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Surface hydrophobicity alteration of fractionated paraffin wax, crude by-product polyolefin wax and their blend

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Abstract−The surface compositions of crude by-product polyolefin wax (wax K) from a naphtha cracking unit, fractionated commercial paraffin wax (wax J) and their blend (wax M) were compared, under various conditions, by using FT-IR. Then a practical criterion was theoretically derived by back-of-the-envelope-calculation to estimate the diffusivity for the surface enrichment of hydrophilic functional groups. The hydrophobicity in terms of chemical structure and functional groups was altered by changing the environment as well as by blending wax K with wax J. The surface properties of wax J and wax M turned out more hydrophobic than that of wax K within the experimental period of water-submerged condition, even though the structure and functional groups on the surfaces of all waxes under ambient atmospheric condition are extremely similar. Thus the blend of wax M behaved unlike wax K but similarly to wax J in terms of alteration of hydrophobicity. Such values of diffusivity as 1.35×10^{-11} cm^2/s and 1.96×10^{-11} cm^2/s are established for wax J and wax M, respectively, under 1 day water-submerged condition. Furthermore, under 1 week water-submerged condition, the values of their diffusivity for wax J, wax K and wax M are estimated as 3.06×10^{-12} cm^2/s, 7.23×10^{-11} cm^2/s and 1.50×10^{-11} cm^2/s, respectively. The obtained values of diffusivity are consistent, in terms of the order of magnitude, with the value of diffusion coefficient of 5.75×10^{-11} cm^2/s obtained, using a very complicated empirical-formula, by Chen et al. for the investigation of surface-modifier enrichment. Thus, the suggested criterion may be very useful and practically applied to clarify the process of surface enrichment from general polymer-blends.

Key words: Crude By-product Polyolefin Wax, Commercial Paraffin Wax, Blend, Surface Hydrophobicity, Diffusivity, Surface Enrichment

INTRODUCTION

Paraffin wax is widely used in applications such as water-repellent treatment of paper and cardboard [1-3], printing inks [4], processing agent for improving rheological property [5], as well as in the food [6], cosmetic [7] and pharmaceutical industries [8]. The characteristics of blends have been investigated mainly in the processing of polymer and wax to improve the unfavored property of a certain material by mixing it with compatible additives in melt state. Mpanza and Luyt [5] compared different paraffin waxes compatible with polyolefins as processing agents for low density polyethylene to improve processing because it is difficult to process polyethylene, especially when it comes to recycling. In their study the effect of blending was the improvement in melt flow and some other physical properties of the blends. In addition paraffin waxes have been developed as phase change materials (PCM) which utilize their latent heat for thermal energy storage (TES) to be used for various heat and cool storage applications [9,10].

Crude by-product polyolefin wax is mainly generated in large scale as a by-product from a naphtha cracking unit or the facilities producing commercial polyethylene or polypropylene, and most crude by-product polyolefin wax is being disposed by the regulation on the waste-material of the ministry of environment of Korea. Therefore, it becomes absolutely necessary to recycle the crude by-product polyolefin wax for the protection of the environment. Not to mention solving such environmental problems, it is important to investigate the possibility that relatively high cost-fractionated paraffin wax may be replaced for its extensive application by its blend with cheap, recycled waste olefin wax. Thus, the huge contribution of this novel blend may be extensively applied to economical and environmental aspects.

Molecular rearrangement has been known to take place to minimize the difference in polarity between the polymer surface and its environment and to lower the interfacial energy by thermodynamic driving force [11-13]. Due to the thermodynamic incompatibility among the components in a polymer blend, the component with the lowest surface energy (hydrophobic polymer) will spontaneously migrate at the air interface to reduce the system's interfacial tension if the blend is equilibrated in air [14]. For immiscible blends the migration is driven by the polymers' surface free energy differences. The component with lower surface free energy is enriched at the surface in order to minimize the polymer/air surface tension [15-17].

In this paper the novel feature of blending of crude by-product polyolefin wax (wax K) and technical grade-commercial paraffin wax (wax J) is presented, where the blend (wax M) of wax K and wax J is suggested to replace wax J. The surface compositions of wax K, wax J and wax M are evaluated and are compared in terms of their chemical structures and functional groups by using FT-IR analysis. In particular, a possible enhancement of hydrophobicity

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in terms of chemical structures and functional groups is expected by blending wax K with wax J. Moreover, regarding the migration of hydrocarbon molecules attached to the hydrophilic functional groups, the order of their diffusivity is estimated for wax J, wax K and their blend (wax M), placed under wet condition.

EXPERIMENTAL

1. Materials

Technical grade paraffin wax, wax J (Mn=585, Polydispersity Index=1.05) was purchased from Nippon Seiro Co. and wax K (Mn =228, Polydispersity Index=29.0) was obtained as crude waste from the naphtha cracking plant located at Yeochun-Chemical Complex, Korea. Wax K and wax J were mixed seven to three in weight ratio at ambient condition. The blend was prepared by melt mixing in a Brabender Platograph at a set temperature of 140 °C and a rotation speed of 30 rpm for 10 min, after which it was cooled slowly at room temperature to prepare wax M. Then the surface of the blend, wax M was kept equilibrated with air at room temperature for at least a month prior to the experiments. For wax J and wax K the same heating and cooling procedures were applied as that of wax M prior to the experiments.

2. Methods

Each 30 g of wax J, wax K and wax M was prepared in 50 ml beaker as a specimen. The beaker was filled with 20 ml of demineralized water for the specimen required under water-submerged condition. The specimens of waxes interfaced with water layer in water-submerged condition were used to observe the alteration of interfacial chemical structure and functional groups of wax J, wax K and wax M, from those of the waxes placed under ambient atmospheric condition before being submerged in water. The structure and functional groups of wax J, wax K and wax M were analyzed by FT-IR spectrometer (Spectrum GX & Auto-Image, Perkin-Elmer) with nitrogen-purge system to provide an environment free from water and carbon dioxide. One milligram of each specimen of wax J, wax K and wax M was taken by scratching its flat surface, placed not only in ambient atmospheric condition but also in the water-submerged conditions for 1 week as well as 1 day, with the flat-end of micro-spatula as shallowly in depth as possible. The scratched depth was measured by digital optical micrometer kit (Model 8400K, J. Chadwic Co.) to range from 30 µm to 50 µm. Then it was used to prepare the pellet according to KBr-pellet technique to obtain the corresponding FT-IR spectrum.

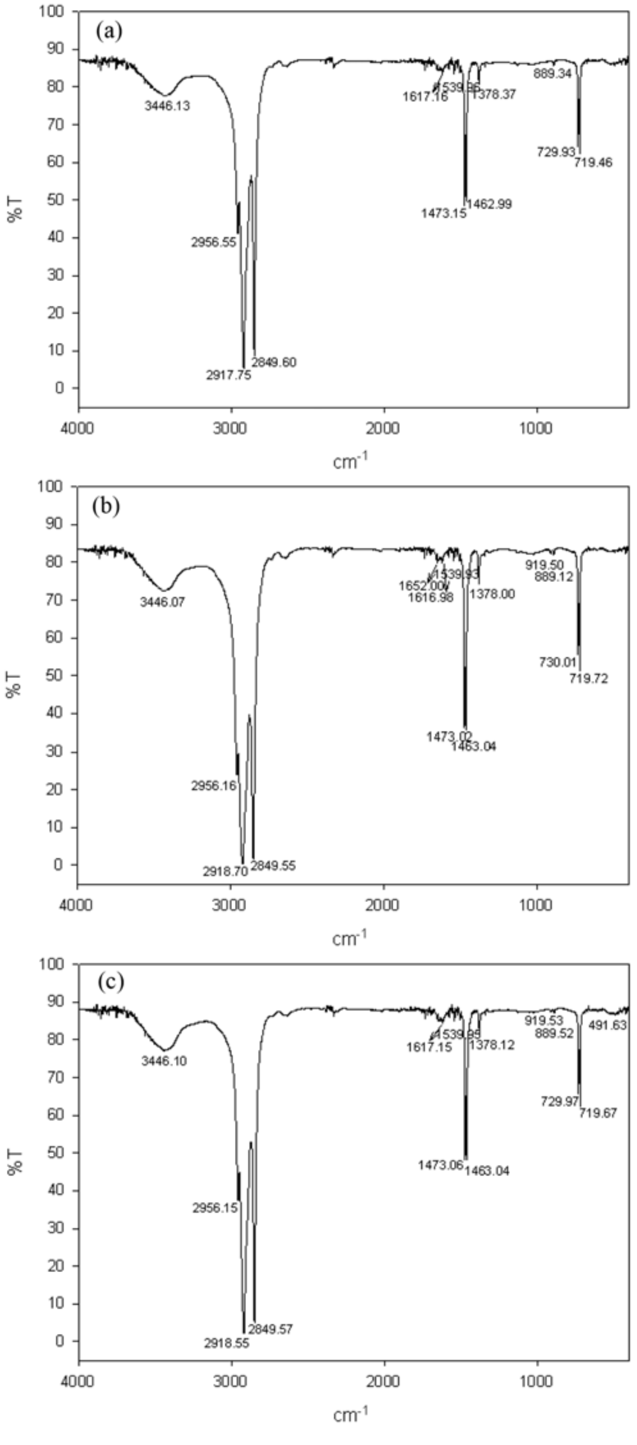


Fig. 1. FT-IR spectrum of % transmittance under ambient atmospheric condition: (a) Wax J; (b) Wax K; c) Wax M.

RESULTS AND DISCUSSION

1. Structure and Functional Groups under Ambient Atmospheric Condition

The structure and functional groups of wax J, wax K and wax M under ambient atmospheric condition were analyzed with FT-IR spectrometer and their FT-IR spectra are shown as in Figs. 1(a), 1(b) and 1(c), respectively. In Figs. 1(a)-(c) the absorption peaks of C-H stretching vibrations of alkane were found in common at the frequencies of 2,956 cm^{-1} , 2,919 cm^{-1} and 2,850 cm^{-1}, which were known as in its typical region of 3,000-2,850 cm^{-1}. These spectra showed typical C-H stretching absorption peaks of paraffin wax as well as polyolefin wax. In fact, the FT-IR spectrum of wax K placed under ambient atmospheric condition was matched to be low density polyethylene (LDPE). The strong peaks for C-H bending of -CH$_2$- and a weak peak for C-H bending of -CH$_3$ were commonly found at the frequencies of 1,473 cm^{-1} and 1,463 cm^{-1}, and 1,378 cm^{-1}, respectively. At both frequencies of 730 cm^{-1} and 719 cm^{-1} these spectra for all waxes exhibited commonly strong absorption peaks of C-H out-of plane bending of alkene. Since the strengths of typical alkane C-H stretching absorption peaks of all waxes seem to be similar to each other, those absorption peaks may be treated as a reference peak to compare the absorption strength of other peaks. Compared to the reference peaks, the strength of such absorption peaks of wax K as C-H bendings of -CH_2- at both frequencies of 1,473 cm^{-1} and 1,463 cm^{-1}, and C-H out-of plane bending of alkene at both frequencies of 730 cm^{-1} and 719 cm^{-1} were found stronger than that of wax J. Besides C=C stretching vibration of alkene was merely observed at the frequency of 1,680-1,600 cm^{-1} (1,652 cm^{-1} and 1,617 cm^{-1}). The structure and functional groups of wax J, wax K and wax M under ambient atmospheric condition were not easily distinguishable. The almost identical structure and non-polar functional groups of wax J, wax K and wax M under ambient atmospheric condition, may be explained by the fact that all the waxes stored under ambient atmospheric condition have their surface interfaced with non-polar air to lower their surface polarity. Nevertheless such a broad polar peak as O-H H-bonded functional group commonly appears around 3,500-3,200 cm^{-1} of FT-IR spectra for all the waxes. However, FT-IR spectra in their fingerprint regions are somewhat different as shown in Figs. 1(a)-(c); both small absorption peaks at 919 cm^{-1} and 889 cm^{-1} exist for wax K and wax M, while only one small absorption peak exists at 889 cm^{-1} for wax J.

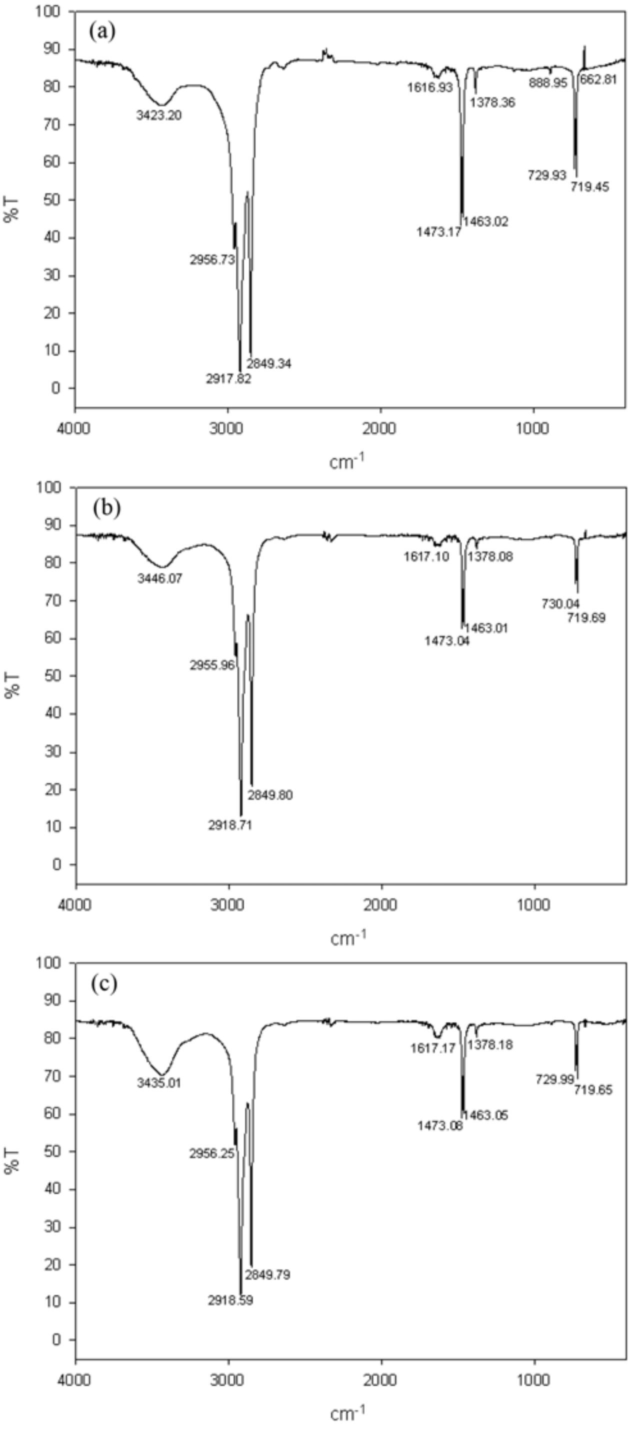


Fig. 2. FT-IR spectrum of % transmittance under water-submerged condition for 1 day: (a) Wax J; (b) Wax K; (c) Wax M.

2. Structure and Functional Groups under 1 Day Water-submerged Condition

The structure and functional groups of wax J, wax K and wax M under 1 day water-submerged condition were also analyzed with FT-IR spectrometer and their FT-IR spectra are shown as in Figs. 2(a), 2(b) and 2(c), respectively. Since polar environment was provided in water-submerged condition this polar environment was expected to increase the surface polarity of the surface of these waxes. As a result, the structure and functional groups of wax J, wax K and wax M under 1 day water-submerged condition were different from those under ambient atmospheric condition in that a few peaks of absorption changed to be relatively weaker or stronger than those under ambient atmospheric condition. Since the strengths of typical alkane C-H stretching absorption peaks of all waxes still seem to be similar to each other and to remain the same as those under ambient atmospheric condition, typically those absorption peaks may be treated as reference peaks to compare the absorption strength of other peaks. Compared to the reference peaks, the strengths of such nonpolar absorption peaks of wax K as 1) C-H bendings of -CH_2- at the frequencies of 1,473 cm^{-1} and 1,463 cm^{-1}; 2) C-H bendings of -CH_3 at the frequencies of 1,378 cm^{-1}; 3) C-H out-of plane bending of alkene at both frequencies of 730 cm^{-1} and 719 cm^{-1}, get weaker than those of wax K under ambient atmospheric condition. However, the strengths of those nonpolar peaks of wax J under 1 day water-submerged condition seem to remain the same as those of wax J under ambient atmospheric condition. Thus, it may be attributed to the more-nonpolar property of wax J than wax K. It is noteworthy that the strength of absorption peaks of C=C stretching vibration of alkene remains the same at the frequencies of 1,617 cm^{-1} for all waxes under 1 day water-submerged condition. In addition wax J produced an additional peak at 663 cm^{-1} under 1 day water-submerged condition.

3. Structure and Functional Groups under 1 Week Water-submerged Condition

Figs. 3(a), 3(b) and 3(c) show FT-IR spectra of wax J, wax K and wax M, respectively, placed under 1 week water-submerged condition. For wax K, C=C stretching vibration of alkene observed at the frequency of 1,617 cm^{-1}, disappears and shifted to 1,631 cm^{-1}. However, for wax J and wax M, the peak observed at the frequency of 1,617 cm^{-1} still remains without the appearance of any new peak. While the absorption peak-growths of hydrophilic O-H H-bonded were observed to develop at a frequency around 3,500-3,200 cm^{-1} for all waxes, the strength of the reference peaks of C-H stretching vibrations of hydrophobic alkane remains the same for all the waxes under 1 week water-submerged condition, as shown in Figs. 3(a)-(c). However, the peak-growths of hydrophilic O-H H-bonded for wax J and wax M were insignificant, while its peak-growth for wax K was prominent. This observation shows the interfacial hydrophilicization of polyolefin wax due to redistribution of functional groups at the interface. The configurational entropy per segment of polymer chains near surfaces is much lower than in bulk polymer systems [18,19]. The difference of conformational entropic penalty between a polymeric chain existing at the surface and that in the bulk, decreases with a decrease in number average molecular weight. Hence, it is reasonable to consider that high polymer molecular weight experiences a large entropy penalty and the polymer layer near the surface would be expected to be depleted in high molecular weight polymer components and enriched in lower molecular weight ones as result of reduced configurational entropic penalty at the surface [20]. Therefore, the hydrophilic functional groups are continuously driven to migrate to the surface of the waxes in order to lower the interfacial free energy by thermodynamic driving force under 1 week-water submerged condition. Since the number-average molecular weight (M_n) of crude wax K is as half as that of fractionated wax J, under the circumstances, the resultant-relatively short chain of wax K-hydrocarbon molecules attached to hydrophilic functional groups would be more helpful for its rapid migration to the wax-surface under water-submerged condition than the relatively long chain of hydrocarbon molecules of wax J. As number-average molecular weight (M_n) decreases, the number density of chain end groups including hydrophilic functional groups increases [17]. Moreover, crude wax K has much more hydrophilic functional groups such as O-H H-bonded functional group than fractionated wax J. Hence the difference of the peak-growth for wax J and wax K may be attributed to the difference of relative condition of waxes regarding the concentration of hydrophilic functional groups in their surfaces and bulk phases, as well as the conformational entropic penalty and the mobility, determined by their molecular weight.

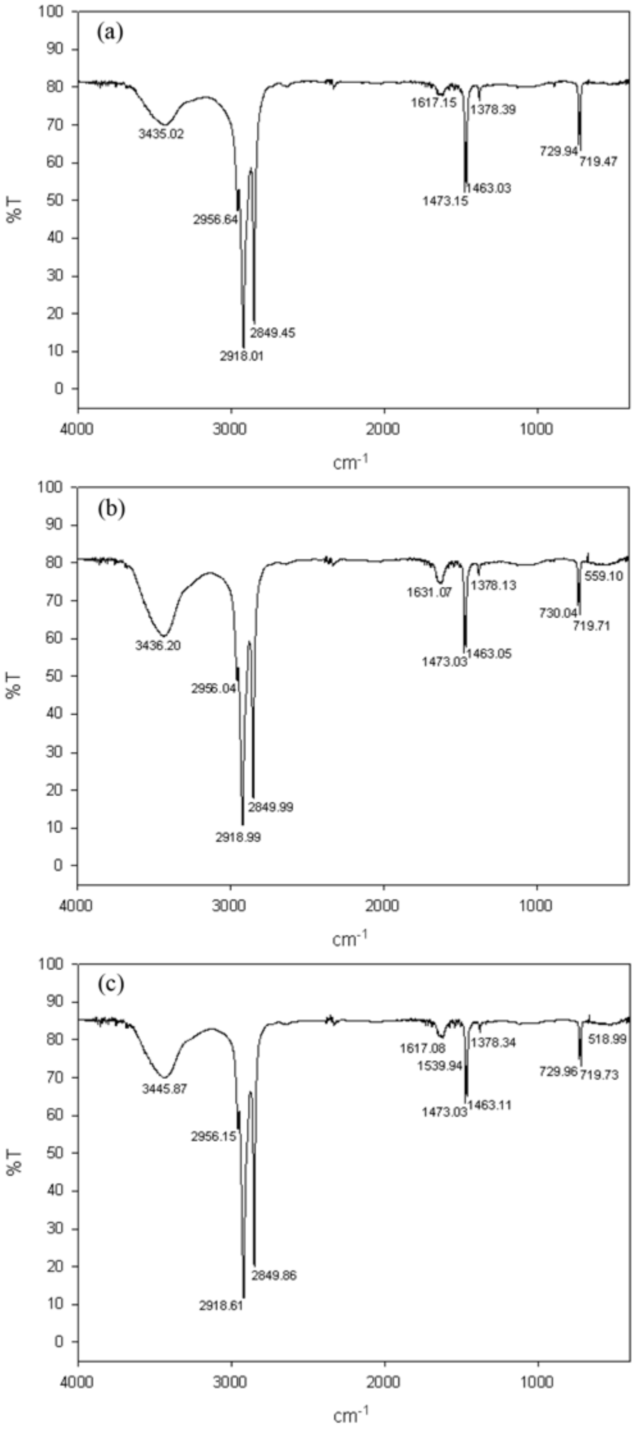


Fig. 3. FT-IR spectrum of % transmittance under water-submerged condition for 1 week: (a) Wax J; (b) Wax K; (c) Wax M.

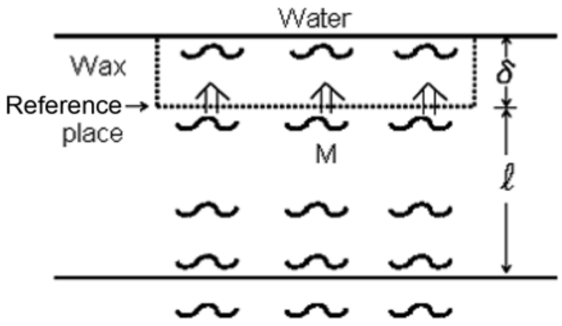
4. Comparison of Hydrophobicity among Wax J, Wax K and Wax M

According to the FT-IR spectra as shown in Figs. 1(a)-(c), Figs. 2(a)-(c) and Figs. 3(a)-(c), the surface properties of wax J and wax M turned out more hydrophobic than that of wax K within the experimental period of water-submerged condition, even though the structure and functional groups on the surfaces of all waxes under ambient atmospheric condition are extremely similar. Thus, the blend of wax M behaved unlike wax K but similarly to wax J in terms of alteration of hydrophobicity. It may be attributed to the fact that the mobility of wax K-molecules from the blend of wax M is hindered by the relatively long chain-conformation of wax J-molecules pertaining to the blend.

5. Estimation on the Diffusivity of Hydrophilic Molecules of the Waxes

It is well known that the mobility of surface-energy reducing additives to polymeric materials is controlled by their diffusion process [21]. Assuming the migration process, toward the wax-surface, of hydrocarbon molecules attached to the hydrophilic functional groups controlled by their diffusion process, one is able to estimate the ballpark figure on their diffusivities on the migration process. The depth of wax-scratch (or the thickness of scratched pieces) after a given period of time, the migration distance of hydrocarbon molecules attached to hydrophilic functional groups to cross over the reference plane at the depth of wax-scratch within the given period of time, their diffusivity, their diffusivity of wax J, wax K and wax M, the absorbance under ambient condition and under water-submerged condition, and their migration time under water submerged condition (i.e., 1 day or 1 week) are denoted as δ, l, D, D_J, D_K, D_M, $A_{ambient}$, A_{water} and t, respectively. The schematic diagram is shown in Figs. 4(a) and 4(b), to describe the migration process of hydrophilic func-

(a) During the period of time, t.



(b) After the period of time, t.

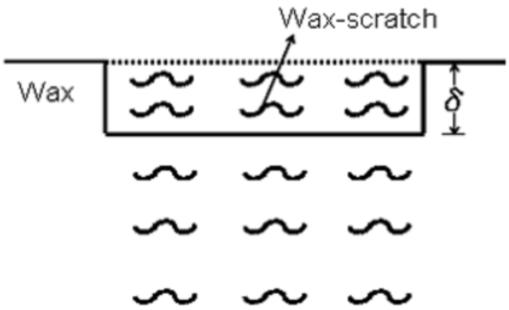


Fig. 4. Schematic diagram on the concept of the suggested criterion to determine their diffusivity with regard to the migration process of hydrophilic functional groups, for surface enrichment, towards wax surface interfaced with water: (a) During the period of time, t; (b) After the period of time, t.
δ: Depth of wax-scratch.
l: Migration distance of hydrocarbon molecules attached to hydrophilic functional groups to cross over the reference plane at the depth of wax-scratch within the given period of time.
M: Hydrocarbon molecules attached to hydrophilic functional groups.

tional groups towards wax surface interfaced with water, and to explain the concept of the suggested criterion to determine their diffusivity. Thus, the diffusivity may be estimated by performing a back-of-the-envelope-calculation in the way $D\sim(l^2/t)$. The absorbance-growth of a hydrophilic functional group takes place with its given peak-width when hydrophilic functional groups migrates cross the plane of the depth (δ) of wax-scratch towards the surface. One may consider the initial amount of hydrophilic functional groups above the unit area of the reference plane to be δ multiplied by its bulk concentration, assuming the depth of δ is deep enough to initially maintain its bulk concentration except near-surface. Therefore, one may assume that the absorbance-growth ratio is equal to the ratio of the sum of the migration distance (l) and the depth (δ), and the depth (δ) in the expression of $(l/\delta)+1\sim(A_{water}/A_{ambient})$. In this manner, the ratio of the migration distance (l) and the depth (δ) may be available for all the waxes. Hence, the diffusivity may be estimated in such a criterion that $D\sim(l^2/t)\sim(\delta^2/t)((A_{water}/A_{ambient})-1)^2$. For the strength of the absorption peaks of hydrophilic O-H H-bonded functional group of all waxes, their values of transmittance were converted to those of absorbance with their absorbance baseline by Beer-Lambert law, as shown in Table 1. For 1 day water-submerged condition, the absorbance-growths of hydrophilic O-H H-bonded functional group were observed for all the waxes except for wax K. Then, using the value of 50 μm as the depth (δ) of wax-scratch, such values as $D_J\sim1.35\times10^{-11}$ cm^2/s and $D_M\sim1.96\times10^{-11}$ cm^2/s are established for wax J and wax M, respectively, under 1 day water-submerged condition. Likewise, under 1 week water-submerged condition, the values of 3.06×10^{-12} cm^2/s, 7.23×10^{-11} cm^2/s and 1.50×10^{-11} cm^2/s are established for the diffusivities of wax J, wax K and wax M, respectively. The established diffusivities of wax J, wax K and wax M are introduced as shown in Table 2. The obtained values of diffusivity are consistent, in terms of the order of magnitude, with the value of diffusion coefficient of 5.75×10^{-11} cm^2/s by Chen et al. [22], who measured the diffusion coefficient of macromolecular surface modifier such as polybutadiene-graft-poly(methyl methacrylate) (PB-g-PMMA) in PB-g-PMMA/PP blends, using very complicated empirical-formula proposed by Quian et al. [23], for the investigation of surface-modifier enrichment.

CONCLUSION

For wax J, wax K and wax M placed under ambient atmospheric

Table 1. Characteristic values of hydrophilic O-H H-bonded functional group from the FT-IR spectrums (3,500-3,200 cm^{-1}) of wax J, wax K and wax M under various conditions

Waxes	Ambient condition			1 Day water-submerged			1 Week water-submerged		
	J	K	M	J	K	M	J	K	M
% Transmittance	77	73	77	75	78	71	70	60	70
Peak height of % transmittance	10	10.5	11	12	9.5	13.5	12	22	15.5
Absorbance baseline	0.061	0.078	0.056	0.061	0.058	0.073	0.086	0.086	0.068
Absorbance	0.053	0.058	0.058	0.064	0.050	0.075	0.069	0.136	0.087

Table 2. Diffusivity values of hydrophilic O-H H-bonded functional group, estimated from the FT-IR spectrums (3,500-3,200 cm^{-1}) of wax J, wax K and wax M under water-submerged condition

Period (water-submerged)	Wax J	Wax K	Wax M
1 Day	1.35×10^{-11} cm^2/s	-	1.96×10^{-11} cm^2/s
1 Week	3.06×10^{-12} cm^2/s	7.23×10^{-11} cm^2/s	1.50×10^{-11} cm^2/s

condition FT-IR spectra showed typical C-H stretching absorption peaks of paraffin wax as well as polyolefin wax. The strong peaks for C-H bending of -CH_2- and a weak peak for C-H bending of -CH_3 were also commonly found. In addition, these spectra exhibited commonly strong absorption peaks of C-H out-of plane bending of alkene. The structure and functional groups of wax J, wax K and wax M under ambient atmospheric condition were not easily distinguishable. Under 1 day-water submerged condition molecular rearrangement was observed to take place at the interface of these waxes. Compared to the reference peaks of C-H stretching vibrations of hydrophobic alkane, the strengths of other nonpolar absorption peaks of wax K get weaker than those of wax K placed under ambient atmospheric condition. However, the strengths of other nonpolar peaks of wax J under 1 day water-submerged condition seem to remain the same as those of wax J placed under ambient atmospheric condition. Thus, it may be attributed to the more-nonpolar property of wax J than wax K. Among all the waxes under 1 week water-submerged condition the peak-growths of hydrophilic O-H H-bonded for wax J and wax M were insignificant, while its peak-growth for wax K was prominent. These observations show the interfacial hydrophilicization of polyolefin wax due to redistribution of functional groups at the interface. The difference of the peak-growth for fractionated wax J and crude wax K may be attributed to the difference of relative condition of waxes regarding the concentration of hydrophilic functional groups in their surfaces and bulk phases, as well as the conformational entropic penalty and the mobility, determined by their molecular weight. To conclude, the surface properties of wax J and wax M turned out more hydrophobic than that of wax K within the experimental period of water-submerged condition, even though the structure and functional groups near the surfaces of all waxes under ambient atmospheric condition are extremely similar. Thus, the blend of wax M behaves unlike wax K but similarly to wax J in terms of hydrophobicity. It may be attributed to the fact that the mobility of wax K-molecules from the blend of wax is hindered by the relatively long chain-conformation of wax J-molecules pertaining to the blend.

The diffusivity may be estimated by performing a back-of-the-envelope-calculation in the way that $D\sim(l^2/t)$. The absorbance-growth of a hydrophilic functional group takes place with its given peak-width when hydrophilic functional groups migrates cross the plane of the depth (δ) of wax-scratch towards the surface. Therefore, one may assume that the absorbance-growth ratio is equal to the ratio of the sum of the migration distance (l) and the depth (δ), and the depth (δ) in the expression of $(l/\delta)+1\sim(A_{water}/A_{ambient})$. Hence the diffusivity may be estimated in such a criterion that $D\sim(l^2/t)\sim(\delta^2/t)((A_{water}/A_{ambient})-1)^2$. Such values as $D_J\sim1.35\times10^{-11}$ cm^2/s and $D_M\sim1.96\times10^{-11}$ cm^2/s are established for wax J and wax M, respectively, under 1 day water-submerged condition. Likewise, under 1 week water-submerged condition, the values of 3.06×10^{-12} cm^2/s, 7.23×10^{-11} cm^2/s and 1.50×10^{-11} cm^2/s are established for the diffusivities of wax J, wax K and wax M, respectively. The obtained values of diffusivity are consistent, in terms of the order of magnitude, with the value of diffusion coefficient (5.75×10^{-11} cm^2/s) of macromolecular surface modifier, obtained, using a very complicated empirical-formula, by Chen et al. for the investigation of surface-modifier enrichment. Thus, the suggested criterion may be very useful and practically applied to clarify the process of surface enrichment from general polymer blends.

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