurement for quantifying and comparing the optical properties of high density polyethylene and low density polyethylene blend films and the effect of blending ratio on these properties. The optical properties of the films indicated the probability of affecting the color spectrum by incorporating low density polyethylene into high density polyethylene. This is the principal reason for changing colorimetric parameters of the films. It was indicated that the presence of more than 25% low density polyethylene in the blend films causes higher L^*-indices comparing to other corresponding blend films. Besides, growing in b^* value of some samples is a sign of a little color shift from white to yellow in the color space. Hue angle of the films containing up to 85% high density polyethylene declined with increasing high density polyethylene content in the blend films. Comparing CIE coordinates proved that hue angle values have significant magnitude, so the difference of blend films and the trend of color intensity variations become more obvious. Whiteness and yellowness indices showed the same trend as L^* and b^* and C^*, respectively. In this paper, it is indicated that YI, WI, hue angle and CI are useful factors to compare the transparent films of polyethylene blends. Prog. Color Colorants Coat. 8 (2015), 219-235 © Institute for Color Science and Technology.

1. Introduction

In polymer industry, color and appearance are influenced by many factors and a variety of appearances are also established depending on the type and the grade of materials. There are some studies on the transparency of materials [1, 2], and it is well known that a transparent polymeric object can be

---

*Corresponding author: A. Yousefi@ippi.ac.ir

prepared if the polymer by itself is transparent, the refractive index of ingredients is close to that of the polymeric matrix and the dispersion domain size of the components is smaller than one fourth of the visible light wavelength [3]. Some polymeric products do not contain any colorant or additive and they are applied in their original/intrinsic color. Optical diversity of resins usually ranges from clear to cloudy and from colorless to pal yellow, amber, and brown. In the case of clear plastics, the percentage of light transmission and the transmission spectrum are commonly measured. Wu and Fan [4] performed some spectral transmission measurements on various types of semi-transparent polymeric thin films. Recently, Philips et al. [5] utilized a range of measurement techniques for optical characterization of transparent films and their ability to diffuse or obstruct the passage of light in terms of light scattering and transmission.

The spectrophotometry technique in both transmission and reflectance modes is a versatile tool to investigate the optical properties of materials [6-9]. Characterization of material's appearance via tristimulus values in CIELAB color system and associated parameters yield advantageous information to describe physical properties of materials and their interaction with light. Ignell et al. evaluated the relation between CIE coordinates and gloss of injection-molded specimens by means of a spectrophotometer and a glossmeter [10]. Berberich et al. showed that the colorimetric parameters in CIELAB color space are quantifiable variables for whiteness of samples [11].

On the other hand, the subject of polymer-polymer incompatibility is a well-known issue in the field of polymer blends. This is not of a prime importance in thick and large polymer blend parts. In polymeric thin films made from blends, however, the optical properties such as clarity, yellowness and light transmission become very important. Therefore, techniques that can distinguish and reveal the differences in behavior of miscible and immiscible blends are helpful in characterizing the blends.

There is a lack of reports on inherent color of polyethylene (PE) films and its characterization through CIE coordinates. Also, no research work was found in literature on the effect of blending on the color stimuli of blown films of blended polyethylene. So, in this work, two PE grades (high- and low-density) were used and the ratio of blending of two constituents was varied with the purpose of investigating its influence on the optical properties of blown films of high density polyethylene/low density polyethylene blend. Following this, the tristimulus values X, Y, and Z of the films were calculated and then optical properties of the samples in color spaces such as CIELAB and CIELCH were compared. In addition, reflectance and transmittance spectra in visible region were investigated to see how composition affects color stimuli.

It is thought that miscibility or homogeneity in polymer blends affects the color stimuli of the blends. This study is important from the standpoint of establishing the suitability of the spectrophotometry method at finding different behaviors of miscible PE blends compared to immiscible counterparts in a wide range of compositions. A series of parameters were determined to observe how considerable (in trend and value) the parameters vs. composition for miscible polyethylene (PE) blend are. This would be a good application of spectrophotometry in characterizing transparent films of the polyethylene blends via color stimuli.

2. Experimental

2.1. Material

In this work, commercial grades of high density polyethylene and low density polyethylene from Iran Petrochemical Co. were used. Some available physical properties of polymers are listed in Table 1.

Table 1: Properties of polymers.

Polymer	HDPE	LDPE
Density (g/cm^3)	0.948	0.918
Melt Flow Index (g/10 min), @190 ^{o}C	0.4	0.8
Melting point (^{o}C)	139	112

2.2. Methods

2.2.1. Preparation of blends and Blown films

The film blowing experiments were conducted on a laboratory scale blown film extrusion line (Brabender Plasticorder, Lab-Station). Blends of high density polyethylene (HDPE) and low density polyethylene (LDPE) were prepared via melt mixing process in a single screw extruder with a screw of length to diameter ratio of 25:1 at the screw speed of 55 rpm. The polymers granules were premixed in a plastic bag and fed into the extruder via its hopper. Extrusion temperature profile from the feed zone to the die was set at 150-210 ^{o}C. The melt homogeneity of HDPE/LDPE blends was checked by rheometry and it was found that there is miscibility for the materials at the melt state [12]. The die diameter was 25 mm and it was fitted with a dual lip ring with air conditioning. The die gap was 0.7 mm. the thickness of produced film was 50 ± 5 µm, by using a blow up ratio (BUR) of 2.5 and a take-off rate of 3 m/min. The composition of the blends is summarized in Table 2.

2.2.2. Color measurement through spectrophotometry

The Optical properties as a mean for physical characterization of the films were determined using a spectrophotometer Color-Eye 7000A (Gretag Macbeth) at a 10^{o} standard observer, with total transmission geometry for transmission mode spectrophotometry and an 8^{o} diffuse geometry for reflectance mode spectrophotometry. To measure the optical properties, a film sample was cut into a rectangular form and placed on the internal side of the spectrophotometer cell. The transmission and reflectance spectra of the PE films were determined in wavelength range of 360 to 750 nm under three different illuminants (D65, TL84 and A). The CIEL*a*b* scale was applied and then the CIELAB coordinates L^{*} (lightness), a^{*} (the red–green axis) and b^{*} (the yellow–blue axis) were determined. Reflectance was measured in specular included mode with a 10^{o} observer. Total light reflectance, i.e., both specular and diffuse reflectance is measured through the reflectance included mode. Reflectance L*a*b* color measurements were carried out on the film samples placed over a white tile background.

2.2.3. Differential scanning calorimetry (DSC)

Miscibility in the blend films was studied through thermal analysis using a NETZSCH DSC 200 F3 differential scanning calorimeter. A film sample was heated from 20 to 170 ^{o}C at a heating rate of 10^{o}C/min and maintained for 5 min at 170 ^{o}C, then cooled to 20^{o}C at a rate of 10^{o}C/min. Endothermic and followed exothermic DSC traces were reported.

Table 2: Composition of the films of blends along with crystallite sizes.

Sample	HDPE (wt %)	LDPE (wt %)	Crystallite size (nm)
H1	100	0	22.0
5L2H	95	5	26.1
10L2H	90	10	19.8
15L2H	85	15	18.7
25L2H	75	25	18.5
50L2	50	50	16.7
25HL2	25	75	14.7
15HL2	15	85	13.4
10HL2	10	90	12.8
5HL2	5	95	12.7
L2	0	100	6.6

3. Theory of quantifying color sensation

Visual scrutiny is unfavorable and problematic since the appearance differences of objects cannot be precisely evaluated via visual perception. Moreover, there is person inaccuracy in visual scrutiny method. Therefore, it has been provided a quantitative measurement method based on color measuring instruments. In 1931, The Commission International de l'Eclairage (International Commission on Illumination), commonly referred to as the CIE, which is an international organization concerned with lighting and color, studied methods for color measurement and they introduced their findings as color specification system. Since 1939, CIE system has been authenticated universally, and many additional recommendations, maintaining the principles, have been made in the field of color measurement. Three light sources have been recommended by the CIE for colorimetry. These light sources approximate noon sunlight and/or average day light. Based on measurement of real daylight, D65 is the most widely used illuminant.

In order to determine the tristimulus values for a reflecting or transmitting sample, the reflectance or transmittance factor of the sample should be combined with a spectral energy distribution of the illuminating light source, E(λ) and spectral sensitivity represented by standard observer functions $\bar{x}(\lambda), \bar{y}(\lambda), \bar{z}(\lambda)$ at each wavelength interval between 400 to 700 nm; therefore, tristimulus values, which are three numbers (X, Y, Z) represented the color of an object, are obtained. Normalized tristimulus values, i.e. $\frac{X}{X+Y+Z}$, $\frac{Y}{X+Y+Z}$, $\frac{Z}{X+Y+Z}$, represent chromaticity coordinates or trichromatic coefficient, x, y, z, respectively. Chromaticity coordinates determine an object color and are designed so that their summation equals one: x + y + z = 1.

Tristimulus value can be easily calculated by a method expressed by CIE. If spectral energy distribution of illuminant is given, the spectral reflectance or transmittance of an object is applied for calculating the tristimulus values:

$$X = k\sum P(\lambda)\bar{x}(\lambda)R(\lambda)$$

$$Y = k\sum P(\lambda)\bar{y}(\lambda)R(\lambda)$$

$$Z = k\sum P(\lambda)\bar{z}(\lambda)R(\lambda)$$

where P(λ) is the relative spectral power distribution of the illuminant at the wavelength of λ, R(λ) is the spectral factor of object at the wavelength of λ, and $\bar{x}(\lambda), \bar{y}(\lambda), \bar{z}(\lambda)$ are the CIE color matching functions for the standard observer at λ. The pre-factor "k" is the luminatory function of a perfect reflectance diffuser and is a normalizing constant given as follows:

$$k = \frac{100}{\sum_{400}^{700} P(\lambda)\bar{y}(\lambda)}$$

The factor k normalizes the tristimulus values so that Y will have a value of 100 for perfect white diffuser – a hypothetical material that reflect or transmits 100 percent of incident light [13]. The tristimulus values X, Y, Z are a base for describing some perceptual color spaces which are often a base for color order systems.

More uniform color spaces by transformation of tristimulus values were developed and the CIE $L^*a^*b^*$ color space (abbreviated CIELAB) was recommended in 1976. $L^*a^*b^*$ system is an important color space which is obtained from X, Y, Z which can also be declared by other inter-convertible systems such as $L^*u^*v^*$, Lab and $L^*c^*h^o$. For paint, plastic and textile industries, the CIELAB color space has been universally employed. The following equation represents CIELAB coordinates:

$$L^* = 116\left(\frac{Y}{Y_n}\right)^{\frac{1}{3}} - 16,$$

$$a^* = 500\left[\left(\frac{X}{X_n}\right)^{\frac{1}{3}} - \left(\frac{Y}{Y_n}\right)^{\frac{1}{3}}\right],$$

$$b^* = 200\left[\left(\frac{Y}{Y_n}\right)^{\frac{1}{3}} - \left(\frac{Z}{Z_n}\right)^{\frac{1}{3}}\right]$$

where X, Y, and Z are the tristimulus values of the object under consideration, respectively, and X_n, Y_n, and Z_n are the tristimulus values of a perfect reflecting diffuser under the same light source, respectively. The values were normalized to that Y_n=100. Lightness (represented by L^*) is called CIE 1976 lightness. One should note that the above equation is limited to $X/X_n>0.000885$, $Y/Y_n>0.008856$, and $Z/Z_n>0.008856$. Otherwise, a modified equation should be used [14].

CIELAB variables form three-dimensional orthogonal coordinates, in which L^* axis correlates with lightness, ranged from 0-100, a^* axis correlates with greenness ($-a^*$) and redness ($+a^*$) and b^* axis represents blueness ($-b^*$) and yellowness ($+b^*$) (Figure 1).

Defining color in cylindrical coordinates is beneficial in most cases and it is possible to calculate parameters of CIELCH system, the C^* (chroma parameter) and h^o (hue angle) which have more correlation with visual perception of color. The values are defined based on a^* and b^* values as

$$C^* = \left[a^{*2} + b^{*2}\right]^{\frac{1}{2}},$$

$$h^\circ = \text{Arctan}\frac{b^*}{a^*} \quad , \quad 0^\circ \le h^\circ \le 360^\circ$$

Ratios such as a^*/b^*, or color coordinates of CIELCH space may better demonstrate color variations than a^* and b^*.

4. Results and discussion

4.1. Comparing characteristics spectra of films

On color percipience, change in light by objects can be described by means of transmission or reflectance spectra (for transparent objects and opaque objects, respectively, and also translucent objects which have both features). These spectra showed that how much light can transmit across an object or reflect at each wavelength, as a light source can also be specified by a spectral power distribution.

The UV-visible spectra of PE films in transmission and reflectance modes are presented in Figures 2 and 3, respectively. In these presentations, the blends did not show any expressive trend in reflectance mode whereas a meaningful trend in transmission mode was observed

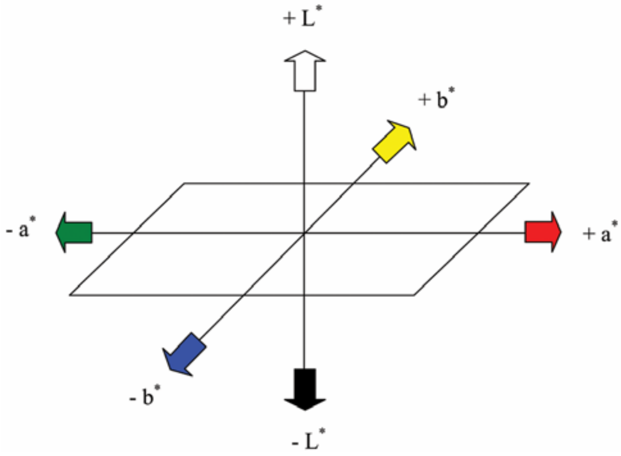

Figure 1: A diagram representing the CIELAB color space.

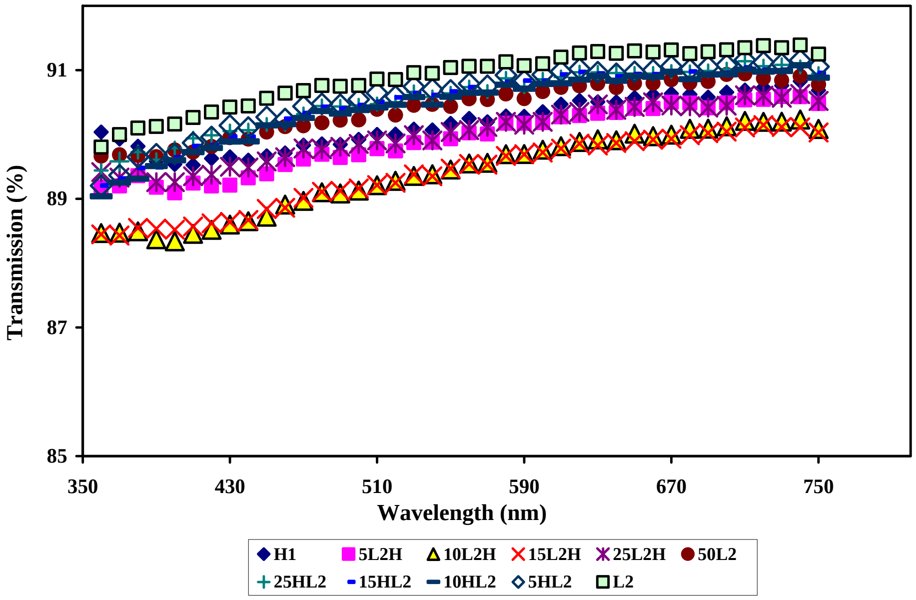

Figure 2: The spectral transmission as a function of the wavelength for samples with different HDPE content.

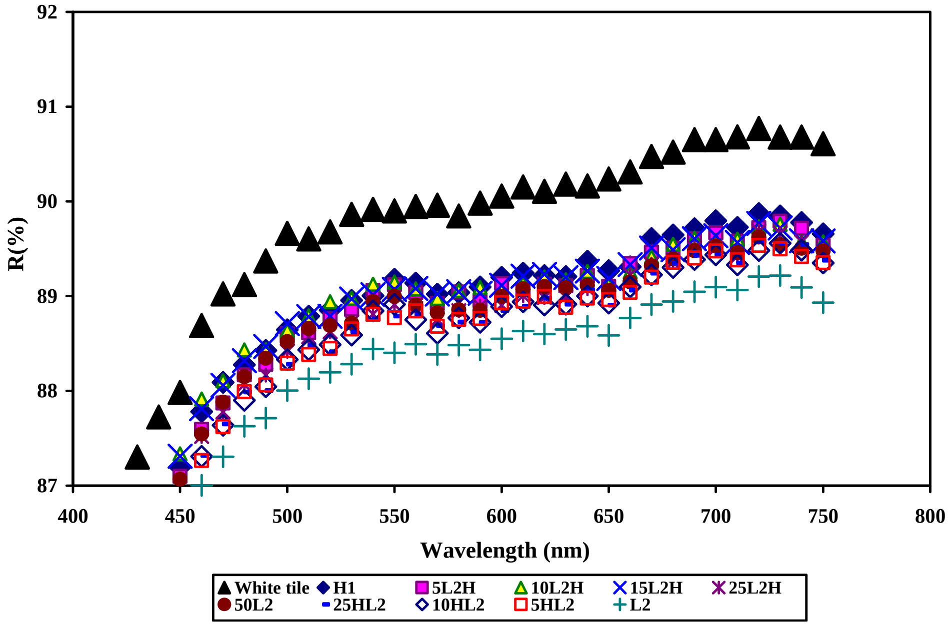

Figure 3: The spectral reflectance as a function of the wavelength for samples containing different amount of HDPE.

Transmission spectra showed that light transmission increased gradually within the wavelength range, demonstrating that the films have a slight transmission inclination towards being colored.

Interestingly, the LDPE polymer forms the most transparent film and its 5 to 25% blends are of a transmission less than that of the HDPE film. With further increasing of LDPE content, the blend film becomes more transparent than the HDPE film.

Light transmission percentage ranges from 89.8 to 91.42 and from 89.5 to 90.8 for LDPE films and HDPE films, respectively. The blend films, especially films of

LDPE-rich blend, showed a growing transmission through the spectrum in comparison with HDPE -rich blend films. The transmittance of all blends with a LDPE-content higher that 25 wt% locates between those of LDPE and HDPE. In this LDPE concentration zone, transmittance of the blend films increases with LDPE content. This might be attributed to the crystalline domains of the films, so that being developed the amorphous regions will result in a better transmission but the crystalline region scatters the light inducing less transmission. Normally, LDPE has lower crystallinity than HDPE which stems from the branched and linear chains of these polyethylenes and their ability towards crystallization [15-18]. The size of polymeric crystallites has an important impact on the wavelength over which they obstruct the passage of light so that small crystallites obstruct short wavelength light [5]. Consequently, with increasing the crystallite size, the wavelength range over which they inhibit the passage of light expands. For that reason, the films having high transmittance at visible light must have crystallite sizes smaller than the wavelengths of visible light. This is supported using values of crystallite sizes calculated from the highest DSC melting peak temperature of the samples (based on the well established Gibbs-Thomson equation according to the work by Wlochowicz and Eder [19]) (see table 2). Crystallite sizes between 6.6 to 26.1 nm were obtained and the LDPE film had the smallest crystallite size which increased with LDPE content in the blend films. So, the values are smaller than the visible light wavelength.

Due to the fact that the studied films without an opaque background do not have a significant light reflectance, the reflectance measurement of the films should be carried out over a standard white tile background. The results indicate that the reflectance spectrum of the background was the principal factor dominating the reflectance spectra of the films.

As can be seen in Figure. 3, the white tile has the highest light reflectance. The films were affected by the color and the reflectance of the background. The reflected light from the white tile was combined with the light scattered within the film while it is reflecting off the background and into the film. Once the incident light reaches the film primary surface, it diffuses through it and then reflects back from the white tile background renters into the films through the opposite surface of the film and finally leaves the primary surface of the films towards measuring device. This originates the complication for the trend of reflectance of the films.

Light reflectance behavior of the films shows that the highest and the lowest reflectance spectrum belongs to HDPE and LDPE films, respectively, and the reflectance spectra for blend films lie between these two extremes. The blend films inclined to reflect more light when HDPE content is augmented.

Using transmission spectrophotometry technique, the wavelength or color dependency of light transmission becomes evident. It may allow establishing an indication of the light scattering effect, different from the opacity of the film. Moreover, judging the color change without considering the influence of the background may also be possible by recording transmission spectra that makes it easier to predict the visual changes [5]. Therefore, the study of optical properties of the films indicates that incorporating LDPE into HDPE may affect the color spectrum.

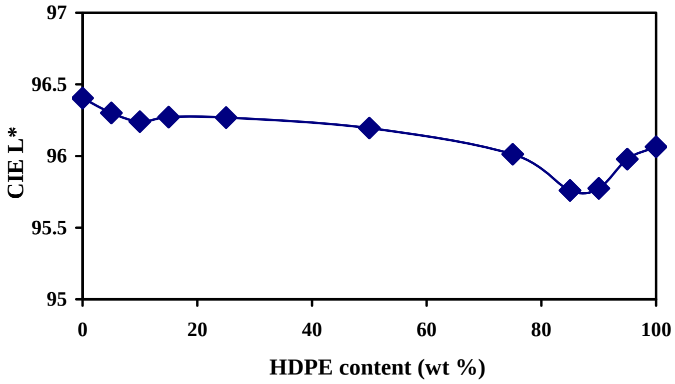

Figure 4: Lightness (CIE L^*) of the blown films of blends with different HDPE weight percent.

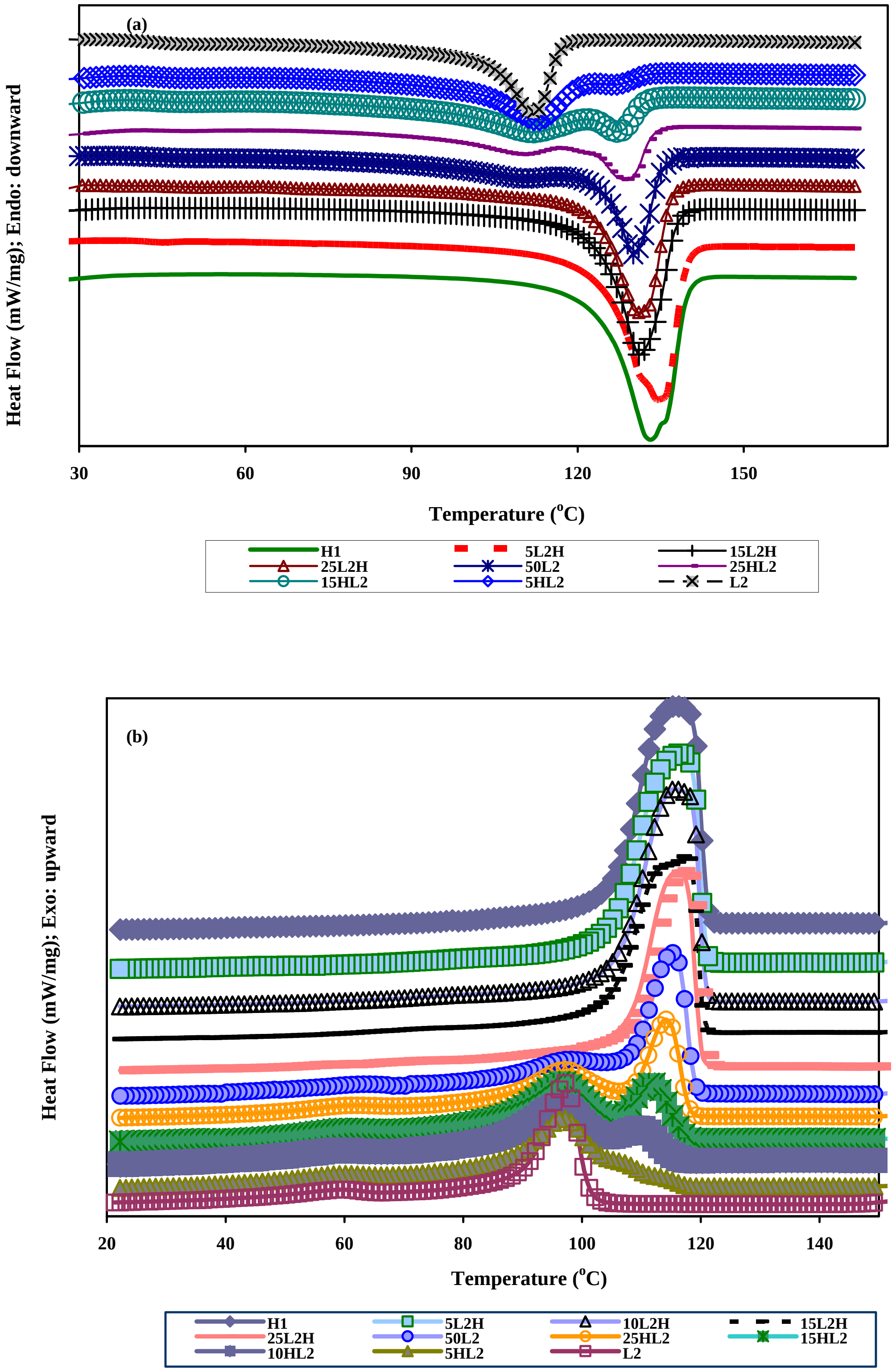

Figure 5: (a) DSC heating (melting) thermograms of PE blend films with different HDPE content (the arrow on each curve of blend films points at the second endothermic peak which is an indication of phase separation and therefore immiscibility). (b) DSC cooling thermograms of PE blend films with different HDPE content.

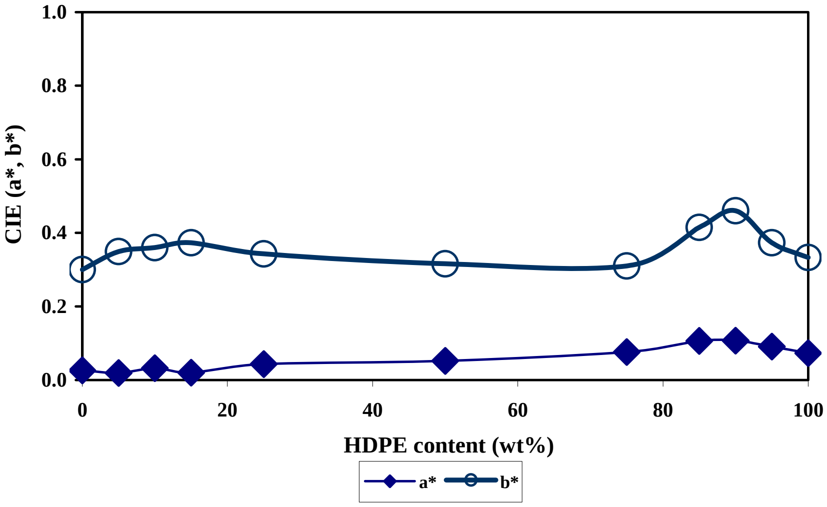

Figure 6: a* and b* variables of the blown films of blends with different HDPE weight percent.

4.2. Lightness

The lightness (L*) of the original LDPE and HDPE films along with the blends are shown in Figure 4. Lightness for LDPE and HDPE was 96.41 and 96.06, respectively. The lowest lightness belongs to the 85% HDPE blend with a value of 95.76. Amongst all samples, LDPE has the highest lightness, while L* values decline by increasing HDPE content in the blend films up to 85%, and then increases from 85% to 100% HDPE. Besides, in transmission mode, the L* value of the blend films decreases up to 15% LDPE and then increases but never exceeds that of the LDPE film.

The repeatability was checked by measuring tristimulus color coordinates CIELAB (obtained by the same operator using the same equipment on the same day) for several samples (pure LDPE and pure HDPE films). It was revealed that there was a repeatability of 0.01 unit of color coordinates CIELAB. This confirms that the observed small differences in the colorimetric parameters for the blend films are valid.

Thermal analysis of the blend films by means of DSC can be a helpful technique for characterizing their melting behavior and detecting the miscibility or immiscibility in solid- state [20, 21]. As illustrated in Figure 5 (a and b), DSC thermograms (both melting and cooling traces) of the films containing lower than 25% LDPE showed only a single endothermic and a single exothermic peak indicating there is no phase separation, which supports homogeneity and miscibility of blends in solid-state, although for other blend films two endothermic and two exothermic peaks were observed reflecting two separated phases which confirms immiscibility in solid-state and is in good agreement with observation reported by Hussein [21].21 Using thermal analysis, he showed that in a blend of HDPE with a branched polyethylene, miscibility exists for HDPE-rich blends. It has been reported that a large number of polyethylene blends are not compatible or only compatible in rather limited extents [20, 22, 23].

The presence of up to 25% LDPE in the HDPE resin due to the miscibility of the blend films in the mentioned composition range bring about diminishing lightness, whereas L* values rise because of immiscibility and more heterogeneity of the mixture in other compositions. It can also be understood that the presence of HDPE in the LDPE matrix causes trivial effect on L* value. For LDPE-rich blend films, the decrease in transmission and associated color change were slighter than that of HDPE-rich blend films.

4.3. Variables a* and b*

The pure polyethylene (LDPE and HDPE) films do not have the same a* values (see Figure 6). Lightness (L* value) was in agreement with general theory of color measurement since transparent and achromatic (or colorless) films should have high lightness and minimum values of a* and b* in color space. a* values which stand for redness (or greenness) in color space were trivial, and even for films containing lower than 15% HDPE was near zero, but by an increase in HDPE content in the blend films, CIE a^* value became slightly larger up to 85 % HDPE in which a^* value reached to 0.11 and then the value remain more and less unchanged. Behavior of blend films containing less than 25% LDPE implies a color change which is a result of light scattering effects. This was corroborated by CIE values which indicated an increase in b^* value and a decrease in L^* value.

In view of the fact that a^* value is positive, it situated in redness area. Because of the low level of redness-greenness of the films, b^* values are more implicative than that of a^*, i.e. because the films are achromatic (or colorless), one of color axis (here b^* axis) can be significant.

It is obvious from the data obtained for the film samples that b^* value in LDPE film is lower than HDPE film. In the case where the films are produced by blending, an interesting behavior was observed. First, with increasing HDPE content from 0 to 75%, b* value slightly increases and then decreases, whereas b^* value for the film with 75% HDPE is equal to that of LDPE film. Thereafter (the 25L2H sample), with further increase in HDPE content, again b^* value increases to reach a maximum and then decreased. As it is obvious, the blend films with 5, 10, and 15% LDPE have the highest yellowness levels; and maximum b^* value is corresponded to the 10L2H sample.

Upon mixing the polymers, a^* and b^* values of the resulting films move towards yellowish and reddish, respectively, and low ratios of LDPE has a clear impact on L^*, a^* and b^* values of HDPE-rich blend films. Again, similar to L^* values, the variations of b^* values of HDPE-rich blend films can be attributed to the miscibility of the blends, whereas immiscibility which strongly occurred in the blend films containing more than 25% LDPE does not cause a significant grow up in b^* value.

4.4. Chroma

Figure. 7 illustrates the plot of chroma vs. HDPE concentration. Minimum chroma (C^*) was obtained for pure LDPE (0 % HDPE) film sample rising with increasing HDPE content in the blend films up to 90 wt%. On the other hand, a predominant HDPE content (90%) results in C^* augmentation reaching a maximum level in 10L2H sample. For the L2 to 10L2H samples, C^* increased from 0.30 to 0.48 and the level of C^* in 50L2 sample was close to that of LDPE sample.

The differences observed in C^* among the films prepared at various HDPE concentrations is effortlessly elucidated by the fact that C^* values are arithmetically stemmed from a^* and b^* values, with b^* largely contributing to the variation of C^* values in the studied samples.

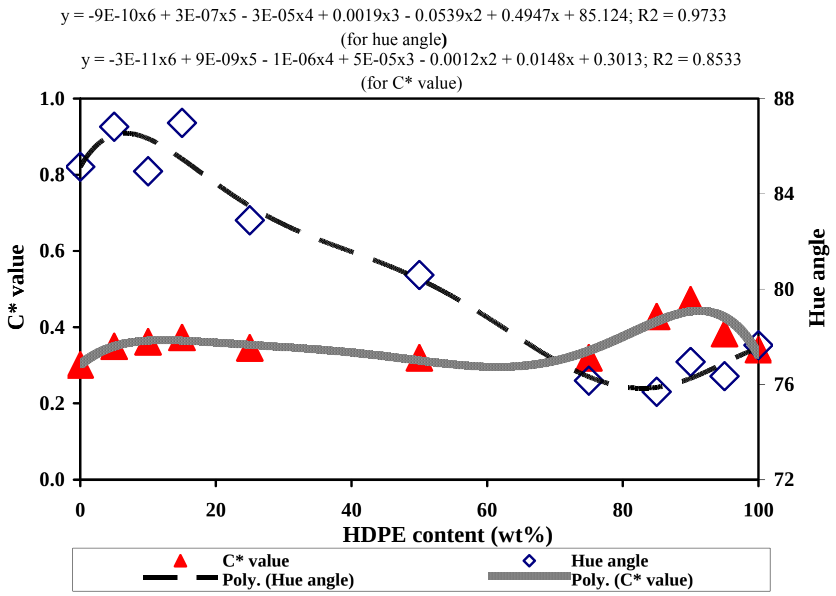

Figure 7: Chroma and hue angle of blend blown films with different HDPE weight percent.

Lightness (L^*) and chromaticity parameters a^* (red–green) and b^* (yellow–blue) of the blend films were reported and then considered for calculating other terms of visual perception of color such as chroma and hue angle. Values of L^*, a^*, and b* are illustrated in Figures 4 and 6. These data correspond to transmission spectrophotometry under standard illuminant D65.

4.5. Hue angle

Hue angle varies within 0-360^o [24]. Hue angle for the samples are located in a part of Cartesian coordinate in which a^* and b^* are both positive, i.e. redness and yellowness region (0-90^o). Regarding the magnitude of the hue angles, it is evinced that the color is located very close to the b^* axis and far from a^* axis which corresponds to yellow color. It means that the saturation or hue of the samples is predominated by b^* and not a^*.

Via incorporating LDPE into HDPE, hue angles shifted to less yellowish; in particular for HDPE-rich blend films in comparison with LDPE-rich blend films. The hue angle for blend films with 15 to 85% HDPE ranged from 87 to 75.7. The value for the angle obtained for LDPE film was higher than pure HDPE film. There was not any significant difference in the hue angle values of samples containing either more than 75% HDPE, or less than 15% HDPE. As illustrated in Figure 7, the hue angle (h^o) shifts towards $+b^*$ (yellowish) by decreasing HDPE content. Comparing the hue angle values of the blends, they generally reached higher levels at lower HDPE contents. As we can see, there is not the same order as described for the hue angle comparing with their L^*, a^*, b^*, C^* counterparts (Figures 4, 6, 7) and also the changes in h^o are more clear and larger. This is because of usefulness of b^*/a^* ratio, by which the color variation in objects is discriminated better than a^* and b^*. Accordingly, hue angle which corresponds to the ratio shows the differences of the films better.

As can be observed for miscible blends (HDPE-rich blends), the hue angle is lower than that of immiscible blends. This may imply the characteristic behavior of the miscible PE blend films which their h^o value is even lower than pure HDPE film.

On the whole, hue angles of the films did not follow the same order as other CIE coordinates. From Figure 7, it is apparent that in composition range of 15-85% HDPE, there is rather a linear relation between hue angle and composition and a dramatic decrease in h^o happens by increasing HDPE content. In fact, hue angle was the only parameter that showed a clear (and rather a linear) composition-dependency just in the ratios of larger than one forth of components. These scrutiny on chroma and h^o corroborates the assertion that chroma could not be used as a remarkable parameter when color is used as a criterion of composition-dependency of blend film properties.

A polynomial is obtained after curve fitting for the plot of hue angle values vs. various HDPE concentrations, which is presented in Figure 7. Using the graph and the fitted equation, prediction of h^o value becomes possible for every HDPE ratio in the blend films. As a result, an implement for predicting hue of two-component blend film samples is offered.

4.6. Color Intensity

Here, we introduce a quantifiable parameter for transparent polymer blends, called color intensity. Color intensity or CI is defined as the difference in color between a point and a central axis in the CIELAB color space (100, 0, 0) and consequently, can be calculated from the following equation [11]:

$$CI = \sqrt{(100 - L^*)^2 + a^{*2} + b^{*2}}$$

The color intensity values for HDPE and LDPE films were 3.95 and 3.61, respectively, but necessarily, for the blown blend films the values do not grow up linearly with HDPE ratio. CI values for HDPE- and LDPE-rich blend films show a prominent trend and HDPE-rich blend films have the most observable CI values. Observations based on CI results showed that CI value increases for samples containing 15- 85% HDPE, and then falls down (Figure 8). CI defined by the above equation is a function which represents a color distance of films from the absolute white point in the CIE space [11]. Moreover, CI values are absolute values like L^*, a^*, and b^* so that each value of CI corresponds to a particular color.

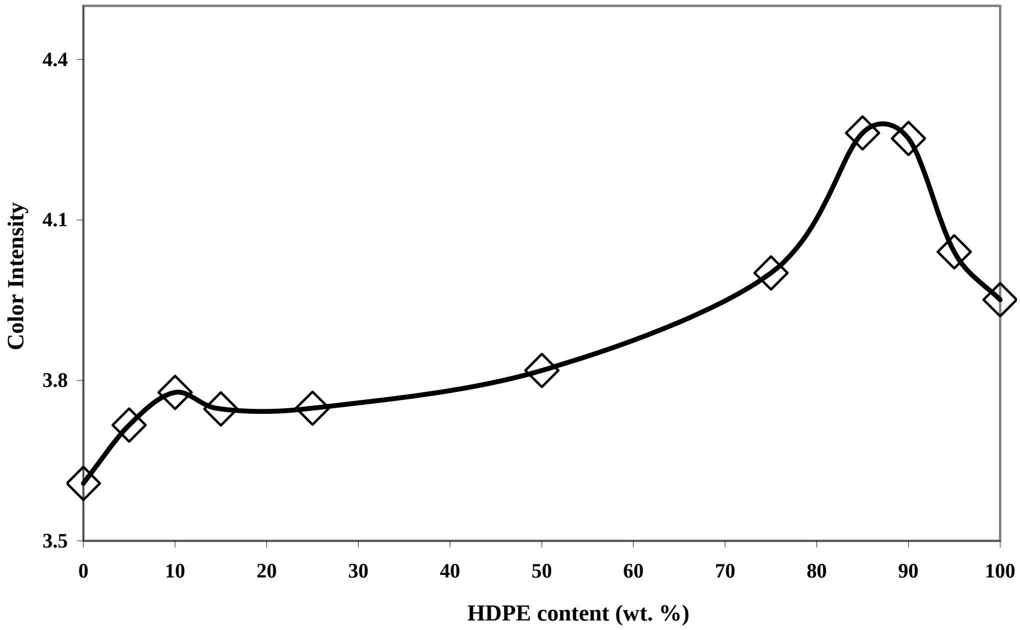

Figure 8: Color intensity of blend blown films with different HDPE weight percent.

Figure 8 shows that CI parameter clearly and typically expresses the optical properties of these blown blend films with variation in second phase content. Color intensity data also show a different and outstanding behavior of the HDPE-rich blend films. Although visual perception of the films can not reveal the difference in their optical properties, CI values shows clear distinction for films containing 5-25% LDPE. Consequently, CI parameter could be a valuable factor which distinguishes optical behavior of the blend films containing various ratios of components.

Because the chromaticity of the films was slight and their lightness was large (higher than 90), color intensity of the films typically reflects the level of their L^* values and it is mostly a measure of lightness of the films. Anyhow, when we deal with colorless (low chroma) films, generally we might not establish a linear relationship between color intensity and the variety of blend composition.

It is noted that although color differences of the samples are not significant, the CI shows difference in the samples at higher order than CIE coordination values; therefore it is a beneficial parameter for comparing transparent films, particularly the blends. Due to the miscibility, HDPE-rich blend films have the highest CI and noticeable trend; however, for immiscible blend films, the CI showed descending trend as HDPE content reduces.

As mentioned earlier, composition and blending conditions can influence the color and the tristimulus values of the final product [5]. In summary, it is clear from Figures 1 to 8 that CIELAB coordinates in transmission mode are affected by composition of the blend films, so that for HDPE-rich blend films, tristimulus parameters are prominent. As a consequence, it purports the presence of low amount of LDPE in HDPE matrix, causing more conspicuous differences in optical behavior of blend films. This is an indication that the HDPE-rich blend films have different structure as compared with that of other blend films and their constituents. This would refer to the influence of miscibility on colorimetric parameters of transparent polymer blend films. Based on our investigations, it is asserted that the color stimuli parameters, in particular h^o and CI, can quantifiably report differences in optical properties stem from miscibility/immiscibility at various compositions of the blend films as a facile mean.

4.7. Comparing films' color under different illuminants

Figures 9 and 10 report CIELAB coordinates of the films under illuminants A and TL84. A similar trend is found with that of illuminant D65 for color stimuli of the blown blend films.

Data of different light sources are reported first to see if the trend of CIE values versus composition of the blend films is affected by light source, and second to find if metamerism phenomenon is observed for any pair of films.

4.8. Inspecting metamerism

CIE coordinates for samples under different illuminants are compiled in Figures 9 and 10. Illuminant metamerism corresponds to the metamerism due to change in illuminants; it means a pair which matches under a specific light source and do not match under other sources. According to Figures 9 and 10 and also Figures 4 and 6 and then by comparing color stimuli of all samples under three illuminants (D65, A, and TL84) it can be inferred that there is no couple of films with identical under a certain illuminant and different color stimuli parameters under another one. Therefore, no illuminant metamerism is concluded for the samples.

Due to the fact that both constituents of the blend films are polyethylene which expressed by the empirical molecular formula $(CH_2)_n$, their close tristimulus values or even the metamerism phenomenon might be probable. Thus, if we dealt with a blend of two different types of polymers with various chemical structures, the $CIEL^*a^*b^*$ coordinates would not be so close [14, 25, 26].

In chemistry, the word “metamerism” is occasionally used to describe structural isomerism. Based on the original description of the term metamerism, this word was probably introduced in color description because similarly the same molecular formula (tristimulus values) yields completely different structural formula (spectral properties) [14]. From this point of view, since HDPE chains are linear and LDPE chains are long and highly-branched, the polymers have different molecular structure. In addition, the degree of polymerization and average molecular weight of the polymers are different, so they do not have the same molecular structure. Consequently, these differences can be a source of dissimilarities in physical properties such as optical properties, so for LDPE and HDPE films, the metamerism phenomenon was not observed. It is also one of the reasons for different color stimuli parameters of their blend films.

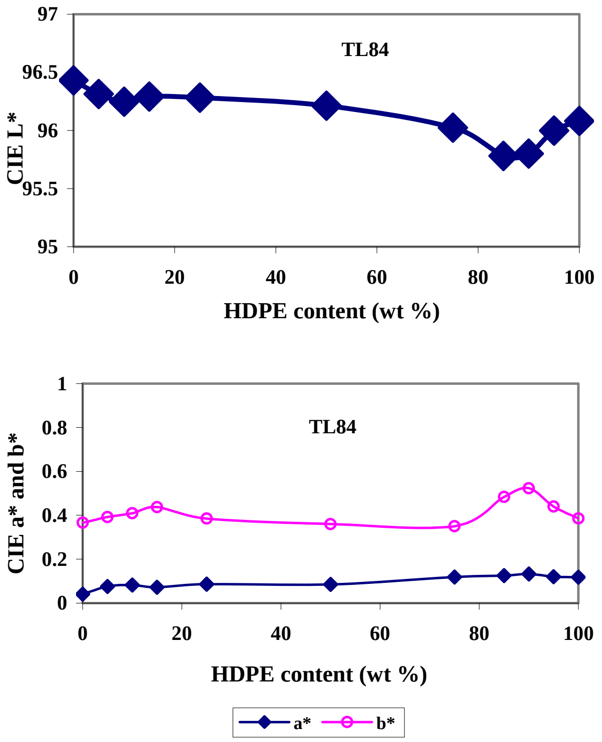

Figure 9: Tristimulus color coordinates CIELAB of the blown films of blends under illuminant TL84 in transmission mode as function of HDPE weight percent.

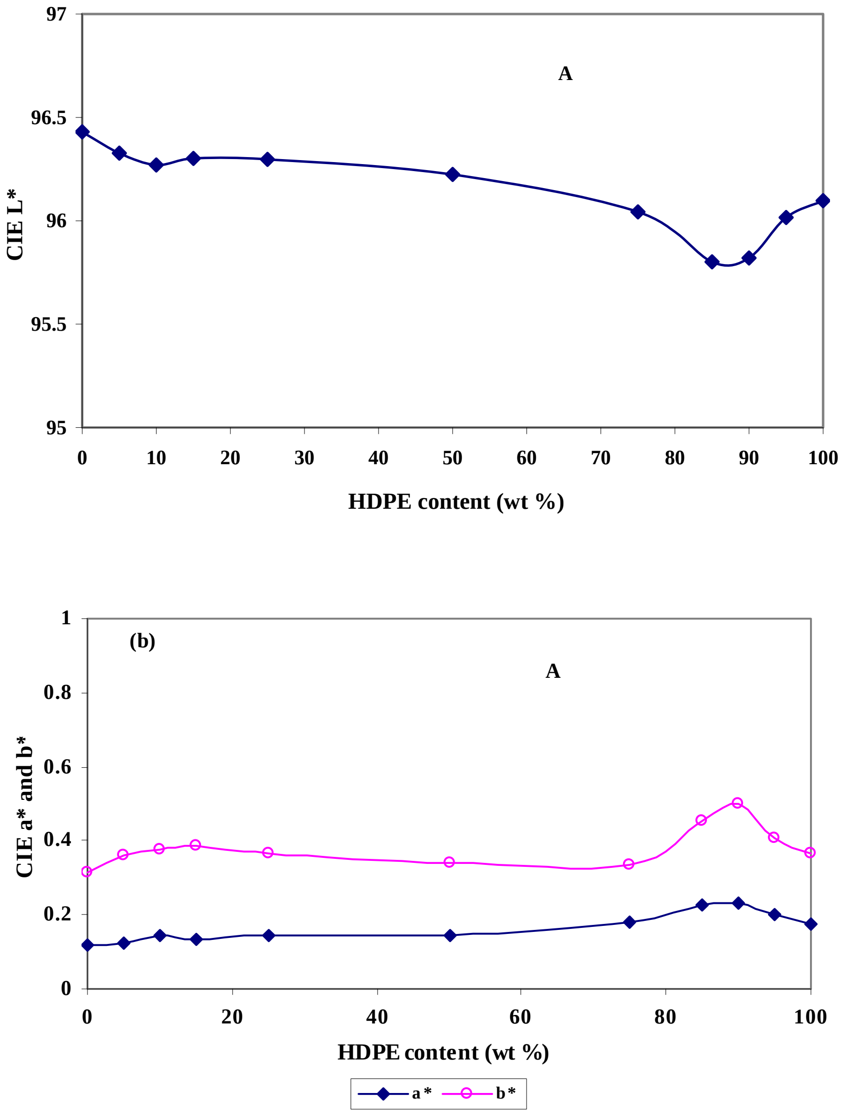

Figure 10: Tristimulus color coordinates CIELAB of the blown films of blends under illuminant A in transmission mode as a function of HDPE weight percent.

4.9. Yellowness and whiteness indices

According to ASTM E313, "yellowness index and whiteness index provide us with numbers that correlate with visual ratings of yellowness or whiteness of white and near white or colorless object-color specimens, perceived in daylight by an observer with a normal color vision. In terminology, *Whiteness index (WI)* is a number, calculated through a certain demarche from colorimetric data, which shows the degree of departure of an object color from that of a preferred white, and, *yellowness index (YI)* is also a number, extracted from colorimetric or spectrophotometric data, which is an indication of the degree of drift of an object color from colorless or from a preferred white, towards yellow" [27].

The indices can be calculated from instrumentally measured color coordinates for illuminant D65 and a 10^{o} standard observer as followings:

$$\mathrm{YI} = \frac{100(1.3013 * \mathrm{X} - 1.1498 * \mathrm{Z})}{\mathrm{Y}}$$

$$\mathrm{WI} = \mathrm{Y} + 800(0.3138 - \mathrm{x}) + 1700(0.331 - \mathrm{y})$$

The indices for blend films are illustrated in Figure 11. As can be seen, the trend of changes in yellowness index and whiteness index versus HDPE content oppose each other. When yellowness index is increasing, whiteness index is decreasing and vice versa. Yellowness index of HDPE and LDPE films were 0.59 and 0.69, respectively. And for blend films YI increases slightly with increasing HDPE content up to 10% and no variation in YI of the blend films containing 10-75% was observed; but the trend of changing YI for HDPE content in the range of 85-100% was outstanding which as mentioned earlier it is due to partial miscibility of the blends in this HDPE content range. This trend coincides that of b^* values which is correspond to the blueness-yellowness axis.

Whiteness index for HDPE and LDPE films was 88.58 and 89.66, respectively. Again here, the trend of variations in whiteness index for blend films with more than 75% HDPE (miscible blends) was outstanding and it was different as compared with that of other compositions. On the whole, the trend of b*, C* and YI versus HDPE content was similar and it was in a reverse order to that of data of L* and WI. Sketching the optical parameters against composition reveals two distinguishable regions:

Region I: less than 25% LDPE composition range (corresponding to the homogeneous or single phase blends)

Region II: more than 25% LDPE composition range (corresponding to the heterogeneous or biphasic blends)

The optical parameters in region I were found to be especially different from those of the region II. Consequently, all L*, b*, C*, CI, WI and YI curves against composition confirm the trends observed in DSC traces, that is the trend of these parameters has coordination with the limit of miscibility of the binary polyethylene blend system. In addition, another advantage of the curves of these colorimetric parameters remains in determination of the critical composition. In the case of the studied blends, 25% LDPE is the critical composition below which the blend is miscible and colorimetric parameters are more pronounced. Whereas at higher LDPE contents the trend changes.

Actually, we comprehended that when two polymer constituents which have relatively similar appearance or there is small difference between their optical properties, what characteristics appear in the final blend of the two constituents. In this paper, it was indicated that hue angle, CI, YI and WI are useful factors which through them the difference in the samples are large enough to compare the transparent films of polyethylene blends.

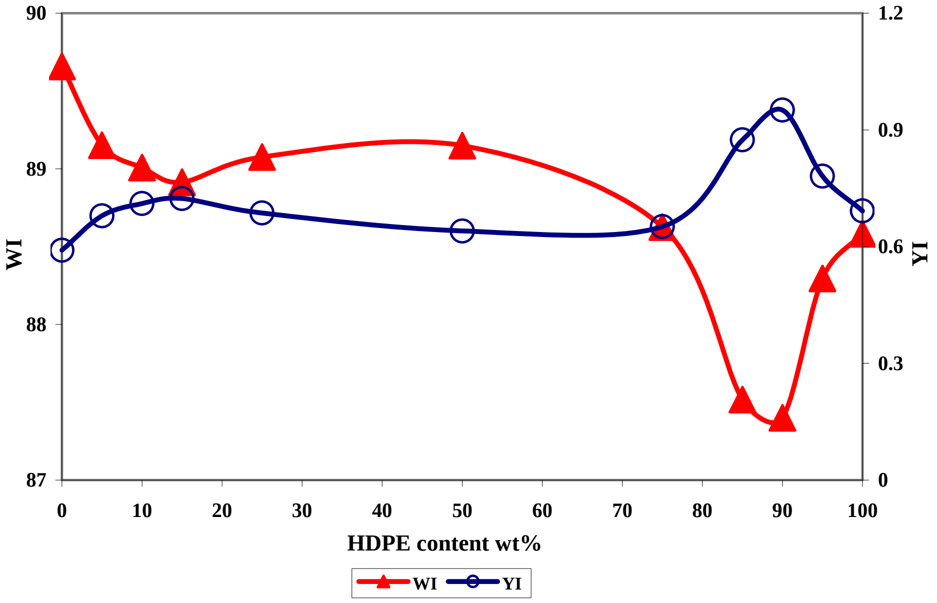

Figure 11: Yellowness and whiteness indices vs. HDPE content for films of blends.

5. Conclusions

We have successfully applied spectrophotometric measurement as a tool for characterizing polymer blend systems. In this paper, we prepared films of LDPE/HDPE blend and then the suitability of spectrophotometry technique for measuring the optical properties of the blend films and the influence of the parameter blending ratio on miscibility, transmittance spectrum and CIE coordinates of the resulting transparent films were investigated. Transmission spectra became a base for quantifying tristimulus color coordinates. Miscibility was revealed via DSC for films of HDPE-rich blends but it was revealed immiscibility in other compositions of the blends. It is distinguishable from lightness (L^*) values that the presence of HDPE constituent in LDPE decreases L^*, and also for blend films containing more than 75% HDPE, there was more obvious change. The Hue angle of the films first descended with increasing HDPE content in the blend films up to 85% and then it increased. The colorimetric parameters obtained from spectrophotometric measurements showed a distinguishable trend for the blend films in miscible composition range compared to that of immiscible blend films. Whiteness and yellowness indices showed the same trend as L^*, b^* and C^*, respectively.

6. References

1. S. Wang, Y. Zhang, W. Ren, Y. Zhang, H. Lin, Morphology, mechanical and optical properties of transparent BR/clay nanocomposites, *Polym Test,* 24 (2005), 766-774.
2. P. B. Harrison, R. R. J. Maier, J. S. Barton, J. D. C. Jones, S. McCulloch, G. Burnell, Component position measurement through polymer material by broadband absolute distance interferometry, *Meas Sci Technol,* 16 (2005), 2066-2071.
3. D. R. Zhang, Z. X. Ma and Q. Z. Yang, *Design of Modern Rubber Recipes*, Chemical Industry Press, Beijing, 1996.
4. H. Wu, J. Fan, Measurement of radiative thermal properties of thin polymer films by FTIR, *Polym Test,* 27 (2008), 122-128.
5. C. O. Phillips, E. H. Jewell, T. C. Claypole, D. T. Gethin, Development of measurement techniques to characterize the optical properties of transparent films with application in in-mould decoration, *Meas Sci Technol,* 19 (2008), 025703.
6. S. G. Lee, R. Shamey, D. Hinks, W. Jasper, Development of a comprehensive visual dataset based on a CIE blue color center: assessment of color difference formulae using various statistical methods, *Col Res Appl,* 36 (2011), 27-41.
7. I. Niskanen, J. Raty, K.-E. Peiponen, *Meas Sci Technol,* 17 (2006), N87-91.
8. B. Yuangsoi, O. Jintasataporn, N. Areechon, P. Tabthipwon, The pigmenting effect of different carotenoids on fancy carp (Cyprinus carpio), *Aquacul. Nutri.* 17 (2011), 306-316.
9. L. Simonot, M. Hebert, D. Dupraz, Goniocolorimetry: from measurement to representation in the CIELAB color space, *Col Res Appl,* 36 (2011), 169-178.
10. S. Ignell, U. Kleist, M. Rigdahl, On the relation between color, gloss and surface texture in injection-molded plastics, *Color Res Appl,* 34 (2009), 291-298.
11. J. Berberich, K. H. Dee, Y Hayauchi, C. Portner, A New method to determine discoloration kinetics of uncoated white tablets occurring during stability testing-an application of instrumental color measurement in the development pharmaceutics, *Int J Pharm,* 234 (2002), 55-66.
12. M. Mohammadi, A. A. Yousefi, M. Ehsani, Thermorheological analysis of blend of high- and low-density polyethylenes, *J Polym Res,* 19 (2012), 9798-9809.
13. K. Nassau, *Color for Science, Art and Technology,* Elsevier science, Amsterdam, 1998.
14. Noborou O, Robertson AR, *Colorimetry: Fundamental and Applications,* John Wiley & Sons, West Sussex, 2005.
15. C. A. Fonseca, I. R. Harrison, An investigation of co-crystallization in LDPE/HDPE blends using DSC and TREF, *Thermochemica Acta,* 313 (1998), 37-41.

16. H. S. Lee, M. M. Den, Blends of linear and branched polyethylene, *Polym Eng Sci,* 40 (2003), 1132-1142.
17. B. Neway, U. W. Gedde, Influence of the method of mixing on homogeneity and crystallization kinetics of blends of linear and branched polyethylene, *J Appl Polym Sci,* 94 (2004), 1730-1736.
18. P. S. Sonawane, S. Radhakrishnan, J. A. Bhangale, A. L. Gadhavi, A. Khare, Development of nanofibrous Morphology in LDPE/LLDPE/PP blends an its effect on mechanical properties of blend films, *J Appl Polym Sci,* 107 (2008), 4005-4012.
19. A. Wlochowicz, Eder M, Distribution of lamella thickness in isothermally crystallized polypropylene and polyethylene by differential scanning calorimetry, *Polymer,* 25 (1984), 1268-1270.
20. A. Siegman, Y. Nir, Structure-property relationships in blended of linear low- and conventional low-density polyethylene as blown films, *Polym Eng Sci,* 27 (1987), 1182-1186.
21. I. A. Hussein, Implication of met compatibility/incompatibility on thermal and mechanical properties of metallocene and Ziegler-Natta linear low density polyethylene (LLDPE) blends with high density polyethylene (HDPE): influence of composition distribution and branch content of LLDPE, *Polym Int,* 53 (2004), 1327-1335.
22. K. Cho, B. H. Lee, K. M. Hwang, H. Lee, S. Choe, Rheological and mechanical properties in polyethylene blends, *Polym Eng Sci,* 38 (1998), 1969-1975.
23. D. Curto, F. P. La Mantia and D. Acierno, The rheological behavior of HDPE/ LDPE blends. I. End effects and shear viscosity, *Rheol Acta,* 22 (1983)**,** 197-208.
24. G. N. Mock, *Modern Concern of Color and Appearance*, Science Publishers, Enfield, 2000.
25. H. Park, T. W. Lee, Y. C. Kim, O. O. Park, J. K. Kim, White polymer light-emitting devices from ternary-polymer blend with concentration gradient, *Chem Phys Let,* 403 (2005), 293-297.
26. Q. Niu, Y. Xu, J. Jiang, J. Peng, Y. Cao, Efficient polymer white-light-emitting diodes with a single-emission layer of fluorescent polymer blend, *J Luminescence,* 126 (2007), 531-535.
27. ASTM E313, *ASTM Standard Practice for Calculating Yellowness and Whiteness Indices from Instrumentally Measured Color Coordinates.* American Society Testing and Materials, 2005.