

Comparison of thermal properties of crude by-product polyolefin wax, fractionated paraffin wax and their blend

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Abstract—The molecular weight and thermal properties of unfractionated by-product polyolefin wax (wax K) from a naphtha cracking unit, fractionated commercial paraffin wax (wax J) and their blend (wax M) were evaluated and were compared with each other using differential scanning calorimetry (DSC), normal and high-temperature gel permeation chromatography (GPC), and wide-angle X-ray diffraction (WAXD). Such properties as molecular weight distribution, melting temperature and degree of crystallization were altered by blending wax K with wax J. By blending with two parts of wax K and one part of wax J to prepare wax M, M_w of wax K was shifted, by half, to that of wax J in order to approach that of wax M, whereas the M_n of wax K remains almost unaltered to become that of wax M. In particular the effect of blending of wax K and wax J turned out co-crystallization for the sharper lower-melting-temperature endothermic peak of the blend, indicating narrower molecular distribution, than that of wax K at the melting temperature shifted even below that of wax J. The total degree of crystallinity for the blend, wax M, turns out less than that before blending wax K with wax J, which may be attributed to the effect of co-crystallization due to blending.

Key words: Crude By-product Polyolefin Wax, Commercial Paraffin Wax, Blend, Molecular Weight Distribution, Melting-temperature Shift, Degree of Crystallization, Co-crystallization

INTRODUCTION

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. Wu et al. [1] investigated the crystalline structure and phase structure of metallocene linear low density polyethylene (mLLDPE) and low density polyethylene (LDPE) blends to show that the blend displayed co-crystallization phenomenon for LDPE of 80 wt% in the blends, indicating good compatibility between the two components under this circumstance. However, as LDPE content decreased, phase separation arose, whereas partial co-crystallization still existed in the blends. Krupa and Luyt [2] reported that linear LDPE/wax blends showed only one endothermic peak in the concentration region from 0 to 40% of wax for both uncross-linked and cross-linked blends. However, according to Mtshali et al. [3], LDPE and paraffin wax are not mutually miscible for 30-40% of wax in the blends even though they are miscible in the crystalline phase in the concentration region of 10% of wax in both uncross-linked and cross-linked blends. Fonseca and Harrison [4] studied co-crystallization in LDPE/HDPE blends to report that in some of their various compositions three endothermic peaks were observed in DSC thermograms, among which the intermediate peak associated with the fusion of a co-crystal formed from LDPE/HDPE was shifted to higher temperature with increasing amount of HDPE. Gao et al. [5] investigated the melting behavior of bimodal medium density polyethyl-

ene (BMDPE)/LDPE blends. According to their investigation the blends have two melting peaks in DSC thermograms; the values of higher peak melting temperature (BMDPE) descend, whereas that of lower peak melting temperature (LDPE) increase with increasing LDPE content in blends. In other words, the values of lower peak melting temperature (LDPE) decrease with decreasing LDPE content in blends. Moreover, when BMDPE is about 20 wt% in blends, the degree of crystallization of blends is reported to be lower than pure LDPE. Small-angle neutron scattering (SANS) and rheological investigations by Ashbaugh et al. [6] have shown that random copolymer of ethylene and butene can interact favorably with the paraffins and modify the crystal morphology to smaller units. Radulescu et al. [7,8] reported that when paraffin wax is mixed with a random copolymer of ethylene and butene in dilute solution, two interaction mechanisms take place: either a polymer-paraffin co-crystallization into 2-dimensional hairy platelets or a paraffin crystallization on the polymer template occur. Hlangothi et al. [9] investigated the thermal property of linear LDPE (LLDPE)/paraffin wax blends up to 40 wt% of wax, where possible co-crystallization of LLDPE and paraffin wax chains occurred even though pure LLDPE showed only a single endothermic peak with a maximum at 132 °C, while paraffin wax showed a triple endothermic peak at lower temperatures. It has been reported that wax favors the crystallization process inducing an increase in the crystallinity of polyethylene-wax binary mixtures because of wax's short and linear chains, compared to those of polyethylene [2,3,10,11]. Wilkinson et al. [12] studied the crystallization behavior of 50/50 polycarbonate (PC)-polybutyleneterephthalate (PBT) blend with added transesterification catalyst. In their study PBT crystallization was inhibited in the blend by both the

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presence of PC and transesterification and increasing transesterification resulted in a reduction in the melting temperature and degree of crystallinity. However, there has not been any reported investigation on the thermal property of the blends composed of different waxes including specially unfractionated crude one. Unfractionated 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. However, most unfractionated 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 unfractionated by-product polyolefin wax for the protection of the environment.

In this paper the novel feature of blending of unfractionated crude by-product polyolefin wax (wax K) and technical grade-commercial paraffin wax (wax J) is presented, where the blend (wax M) of wax J and wax K is suggested to replace wax J. The properties of wax J, wax K and wax M are evaluated and are compared with each other in terms of their molecular weight distribution and thermal characteristics in connection with their crystallinity, using normal and high-temperature gel permeation chromatography (GPC) analysis, differential scanning calorimetry (DSC) analysis and wide-angle X-ray diffraction (WAXD) analysis. In particular, the possible alteration of such properties as molecular weight distribution and thermal properties including melting temperature, the degree of crystallization and so on, is expected by blending wax K with wax J.

EXPERIMENTAL

1. Materials

Technical grade paraffin wax, wax J was purchased from Nippon Seiro Co. and wax K was obtained as unfractionated waste from the naphtha cracking plant located at Yeochun-chemical complex located in Korea. Wax K and wax J were mixed with the weight ratio of seven to three 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 rev/min for 10 min, after which it was cooled slowly at room temperature to prepare wax M. The blend, wax M, was kept at room temperature for at least 24 hrs prior to the experiments.

2. Methods

2-1. Identification of Thermal Characteristics

Differential scanning calorimetry (DSC) analyses of wax J, wax K and wax M were carried out using a thermal analyzer (TA instrument DSC2010) in nitrogen atmosphere. The samples were heated from 25 °C to 180 °C at the rate of 10 °C/min, for wax J, wax K and wax M.

2-2. Measurement of Molecular Weight

The molecular masses, number-average molecular weight (M_n), weight-average molecular weight (M_w) and Z-average molecular weight (M_z) of the waxes were analyzed with gel permeation chromatography (GPC) (Agilent, HPLC 1200 series equipped with Viscotek TD302) and high temperature-GPC (Polymer Laboratories (PL), PL GPC 220) maintained at room temperature and 160 °C, respectively. The detector for GPC was composed of refractive index (RI), viscometer (Viscotek, TD302) and light scattering detector, while the detector for high temperature-GPC was of RI and vis-

cometer. Two PL gel 5 μm (pore size of 50 Å) MIXED-C columns (300×7.5 mm) were used for normal GPC analysis while two PL gel 10 μm (pore size of 50 Å) MIXED-B columns (300×7.5 mm) thermostated at 160 °C were used for high temperature GPC analysis. Tetrahydrofuran (THF) was used as effluent at the flow rate of 1 mL/min, for normal GPC analysis. In normal GPC operation narrow-molecular-weight polystyrene (PS) standards (Polymer Laboratories, PL polystyrene calibration kit, S-M2-10 for GPC) were used with their least M_w of 580. In addition 1,2,4-trichlorobenzene (TCB) was used as effluent at the flow rate of 1 mL/min, for high temperature GPC analysis. In high temperature GPC operation, 1) narrow-molecular-weight PS standards (Polymer Laboratories, PL polystyrene calibration kit, S-H2-10 for high temperature GPC) were used with their least M_w of 580, or 2) the broad polyethylene (PE) standard (National Bureau of Standards, NBS-1476) was used with its M_w of 110,000 and poly-dispersity index of 4.18. The molecular masses (M_n , M_w and M_z) of wax J, wax K and wax M were analyzed against the universal calibration curve and the broad standard calibration curve, generated with high temperature-GPC data obtained by the narrow PS standards and the broad PE standard, respectively. In addition, those molecular masses of wax J were analyzed one more time against the calibration curve, generated with normal GPC data obtained by the narrow PS standards.

2-3. Crystallization Characteristics of Waxes

Wide-angle X-ray diffraction (WAXD) intensity patterns were collected on an X-ray diffractometer (Rigaku, DMAX 2000) equipped with RINT2000 wide angle goniometer and standard sample holder. The monochromatized X-ray beam was Cu K α radiation ($\lambda=1.5406$ Å). The operating condition of the X-ray source was set at the voltage of 60 kV and the current of 100 mA. Sample of the waxes were scanned into 2θ ranges from 10° to 90°. The obtained WAXD intensity patterns were used to estimate the apparent degree of the wax-crystallinity by the integration of intensities of the pattern associated with the crystalline structure and the amorphous halo with the aid of the software of Origin (Ver. 7.0).

RESULTS AND DISCUSSION

1. Determination of Molecular Weight of Waxes

Three kinds of masses for wax J were measured using normal GPC with narrow PS standards as well as high temperature GPC with the broad and universal calibration curves, as shown in Table 1. However, the least M_w of narrow PS standard was 580, which should be less than the M_w of wax J measured, as in Table 1, except for the case when using high temperature GPC with the broad PE standard. Thus, the measured M_n , 614 of wax J measured using GPC with narrow PS standards was acceptable, while the measured M_w , 500 of wax J measured using high temperature GPC with the uni-

Table 1. Molecular masses of wax J (commercial paraffin wax)

Method	Standard (calibration)	M_n	M_w	M_z
Normal GPC	PS narrow	585	614	648
High temperature GPC	PE broad (Broad)	257	312	362
High temperature GPC	PS narrow (Universal)	44	500	615

* The accepted ones are shown in bold character

Table 2. Molecular masses of wax K (unfractionated byproduct-polyolefin wax)

Method	Standard (calibration)	M_n	M_w	M_z
High temperature GPC PE broad (Broad)		228	6613	1168953
High temperature GPC PS narrow (Universal)		161	2461	322260

※ The accepted ones are shown in bold character

Table 3. Molecular masses of wax M (blend of wax J and wax K)

Method	Standard (calibration)	M_n	M_w	M_z
High temperature GPC PE broad (Broad)		226	3116	482550
High temperature GPC PS narrow (Universal)		298	2719	511670

※ The accepted ones are shown in bold character

versal calibration curves was rejected, as in Table 1. The value of poly-dispersity index (PI) of wax J, M_w/M_n , was obtained as 1.05 when using GPC with the narrow PS standard. It showed so narrow molecular weight distribution consistent with that of fractionated commercial paraffin wax that M_w of 614 may be accepted excluding the measurement of M_w , 312 when using high temperature GPC with the broad P.E. standards.

Those masses for wax K and wax M were measured using high temperature GPC with the broad and universal calibration curves as shown in Tables 2 and 3, respectively. Due to that the universal calibration-based-value of M_n , 161 of wax K was less than 580, the least M_n of the narrow PS standards, the measured values of average molecular weights, using high temperature GPC with the universal calibration curves, should be rejected, while those using high temperature GPC with the broad calibration curves may be accepted as in Table 2. Thus, the accepted measured values of M_n , M_w and M_z for wax K were 228, 6,613 and 1,168,953, respectively, with its PI value of 29.0. This relatively high PI value for wax K meets the characteristics of unfractionated crude by-product polyolefin wax.

Since the ratio of blending with wax K and wax J was two to one to prepare wax M, we can roughly estimate not only number-average molecular weight but also weight-average molecular weight with the values of molecular weight from Tables 1 and 2. We can apply 585 and 614 as M_n and M_w , respectively, for wax J and may apply 228 and 6,613 as M_n and M_w , respectively, for wax K. For wax M, M_n and M_w may be calculated as:

$$M_n = \frac{1+2}{\frac{1}{585} + \frac{2}{228}} = 286 \quad (1)$$

$$M_w = \frac{1}{3}(614) + \frac{2}{3}(6613) = 4,613 \quad (2)$$

$$PI = \frac{4613}{286} = 16.1 \quad (3)$$

We can compare the roughly-estimated molecular weights to the measured ones using high temperature GPC with the broad and universal calibration curves as shown in Table 3. Due to that the universal calibration-based-value of M_n , 298 of wax M was less than 580, the least M_n of the narrow PS standards, the measured values of

average molecular weights using high temperature GPC with the universal calibration curves should be rejected, while those using high temperature GPC with the broad calibration curves may be accepted as in Table 3. Thus, the accepted measured values of M_n , M_w and M_z for wax M were 226, 3,116 and 482,550, respectively, with the PI value of 13.8. The estimated ball park figures for M_n , M_w and PI were close to the accepted measured average molecular weights within the error-range of 26.5%, 48.0% and 16.7%. It is noteworthy that by blending with two parts of wax K and one part of wax J to prepare wax M, the accepted M_w of wax K was shifted, by half, to that of wax J in order to approach that of wax M, whereas the accepted M_n of wax K remains almost unaltered to become that of wax M.

2. DSC Thermal Properties of Waxes

Thermal characteristic of wax J, wax K and wax M was identified by performing differential scanning calorimetry (DSC) analyses, the results of which are shown in Figs. 1(a)-(c). The melting temperature was estimated by the tangent at the point of the greatest slope on the face portion of the peak of the DSC curve. DSC analysis of wax J showed two peaks composed of the larger and sharp peak, and the smaller and blunt peak as in Fig. 1(a). The larger and sharp endothermic peak illustrates narrow molecular weight distribution where its onset and peak melting temperatures and the corresponding melting enthalpy were 58.80 °C, 64.10 °C and 137.0 J/g, respectively, whereas the smaller and blunt peak does wide one where its onset and peak melting temperatures and the corresponding melting enthalpy were 39.99 °C, 47.56 °C and 19.8 J/g, respectively. According to Regin et al. [13], the larger peak of the two DSC peaks of technical grade paraffin wax was interpreted due to solid-liquid phase change and the smaller peak was due to solid-solid phase transition below the main melting temperature (referred to as melting temperature hereinafter) of the larger peak. Nevertheless, it is clear that the smaller peak should be treated as minor endothermic peak showing another minor melting temperature (referred to as minor melting temperature hereinafter). Sharma et al. [14] reported that the melting points and the heats of fusion of various paraffin waxes including commercial and laboratory paraffin waxes ranged at 42-68 °C and 146-210 J/g, respectively. Accordingly, thermal properties of wax J were believed to have relatively high peak melting temperature and low heat of melting as paraffin wax. Thus, wax J, a commercial paraffin wax was estimated to have relatively high molecular weight and low degree of crystallinity according to the paraffin wax-experiment of Shama et al. [14].

DSC analysis of wax K as in Fig. 1(b) illustrated that it has two endothermic peaks showing different melting temperatures, which is indicative of phase separation in crystalline structure. Its lower onset and peak melting temperatures and the corresponding melting enthalpy were 48.75 °C, 73.16 °C and 116.2 J/g, respectively, and its higher onset and peak melting temperatures and the corresponding melting enthalpy were 113.52 °C, 116.88 °C and 4.424 J/g, respectively. It has been known that among the properties of various polyethylene, the approximate % crystallinity and the crystalline melting point of low density polyethylene (LDPE) are 42-53% and 110-120 °C, respectively, while the approximate % crystallinity and the crystalline melting point of high density polyethylene (HDPE), are 64-80% and 130-136 °C, respectively [15]. Furthermore, Chatterjee et al. [16] claimed that the melting point and the degree of

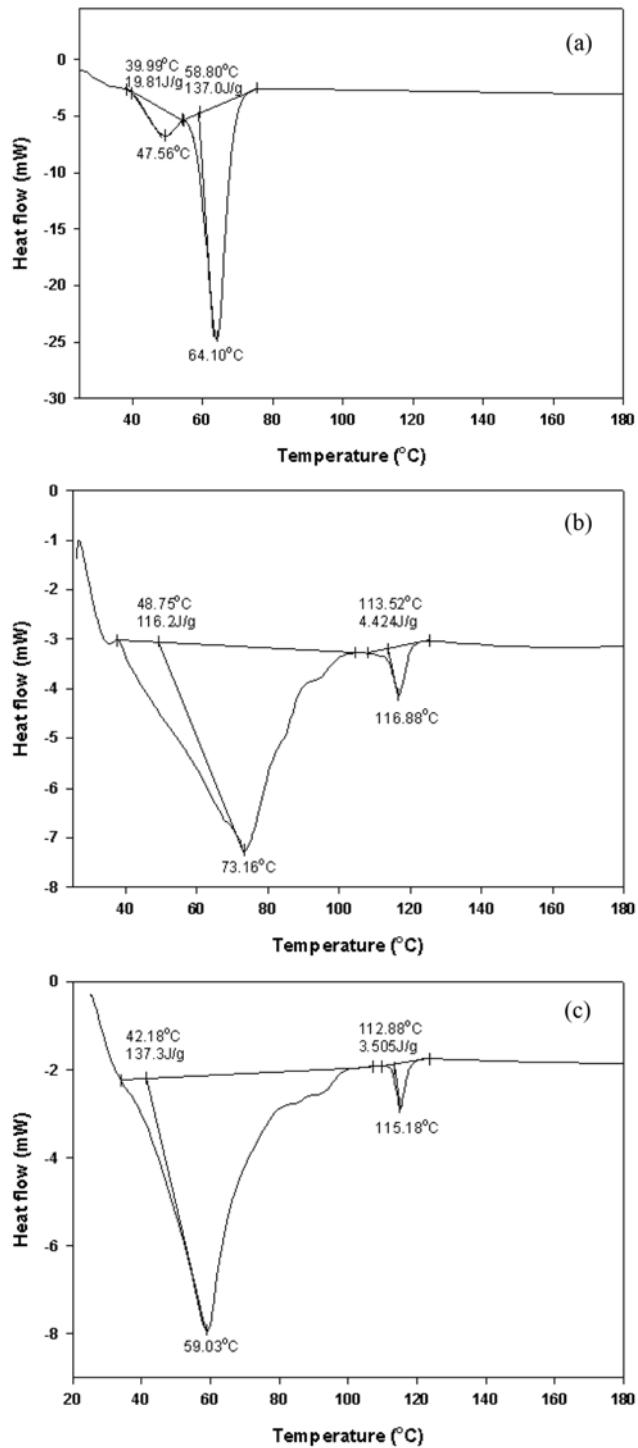


Fig. 1. DSC heating curves: (a) Wax J (commercial paraffin wax); (b) Wax K (unfractionated byproduct-polyolefin wax); (c) Wax M (blend of wax J and wax K).

crystallinity for pure polyethylene wax ($M_n=700$ g/mol) were 85.3 °C and 74.2%, which was calculated based on the standard (100% crystallinity) heat of fusion value of polyethylene ($\Delta H_m^f=290$ J/g). Hence, wax K was found to consist of a large portion of wax-grade lower molecular-weight crystal and a small portion of polymer (LDPE)-grade higher molecular-weight crystal. According to Ozawa [17] the degree of crystallinity is defined in terms of melting enthalpy as:

$$X_c = \frac{\Delta H_m}{\Delta H_m^f} \quad (4)$$

where ΔH_m is the melting enthalpy of the crystallinity of X_c ($\times 100\%$) and ΔH_m^f is the melting enthalpy of 100% crystallinity-substance.

He measured the degree of crystallinity of polyethylene with ΔH_m of 273 J/g; Hlangothi et al. [9] adopted 293 J/g as ΔH_m^f of polyethylene. Thus, assuming ΔH_m^f of polyethylene to be 270 J/g, the % crystallinity of polymer (LDPE)-grade crystal of wax K may be calculated as a very small portion of 1.53%.

The thermal behavior of wax M, the blend of wax K and wax J was obtained as shown in Fig. 1(c). It resembles the thermal behavior of wax K to have two endothermic peaks, showing two different melting temperatures and the corresponding melting enthalpy were 112.88 °C 115.18 °C and 3.505 J/g, respectively. Furthermore, it also behaved as wax J, a commercial paraffin wax. Its lower onset and peak melting temperatures (which are lower than that of wax K) and the corresponding melting enthalpy were 42.18 °C, 59.03 °C and 137.3 J/g, respectively, which is indicative of narrower and broader molecular weight distributions than those of wax K and wax J, respectively. Thus the effect of blending wax K with wax J turned out to resemble the thermal property of wax J. Moreover, it led to co-crystallization, which represents miscibility in the crystalline phase, for the lower-melting-temperature endothermic peak of the blend. Strikingly, it turned out to lower the melting temperature even below that of wax J, even though wax K constitutes the mass fraction of two-thirds for wax M. However, wax M, a blend of wax K and wax J, still carried the thermal property of the higher melting-temperature endothermic peak of wax K. The result of co-crystallization is consistent with the results of Hlangothi et al. [9] who investigated thermal property of LLDPE/paraffin wax blends. Even though there exists the co-crystallization for lower endothermic peak of the blend, its melting temperature-shift may be substantiated by the investigation of Gao et al. [5], where the values of lower peak melting temperature (LDPE) decrease with decreasing the LDPE content in blends. It may be further supported by the SANS and rheological investigations by Ashbaugh et al. [6] that random copolymer of ethylene and butene can interact favorably with the paraffin and modify the crystal morphology to smaller units. It was also found to be very similar to the influence of co-polymerization on thermal properties, by which the random incorporation of minor amounts of repeating unit B with A would disrupt the A lattice, lowering the melting temperature beneath that of homo-polymer A, and vice versa [15].

3. XRD Analysis on Waxes

The wide-angle X-ray diffraction (WAXD) intensity patterns for wax J, wax K and wax M were obtained by X-ray diffractometer (XRD) as in Figs. 2(a)-(c). The apparent degree of the wax-crystallinity was estimated by the integration of intensities of the pattern associated with the crystalline structure and the amorphous halo with the aid of the software of Origin (Ver. 7.0). X-ray diffractogram for wax J shows a major and a minor intensity peak, as in Fig. 2(a), at the scattering angles; $2\theta=21.48^\circ$ and $2\theta=23.88^\circ$, respectively, while the X-ray diffractogram for wax K shows those peaks at the scattering angles, $2\theta=21.48^\circ$ and $2\theta=23.84^\circ$, respectively, as in Fig. 2(b). It is interesting that the X-ray diffractogram for wax M (Fig. 2(c)) shows them at exactly the same values of 2θ as those of wax K. Intensity value of the major peak for wax K was almost double

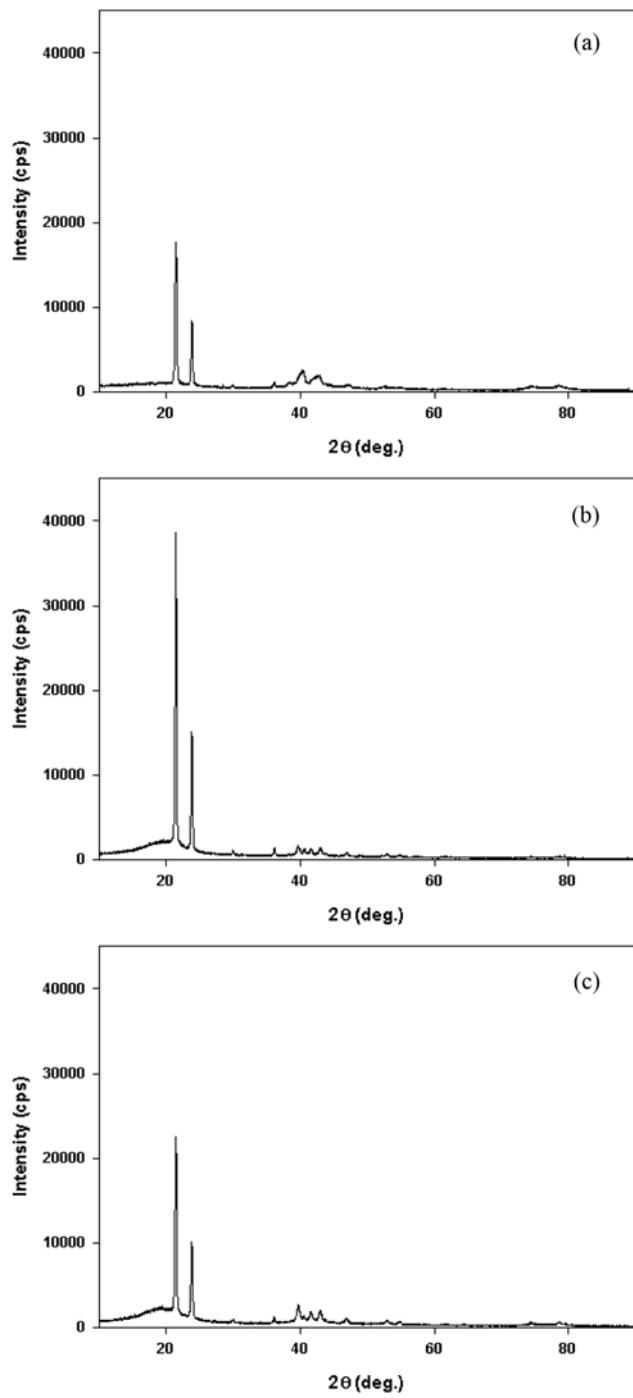


Fig. 2. Wide angle X-ray scattering curve showing crystalline peaks and amorphous halo: (a) Wax J (commercial paraffin wax); (b) Wax K (unfractionated byproduct-polyolefin wax); (c) Wax M (blend of wax J and wax K).

of that for wax J, whereas the intensity values of the minor peaks were close to each other. Umare et al. [18] synthesized low molecular weight polyethylene waxes by a titanium BINOLate-ethylaluminum sesquichloride catalyst system. Its X-ray diffractogram showed that a major and minor intensity peak were located at $2\theta=21.6^\circ$ and $2\theta=24^\circ$, respectively.

According to Ryan et al. [19], the degree of crystallinity, X_c , ex-

pressed as the mass fraction of crystalline component, is given as:

$$X_c = Ac/(Ac+As) \quad (5)$$

where As is the area under the amorphous halo and Ac is the area remaining under the crystalline peaks.

Accordingly, the degree of crystallinity, X_c , expressed as the mass fraction of crystalline component for wax J, wax K and wax M, was calculated to be 45.7%, 42% and 38%, respectively. It is noteworthy that the degree of crystallinity, X_c , decreased from 42-46% to 38% by blending wax K with wax J to prepare wax M. This phenomenon may be related to the aforementioned observed fact that the effect of blending wax K with wax J turned out 1) to make the minor endothermic peak from wax J disappear and 2) to lower the melting temperature for the lower endothermic peak of wax M, even than that at the main endothermic peak of wax J, even though wax K constitutes the mass fraction of two-thirds for wax M. The blending of two parts, wax K with one part, wax J, might disrupt the lattice of wax K for its lower endothermic peak and vice versa in a similar manner to the effect of the aforementioned co-polymerization. This phenomenon is again very comparable to the investigation of Gao et al. [5], where the degree of crystallization of blends is lower than pure LPDE when BMDPE is about 20 wt% in blends.

4. Analysis by Coupling DSC Thermal Properties with the Available Degree of Crystallinity

Since the blend was prepared by melt mixing in a Brabender Plastograph at a set temperature of 140 °C for 10 min, after which it was cooled slowly at room temperature to prepare wax M, its development of crystallization did not belong to isothermal crystallization following quenching to a certain temperature of measurement, but to the fashion of non-isothermal crystallization. It is well known that the rate of crystallization increases as the temperature decreases below its melting temperature, reaching a maximum and decreasing again when the temperature is lowered still further [20]. It has been reported by Kim and Kim [21] that the degree of crystallinity of the blend increased with increased holding time between 90 and 100 °C; above 100 °C, there was a single liquid solution, which separated into two fractions on cooling between 90 and 100 °C.

Assuming wax J, wax K and wax M were provided with the same condition to crystallize, one may derive the degree of crystallinity of wax M using the experimental results from DSC and XRD analyses for wax K and wax J. Then the calculated degrees of crystallinity of wax M in various ways may be compared with the experimental results from DSC and XRD analyses for wax M, and the deviation that takes place may be further investigated to obtain a plausible explanation. Combining the results of DSC thermal analysis and the obtained degree of crystallinity on those waxes, one may formulate the following and may estimate their thermal properties including the enthalpy of fusion of 100% crystalline.

$$L_0 X_0 = 19.8 \text{ J/g} \quad (6)$$

$$L_1 X_1 = 137 \text{ J/g} \quad (7)$$

$$X_0 + X_1 = 0.457 \quad (8)$$

where L_0 , L_1 , X_0 , X_1 denote the enthalpy of fusion of 100% crystalline at the minor melting point and the main melting point of wax J, respectively, and the degree of crystallinity at the minor melting point and the main melting point of wax J, respectively.

Assuming both the value of L_0 and L_1 are the same, the enthalpy of fusion of 100% crystalline, X_0 and X_1 of wax J may be estimated as 343.1 J/g, 0.057 and 0.40 since the degree of crystallinity for wax J was obtained as 0.457 in the previous XRD analysis (Fig. 2(a)).

Since the total degree of crystallinity of wax K was obtained as 0.42 in the previous XRD analysis (Fig. 2(b)), the following relationships are established combining the results of DSC thermal analysis.

$$L'_1 X'_1 = 116.2 \text{ J/g} \quad (9)$$

$$L'_2 X'_2 = 4.424 \text{ J/g} \quad (10)$$

$$X'_1 + X'_2 = 0.42 \quad (11)$$

where L'_1 , L'_2 , X'_1 and X'_2 denote the enthalpy of fusion of 100% crystalline of wax K for its lower and higher DSC endothermic peaks, respectively, and the degrees of crystallinity of wax K for its lower and higher DSC endothermic peaks, respectively.

One may regard the enthalpy of fusion of 100% crystalline of wax K at the melting temperature of its lower and higher endothermic peaks as $\Delta H_m^f = 290 \text{ J/g}$ according to Chatterjee et al. [16]. Then the degrees of crystallinity of wax K for its lower and higher melting-temperature DSC-endothermic-peaks may be separately obtained, from Eqs. (9) and (10), as 0.401 and 0.015, respectively. Then these obtained degrees of crystallinity are verified with satisfying the requirement of the total degree of crystallinity of wax K measured as 0.42 ($=X'_1+X'_2$) in the previous XRD analysis (Fig. 2(b)). Thus, the aforementioned assumption of both L'_1 and L'_2 equal to 290 J/g for wax K, is justified by this verification.

Furthermore, using the measured thermal quantities of melting enthalpy for wax M, one can estimate each degree of crystallinity per each endothermic peak of wax M as follows.

$$L''_1 X''_1 = 137.3 \text{ J/g} \quad (12)$$

$$L''_2 X''_2 = 3.505 \text{ J/g} \quad (13)$$

$$X''_1 + X''_2 = 0.38 \quad (14)$$

where L''_1 , L''_2 , X''_1 and X''_2 denote the enthalpy of fusion of 100% crystalline of wax M for its lower and higher DSC endothermic peaks, respectively, and the degrees of crystallinity of wax M for its lower and higher DSC endothermic peaks, respectively.

Assuming blending did not affect the thermal behavior of wax K at the melting temperature of its higher endothermic peak that wax J does not have, one can still regard the enthalpy of fusion of 100% crystalline of wax M at the melting temperature of its higher endothermic peak as $\Delta H_m^f = 290 \text{ J/g}$ according to Chatterjee et al. [16]. Hence, the degrees of crystallinity of wax M for its higher DSC endothermic peak may be estimated with the assumed value of L''_2 of 290 J/g as 0.0121. Then the degree of crystallinity of wax M for its lower DSC endothermic peak may be obtained as 0.368 since the total degree of crystallinity of wax M was measured as 0.38 by previous XRD analysis. Blending may affect the thermal behavior of wax K at the melting temperature of its lower endothermic peak since blending wax K with wax J turned out to lead to co-crystallization, which represents miscibility in the crystalline phase, for the lower endothermic peak of wax M. Thus, the enthalpy of fusion of 100% crystalline of wax M at the melting temperature of its lower endothermic peak may be estimated as $\Delta H_m^f = 373.1 \text{ J/g}$, which is greater than that (i.e., 290 J/g) of wax K and is close, even greater than, to that (i.e., 343.1 J/g) of the main endothermic peak of wax

J. Hence, it is noticeable that blending caused the enhancement of the enthalpy of fusion of 100% crystalline of wax M at the melting temperature of its lower endothermic peak, even though the degree of crystallinity of wax M for its lower DSC endothermic peak was reduced by 0.03 from the value of 0.40 before blending.

Neglecting the effect of blending and assuming that negligible re-crystallization occurred in the heating process, the degrees of crystallinity of wax M for its lower and higher melting-temperature DSC endothermic peaks may be estimated in the other way, according to the ratio of blending, i.e., two parts of wax K and one part of wax J.

$$X''_1 = 0.3(X_0 + X_1) + 0.7X'_1 = (0.3)(0.457) + (0.7)(0.401) = 0.417 \quad (15)$$

$$X''_2 = 0.7X'_2 = (0.7)(0.015) = 0.0105 \quad (16)$$

Thus the sum is obtained from Eqs. (15) and (16) as below..

$$X''_1 + X''_2 = 0.4275 \quad (17)$$

However, the sum of 0.4275 remains higher than the measured quantity of 0.38 by XRD analysis. Thus, the total degree of crystallinity for wax M turns out less than that before blending wax K with wax J. The degrees of crystallinity (i.e., 0.417 and 0.0105) of wax M obtained according to the ratio of blending give the more and less value by 13% than the previously estimated values (0.368 and 0.0121), respectively. This increase and decrease in the degree of crystallinity may be attributed to the effect of co-crystallization due to blending and the possible re-crystallization during the heating process (or the increase may be just within the range of experimental error), respectively. According to Radulescu et al. [7,8], when paraffin wax is mixed with a random copolymer of ethylene and butene in dilute solution, there exists a polymer-paraffin co-crystallization into 2-dimensional hairy platelets for the case of high paraffin contents. Since the effect of blending of wax J and wax K turned out to lead to co-crystallization, which represents miscibility in the crystalline phase, for the lower endothermic peak of the blend, one may suggest it complies with the results of Radulescu et al. [7]. Thus, the phenomenon of decreased degree of crystallinity for wax M may be explained in a similar way to the influence of co-polymerization on thermal properties, by which the random incorporation of minor amounts of repeating unit B with A would disrupt the A lattice, and vice versa [15]. Moreover, it may be inferred that with the presence of such a functional group as alcohol and ester in the blend of wax M, a possible reaction occurs in a similar manner to the investigation of Wilkinson et al. [12], to which a reduction in the melting temperature and the degree of crystallinity of the blend, wax M, may be attributed.

CONCLUSION

Molecular masses for wax J, wax K and wax M were measured using normal gel permeation chromatography (GPC) and high temperature GPC. The M_w of 614 and poly-dispersity index (PI) of 1.05 were obtained for wax J, which shows a narrow molecular weight distribution and meets the requirement of commercial paraffin wax. The measured values of M_n , M_w and M_z for wax K were 228, 6,613 and 1,168,953, respectively, with its PI value of 29.0. This relatively high PI value meets the characteristics of unfractionated crude by-product polyolefin wax. The measured values of M_n , M_w and M_z for wax M were 226, 3,116 and 482,550, respectively, with its PI

value of 13.8, which was confirmed by the ball park estimation of its molecular masses. It is noteworthy that by blending with two parts of wax K and one part of wax J to prepare wax M, the M_w of wax K was shifted, by half, to that of wax J in order to approach that of wax M, whereas the M_w of wax K remains almost unaltered to become that of wax M.

Differential scanning calorimetry (DSC) analysis showed that 1) wax K consists of a large portion of wax-grade lower-molecular-weight crystal and the small portion of polymer (LDPE)-grade higher molecular-weight-crystal, and that 2) the effect of blending wax K with wax J, turned out to resemble the thermal property of wax J and further to lead to co-crystallization, which represents miscibility in the crystalline phase, for the sharper lower-melting-temperature endothermic peak of the blend than that of wax K. It indicates narrower molecular distribution of the blend, wax M, than that of wax K at the melting temperature even below that of wax J, even though wax K constitutes a mass fraction of two-thirds for wax M. However wax M, the blend of wax K and wax J, still carried the thermal property of the higher-melting-temperature endothermic peak of wax K.

The intensity patterns of wide angle X-ray diffraction (WAXD) show that a major and minor peak were located at $2\theta=21.48^\circ$ and 23.88° , respectively, for wax J, and were located at $2\theta=21.48^\circ$ and 23.84° , respectively, for both wax K and wax M. The degrees of crystallization for wax J, wax K and wax M were found to be 45.7%, 42% and 38%, respectively. The degrees of crystallinity of wax K for its lower and the higher melting-temperature DSC endothermic peaks were obtained from the relationships established from the results of DSC thermal analysis as 0.401 and 0.015, respectively, which satisfies the requirement of the total degree of crystallinity of wax K measured as 0.42 in XRD analysis. The degree of crystallization of the blend, wax M, was observed to decrease lower than the value estimated by the simple mass balances, according to the ratio of blending, for its lower and higher melting-temperature DSC endothermic peaks, neglecting the effect of blending and the possible re-crystallization that occurred in the heating process. Thus, the total degree of crystallinity for wax M turns out less than that before blending wax K with wax J. The degrees of crystallinity (i.e., 0.417 and 0.0105) of wax M obtained according to the ratio of blending give the more and less values by 13% than the corresponding values (0.368 and 0.0121) estimated with the measured quantity of the degree of crystallinity of wax M, respectively. The more and less values may be attributed to the effect of co-crystallization due to blending and the possible re-crystallization during heating process (or just experimental error), respectively, or may be attributed to a possible reaction to result in a reduction in the melting temperature and degree of crystallinity.

Thus, blending wax K with wax J altered such properties as molecular weight distribution, melting-temperature and the degree of crystallization. In particular 1) the effect of blending wax K with wax J turned out co-crystallization for the sharper lower-melting-temperature endothermic peak of the blend, indicating narrower molecular distribution, than that of wax K at a melting temperature even below that of wax J; 2) Latent heat of fusion of 100% crystalline of blend, wax M, was enhanced even higher than that of wax J, at the expense of reducing the total degree of crystallinity, by the co-

crystallization. To conclude, it is suggested that costly commercial paraffin wax may be replaced by its blend with cheap recycled waste olefin wax for its extensive applications, not to mention solving environmental problems. Furthermore, the enhancement of latent heat of fusion of 100% crystalline of the blend, wax M, exhibits the possibility of its application to thermal energy storage (TES) as phase change materials (PCM), to be explored. Thus, it is very important that the huge contribution of this novel blend is expected to extensive economical and environmental aspects.

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REFERENCES

1. T. Wu, Y. Li and G. Wu, *Polymer*, **46**, 3472 (2005).
2. I. Krupa and A. S. Luyt, *Polym. Deg. Stab.*, **70**, 111 (2000).
3. T. N. Mtshali, I. Krupa and A. S. Luyt, *Thermochimica Acta*, **380**, 47 (2001).
4. C. A. Fonseca and I. R. Harrison, *Thermochimica Acta*, **313**, 37 (1998).
5. J. G. Gao, M. S. Yu and Z. T. Li, *European Polymer Journal*, **40**, 1533 (2004).
6. H. S. Ashbaugh, A. Radulescu, R. K. Prud'homme, D. Schwahn, D. Richter and L. J. Fetter, *Macromolecules*, **35**, 7044 (2002).
7. A. Radulescu, D. Schwahn, D. Richter and L. J. Fetter, *J. Appl. Crystal.*, **36**, 995 (2003).
8. A. Radulescu, D. Schwahn, M. Monkenbusch, D. Richter and L. J. Fetter, *Physica B. Condensed Matter*, **350**, e927 (2004).
9. S. P. Hlangothi, I. Krupa, V. Djokovi and A. S. Luyt, *Polym. Deg. Stab.*, **79**, 53 (2003).
10. I. Krupa and A. S. Luyt, *Polym. Deg. Stab.*, **73**, 157 (2001).
11. I. Krupa and A. S. Luyt, *Polymer*, **42**, 7285 (2001).
12. A. N. Wilkinson, S. B. Tattum and A. J. Ryan, *Polymer*, **38**, 1923 (1997).
13. A. F. Regin, S. C. Solanki and J. S. Saini, *Renew. Energy*, **31**, 2025 (2006).
14. A. Sharma, S. D. Sharma and D. Buddhi, *Energy Conversion and Management*, **43**, 1923 (2002).
15. S. L. Rosen, *Fundamental principles of polymeric materials (2nd Ed.)*, John Wiley & Sons, Inc., Singapore (1993).
16. J. Chatterjee, Y. Haik and C. J. Chen, *J. Mag. Mag. Mater.*, **246**, 382 (2002).
17. T. Ozawa, *Polymer*, **12**, 150 (1971).
18. P. S. Umare, R. Antony, K. Gopalakrishnan, G. L. Tembe and B. Trivedi, *J. Molecul. Catal. A: Chem.*, **242**, 141 (2005).
19. A. J. Ryan, J. L. Stanford, W. B. Thomas and M. W. Nye, *Polymer*, **38**, 759 (1997).
20. D. W. Van Krevelen and P. J. Hoflyzer, *Properties of polymers: Their estimation and correlation with chemical structure (2nd Ed.)*, Elsevier Scientific Publishing Company, Amsterdam (1976).
21. J. K. Kim and B. K. Kim, *J. Jpn. Soc. Powder/Powder Metall.*, **46**, 823 (1999).