Extrusion Coating Performances of iPP/LDPE Blends

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ABSTRACT: The performance of iPP/LDPE blends in an extrusion coating process was investigated in the terms of coating width and draw-down ability. It is well known that iPP alone is not proper because of lower draw-down ability with severe draw resonance in elongational flow. To obtain higher draw-down ability, iPP was blended with LDPE. Additionally, iPPs having different molecular weight distribution (MWD) were used in this study to find out the effect of MWD of iPP on neck-in and draw-down ability. It was observed that iPP/LDPE blend with narrower MWD exhibits narrower coating width and higher draw-down ability. Neck-in and draw-down ability were correlated with shear and elongational properties obtained by several rheological measurements. From this study, the major rheological parameters affecting extrusion performance in iPP/LDPE blends could be assessed. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 3121–3127, 2009

Key words: blends; coating; extrusion

INTRODUCTION

Polypropylene (PP) is a very versatile material in packaging industry, and it is transformed into useful products by a wide variety of processes such as film forming, fiber spinning, sheet molding, blow molding, injection molding, and extrusion coating processes. PP is frequently used for film applications, because it provides many good properties such as high heat resistance, low density, chemical resistances, high stiffness, etc. Extrusion coating process has been widely used for production of both food packaging and industrial packaging. Although PP has many good features, PP alone is not suitable for extrusion coating process because it shows pronounced flow instability called draw resonance in extrusion coating processes.[1,2] Even though low-density polyethylene (LDPE) has better processability than PP,[3] it has its own deficiency for packaging purpose because of low mechanical strength, grease and oil resistance, barrier properties, abrasion resistance, and thermal resistance.

In the extrusion coating process schematically shown in Figure 1, polymer melt is vertically extruded through a slit die and coated onto a moving web in a nip created by rubber pressure roll and chrome-plated steel chill roll. Because the take-up velocity at the chill roll is greater than the extrusion velocity at the die, the melt flow is stretched along the machine direction. Ratio of take-up velocity to extrusion velocity is defined as a draw-down ratio (DDR). High draw-down ability is directly related to the high productivity. High DDR is limited by a draw resonance and edge tear phenomena. In melt spinning or film forming process, a periodic variation of filament radius or film thickness is observed at higher processing rate. This is called a draw resonance.[4,5] In extrusion coating process, the draw resonance, cause of nonuniform coating thickness and width, is a serious problem especially for linear polymers. Neck-in is defined as a difference between die lip width and coated film width. It determines how wide film can be obtained in the fixed die width and influences the economy of extrusion coating process in given machine dimension. Lower neck-in means wider film width. Therefore, low neck-in and high DDR are important aspects in extrusion coating process.

LDPE is suitable material for extrusion coating because of its lower neck-in and relatively high draw-down ability. It was reported that the draw resonance seldom occurs in extrusion coating of LDPE, which is attributed to a strain hardening and extension thickening behavior in elongational rheology because of its long-chain branched structure.[6,7] Incorporation of LDPE into linear polymers is an effective way, reducing the draw resonance.[8–10] It is known that the polymer having broader molecular distribution shows lower neck-in.[11] The long-chain branching is also known to reduce the neck-in. The

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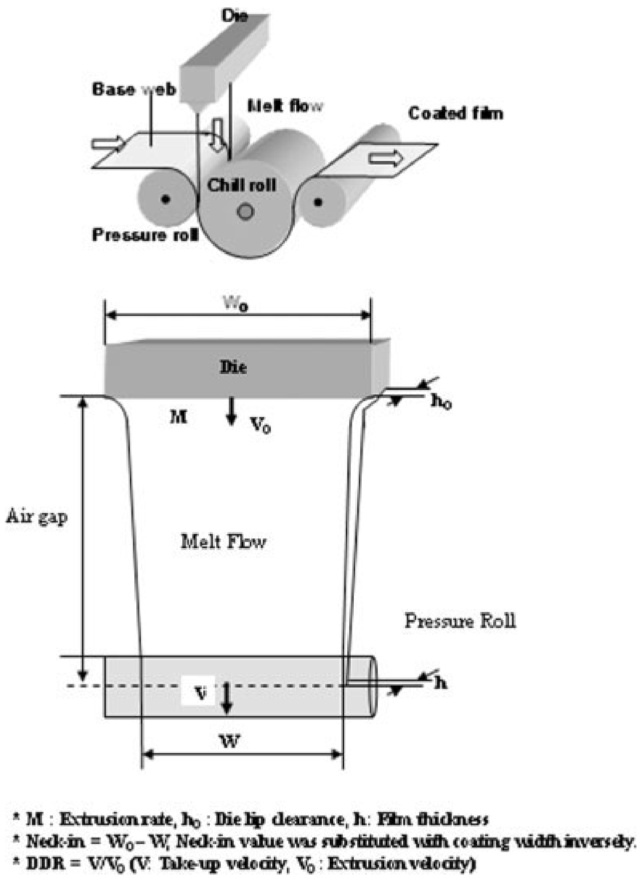

Figure 1 Schematic diagram of an extrusion coating.

long-chain branches act as anchors to maintain resin flow stability with lower neck-in behavior.[12] Toft and Rigdahl[13] investigated the neck-in properties of metallocene-catalyzed polyethylenes (mPE). They reported that the neck-in decreases with the elasticity of the mPE. This result indicates that a low shear viscosity and a high Trouton's ratio provide optimal processability with regards to neck-in and draw-down ability.

PP is usually known to show higher neck-in and severe draw resonance compared with LDPE. To overcome these shortcomings, introduction of long-chain branches to PP[1,14] and blending with LDPE[2,15] have been studied. Yoo[1] investigated relations between the coating performance and rheological properties of high melt strength PP (HMS PP). It was observed that the neck-in is related to the elasticity of the polymer, whereas the draw-down ability is more dependent on the viscosity. Since HMS PP is relatively expensive because of the high cost of branching process, blending of PP and LDPE is advantageous in an economical aspect. Although many studies have shown that shear (viscosity, elasticity, etc) and elongational properties (melt tension, elongational viscosity, strain hardening, etc.) are related to the draw-down ability and flow instabilities in melt spinning,[16–19] thermoforming[20] and film blowing process,[21] the study on the neck-in and draw-down ability using an extrusion coating equipment is rare.

In previous studies[2,15] on the extrusion process of PP/LDPE blends, the correlations between rheological properties and the extrusion coating performances are not assessed in detail. The objective of this study is to understand major rheological factors determining the processability of isotactic PP (iPP) and its blends with LDPE using an extrusion coating equipment. Rheological properties were studied to correlate resin properties to the extrusion coating performances. The effect of different molecular weight distribution (MWD) of iPP in iPP/LDPE blends is also investigated.

EXPERIMENTAL

Materials

Three different polypropylenes having similar number-average molecular weight and different MWD were used in this study. Among them, iPP of broadest MWD was unmodified one supplied from Honam Petrochemical Corporation.

The other two iPPs, supplied from Honam Petrochemical Corporation (Seoul, Korea), were modified by a peroxide (2,5-dimethyl-2,5-di-*tert*-butylperoxy hexane, M_w = 290.4, Akzo Chemicals Trigonox 101^{TM}). It is well known that peroxide treatment reduces M_w and MWD by inducing β-scission effectively in high molecular weight iPP.[22,23] LDPE was obtained from Hanwha Petrochemical Corporation. The relevant physical and molecular properties of these resins are summarized in Table I.

Preparation of blends

iPPs and LDPE with an 9/1 ratio in weight were dry blended in the Henschel mixer for 3 min, followed by melt-mixing in a 40-mm dulmage type single-screw extruder at 210°C. Antioxidant (Irganox 1010, Ciba) of 0.1 phr was added in the blends to ensure that the molecular weights of iPP and LDPE were not much changed. Finally, extrudate from die was cooled in water bath and pelletized. The characteristics of the blends are summarized in Table II.

Extrusion coating experiments

Extrusion coating experiments were carried out at die temperature of 230°C in extrusion coating equipment, which consists of 60-mmφ single screw and a rectangular die of 440 mm in width and 0.75 mm in height. BOPP (biaxially oriented PP) film of 25 μm

TABLE I
Characteristics of Materials Used in This Study

Sample	PP-wide	PP-middle	PP-narrow	LDPE
Type	iPP[a]	iPP[b]	iPP[c]	LDPE[d]
MFR (g/10 min)	17	17	18	10
M_n	54,300	56,700	58,500	30,500
M_w	246,000	214,000	203,000	223,000
MWD	4.53	3.77	3.47	7.31

[a] SJ-160, Honam petrochemical corp.
[b] Peroxide treatment with SJ-150 (Honam petrochemical corp. MFR = 10).
[c] Peroxide treatment with SY-130 (Honam petrochemical corp. MFR = 4).
[d] LDPE 960 (Hanwha petrochemical corp.).

was used as a coated base web. Extrusion rate was 600 g/min corresponding to a linear extrusion velocity of 2.4 m/min and apparent shear rate of 240 s^{-1} in the die. DDR is defined as follows:

$$\mathrm{DDR} = V/V_o$$

where V_o is a linear extrusion velocity and V is a maximum take-up velocity beyond which the coated film shows unstable draw resonance.

Characterizations

A conventional capillary viscometer (Instron 4467 UTM) equipped with infrared apparatus was used to measure an extrudate swell ratio. Measurements were carried out at 230°C using a capillary die of L = 25.4 mm and D = 0.76 mm. Dynamic shear test were performed by ARES system from Rheometrics Scientific. Tests were performed on 25-mm parallel plate fixture at 230°C. The frequency window was 0.1–100 rad/s with a strain of 10% in a nitrogen atmosphere. Measurement of a time-dependent elongational viscosity ($\eta_e^+(t)$) was carried out at 170°C by an extensional viscosity fixture (EVF) in the ARES. Elongational rates for the measurement were 0.5, 1.0, and 3.0, respectively. The detailed features of the equipment was reported elsewhere.[24]

Melt strength, draw-down ability, and the indication of draw resonance were evaluated in melt strength tester, which consists of a single-screw laboratory extruder equipped with a capillary die and a take-up device from Goettfert Rheotens™. Take-up device consists of two counter rotating wheels, which are mounted on a sensitive balance beam. A melt strand extruded vertically downward from an extruder is pulled by rotating wheels with increasing velocity (constant acceleration) and the draw-off force is determined. The melt strength at the time of breakage or the commencement of any instability was measured. Dimensions of the capillary die used were 1 mm in diameter, 30 mm in length, and 90° in entrance angle. All measurements were carried out at 170°C and acceleration speed of 2.4 mm/s^2.

RESULTS AND DISCUSSION

Table I shows characteristics of iPP and LDPE used in this study. Three different iPPs having various MWD but similar number-average molecular weights were used. By peroxide treatment, M_w and MWD of these iPPs were modified. PP-narrow and PP-middle have narrower MWD than those of PP-wide by this treatment as indicated in Table I. The results of dynamic shear test of three iPPs obtained are shown in Figure 2. As expected, complex viscosity and storage modulus increase with the MWD. Extrudate swell ratios (D/D_0) of three iPPs are also shown in Figure 3. Broader MWD PP (PP-wide) shows higher extrudate swell ratio than narrower MWD PP, which is attributed to the higher elasticity of PP-wide.

Table III and Figure 4 show film width of pure iPPs and its blends with LDPE as a function of draw-down ratio. It is noteworthy that materials having higher viscosity and storage modulus show wider film width and consequently lower neck-in,

TABLE II
Characteristic of iPP/LDPE Blends Investigated in This Study

Sample	PP- wide /LDPE	PP- middle /LDPE	PP-narrow /LDPE
iPP content (%)	90 (PP-wide)	90 (PP-middle)	90 (PP-narrow)
LDPE content (%)	10	10	10
MFR (g/10 min)	18	17.5	19

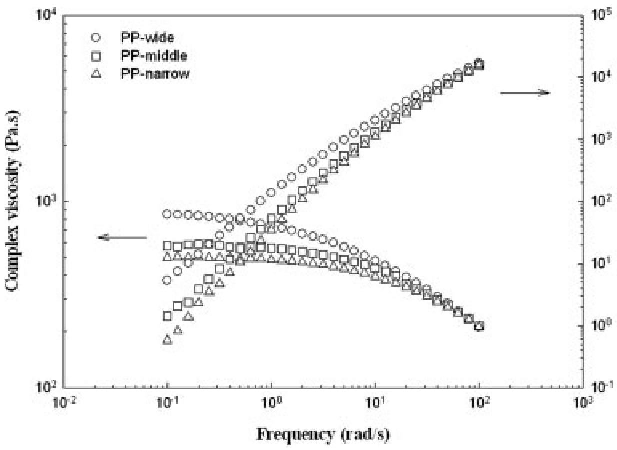

Figure 2 Storage modulus and complex viscosity of iPP.

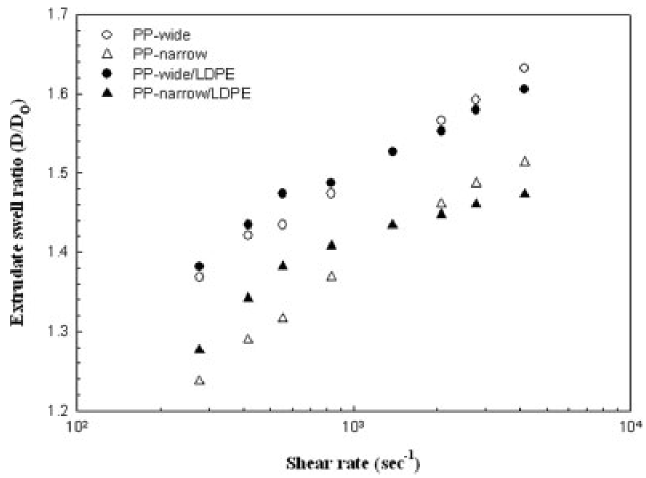

Figure 3 Extrudate swell ratio and shear viscosity measured in capillary rheometer.

but lower draw-down ability. This is consistent with the previous studies.[1,13]

Pure iPPs (not blended with LDPE) exhibit remarkably low draw-down ability. For example, maximum draw-down ratios of PP-wide and PP-narrow are 14.6 and 18.8, respectively. Above these ratios, the melt flow exhibits unstable behavior of draw resonance where width and thickness of the films fluctuate along the film length. This phenomenon was observed at one side of die region at low DDR, followed by propagation to entire region upon further increase of the DDR. iPP with narrower MWD shows higher draw-down ability than broader MWD iPP. This is consistent with previous studies on melt spinning, which reported the advantages of narrow MWD resin in elongational flow-dominant process.[16,25] Minoshima et al.[25] investigated the effect of MWD on the instability phenomena in a melt spinning process.They reported that polymer having narrower MWD provides weaker elongational thinning effect (higher power law index, *n*, in elongational viscosity vs. elongational rate curve) and stabilizes the spinning process at the higher spinning rate. Tzokanakis et al.[26] also reported that elongational viscosity of the polymer with narrower MWD is less dependent on elongational rate, maintaining higher elongational viscosity and thus show stable spinning process even at high speed spinning rate.[6]

In our study, pure iPP without incorporation of other materials does not show enough draw-down ability although narrower MWD obtained by the peroxide treatment could improves draw-down ability to a certain extent. Incorporation of LDPE into iPP phase would be one of solutions.

Extrusion coating performance of iPP blended with LDPE - neck-in property

As shown in Table III and Figure 4, the film width of iPP/LDPE blends increase in the order of PP-wide/LDPE > PP-middle/LDPE > PP-narrow/LDPE in extrusion coating experiment.

The results of dynamic shear test of three iPP/LDPE blends are shown in Figure 5. It is observed that blends containing broader MWD iPP show higher G' (higher elasticity) due to longer relaxation time of high molecule weight components of iPP in

TABLE III
Film Width[a] of Samples in Extrusion Coating (unit : mm)

	PP- wide	PP- narrow	PP- wide /LDPE	PP-middle/LDPE	PP- narrow /LDPE
8.3	**323**	**295**	**324**	**320**	**301**
12.5	**304**	**299**	**323**	**322**	**313**
16.7	n.a.[c]	**287**	**323**	**320**	**315**
20.8	n.a.[c]	n.a.[c]	**323**	**320**	**315**
25.0	n.a.[c]	n.a.[c]	n.a.[c]	**319**	**314**
33.3	n.a.[c]	n.a.[c]	n.a.[c]	n.a.[c]	**316**
Max DDR[b]	14.6	18.8	22.9	27.1	37.5

[a] Related to neck-in inversely.
[b] Related to draw-down ability, it means the commencement point occurring draw resonance.
[c] Film width cannot be evaluated in this DDR due to draw resonance.

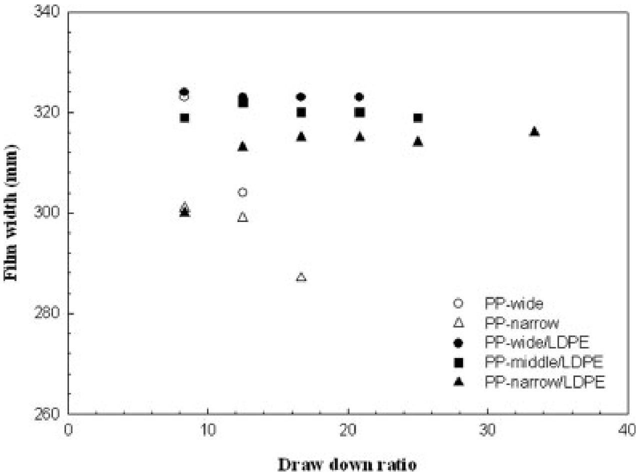

Figure 4 Results of extrusion coating showing neck-in and draw-down ability.

this resin. Therefore, it is inferred that iPP with higher elasticity provides low neck-in performance.

Figure 6 shows melt strength and apparent elongational viscosity obtained from a Rheotens test. Many researchers have reported many interesting results with this apparatus such as effect of melt strength on bubble stability[9] and thermoforming,[16] melt extensibility of polypropylene,[19,27] melt strength behavior of polyethylene blend,[28,29] Rheotens master curves of polymer melt,[30,31] and melt rupture phenomena.[32] In our test, large fluctuation of melt strength near maximum draw speed indicates the draw resonance. PP-wide/LDPE exhibits highest melt tension and apparent elongational viscosity, which is related to the neck-in property. On the other hand, the apparent elongational viscosity of PP-narrow/LDPE (which shows the highest neck-in) is lowest among four samples. It seems that higher melt tension and apparent elongational viscosity provides wider coating width (low neck-in). From these results, it is assessed that the neck-in property is related not only to elasticity but also to elongational properties.

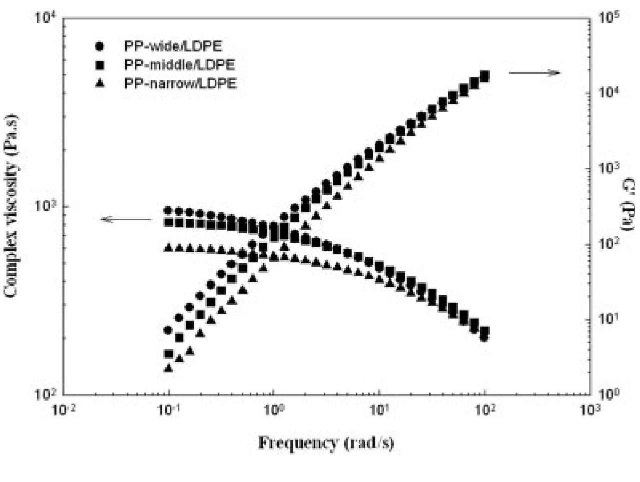

Figure 5 Storage modulus and complex viscosity of samples.

Extrusion coating performance of iPP blended with LDPE - draw-down ability

In extrusion coating performance, draw-down ability must be considered together with neck-in property. As seen in Table III and Figure 4, PP-wide/LDPE provides lowest draw-down ability and best neck-in performance (wider film width), whereas PP-narrow/LDPE provides best draw-down ability and lowest neck-in performance. It is noteworthy that incorporation of LDPE into pure iPPs reduces the draw resonance, improving the draw-down ability. Since LDPE has high level of entanglement because of the long-chain branching (LCB), blend of LDPE induces strain hardening and reduces draw resonance in melt spinning as mentioned by Yoo.[17] Several authors agree that the LCB reduces draw resonance by similar mechanism.[1,6] Our studies in

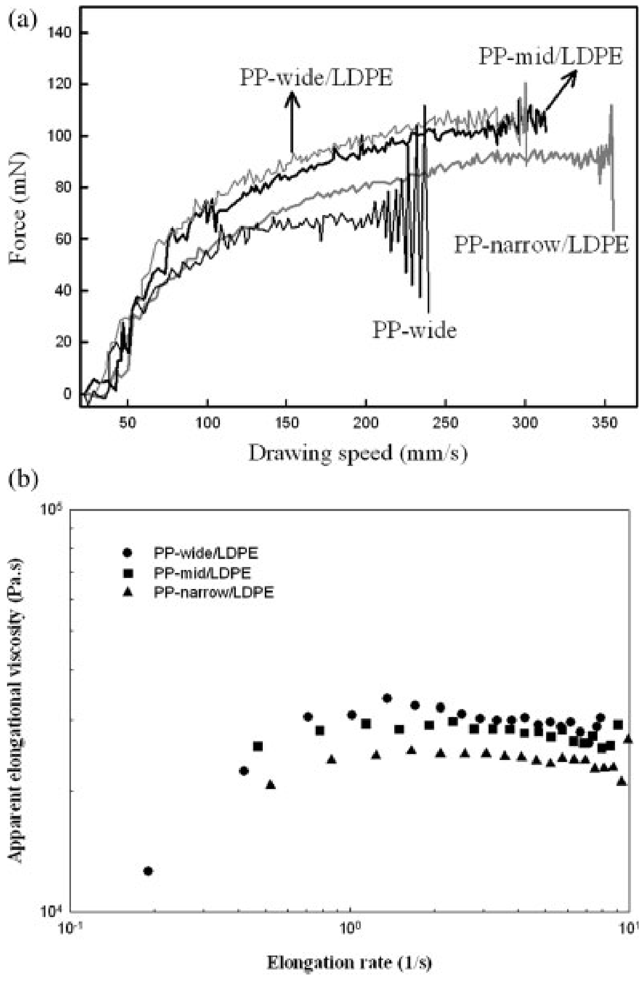

Figure 6 Melt strength and apparent viscosity measured by Rheotens. (a) Melt tension versus draw speed. (b) Apparent elongation viscosity versus elongational rate.

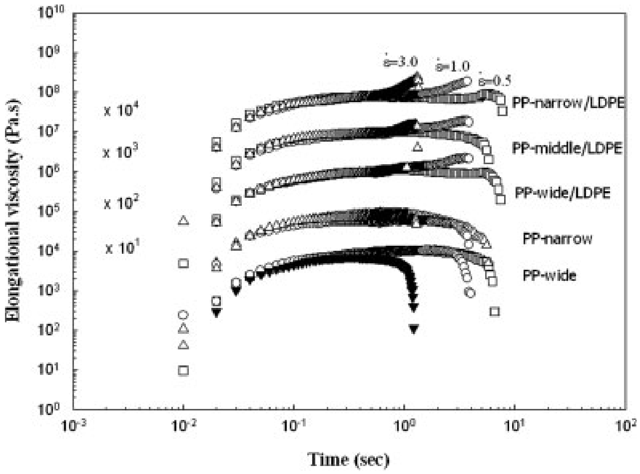

Figure 7 Time-dependent elongational viscosities of iPP and iPP/LDPE blends.

extrusion coating process seem to be consistent with these opinions.

Focusing on the Rheotens experiments of three iPP/LDPE blends in Figure 6, it was observed that the sample showing high melt strength provides lower draw-down ability. This is in agreement with previous study.[19] On the other hand, PP-wide shows lowest draw-down ability in Rheotens experiment and extrusion coating experiment even though it shows very low melt strength and apparent elongational viscosity. Thus, it is expected that only low melt tension cannot provide high draw-down ability. Time-dependent elongational viscosity gives clue for this discrepancy.

Time-dependent elongational viscosities of two iPPs and three iPP/LDPE blends are shown in Figure 7. iPP/LDPE blends show strain hardening behaviors at elongational rate of 1 and 3 s^{-1}, whereas pure iPPs do not show this behavior. For quantitative analysis of the strain hardening behavior of polymers, a extensional viscosity index (EVI) was introduced, which was defined as a ratio of elongational viscosity at the Henky strain of 3 to that of 1 at strain rate 1 s^{-1} by Ivanov et al.[33] In our evaluation, modified EVI which is a ratio of elongational viscosity at the Henky strain of 3 to that of 1 at strain rate 3 s^{-1} was used. EVIs of PP-wide/LDPE, PP-middle/LDPE, and PP-narrow/LDPE are 1.38, 1.53 and 2.07, respectively, and those of PP-wide and PP-narrow are 0.56 and 0.98. From these results, it is believed that the strain hardening is necessary to provide higher draw-down ability along with reducing draw resonance. Strain hardening is also the crucial factor in other elongational flow-dominant process such as film blowing,[25] BOPP film manufacturing,[34] and foaming process.[35] Film width of PP-narrow/LDPE shows highest EVI increases with DDR, whereas those of PP-middle/LDPE and PP-wide/LDPE decreases slightly as shown in Figure 4. Therefore, it could be concluded that the polymer should have low melt strength and strain hardening behavior to be used for extrusion coating process.

CONCLUSIONS

PP is susceptible to occurrence of draw resonance in extrusion coating process. This shortcoming can be overcome through blending with LDPE. iPP/LDPE blends exhibit reduced draw resonance and stable extrusion coating performance even in high draw-down ratio. It would be due to strain hardening properties of samples in elongation caused by LDPE blending, as verified in our EVF test. Neck-in and draw-down ability, which are important performance factors in extrusion, are also affected by MWD of iPP in iPP/LDPE blends. Blend sample containing narrower MWD iPP (PP-narrow/LDPE) exhibits narrower film width and higher draw-down ability, which resulted from lower elasticity and lower melt strength. From several rheological measurements, it can be concluded that neck-in is affected not only by elasticity but also by elongational properties such as melt strength and apparent elongational viscosity. In addition, high draw-down ability can be achieved with material which has lower melt strength and strong strain hardening.

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