Hot Tack of Metallocene Catalyzed Polyethylene and Low-Density Polyethylene Blend

HSI-HSIN SHIH, CHANG-MIN WONG, YU-CHI WANG, CHI-JOU HUANG, CHANG-CHONG WU

Union Chemical Laboratory, Industrial Technology Research Institute, 321 Kuang-Fu Rd. Section 2, Hsin-Chiu, Taiwan, ROC

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ABSTRACT: Films made of metallocene catalyzed polyethylene (mPE), low-density polyethylene (LDPE), and their blend were prepared to investigate how LDPE influences the hot tack of film. Experimental results showed hot tack is independent of film thickness. The addition of 30 wt % of LDPE can increase the hot tack of mPE film. The thermograms of differential scanning calorimetry (DSC) suggest the respective partial melting and recrystallization of those smaller size crystals at the bond forming and joint fracture stages play very important roles. The large amount of partial melting and high flow may induce a higher degree of molecular diffusion. Higher residual crystallinity and recrystallization at the hot tack testing process may induce higher resistant to bond fracture. Those two positive influences show that the mPE/LDPE film has the higher hot tack. The evidence from optical (higher optical transmission and lower haze) as well as viscoelastic (higher storage modulus and lower melt viscosity) properties further support this hypothesis. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1769–1773, 1999

Key words: hot tack; metallocene; morphology; polyethylene

INTRODUCTION

Polyethylene has long been polymerized with Zieglar–Natta catalyst and is classified by his levels of density, as high, medium, low, and linear low polyethylenes, respectively. Recently, metallocene catalyzed polyethylene (mPE) has been commercialized by some companies; among them, Exxon and Dow. This polyethylene has a molecular weight distribution around two, uniform short side chain distribution, and controllable long chain branch. This unique molecular structure means that mPEs have superior heat sealing properties (hot tack and heat seal strength) as compared to low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE).¹

Many products are sealed in various flexible plastic films using a heat sealing method. One of the most important film characteristics is its heat sealing property. Hot tack dominates the packaging speed, and heat seal strength controls the load of the contents. The heat sealing mechanisms have been investigated by Meka and Stehling.²⁻⁴ Who found that the heat sealing strength is dominated by the interfacial temperature, dwell time during the sealing process,² the melting behaviors of polyethylene films,³ and the presence of the crosslinking rather than that of the functional group.⁴ The latest finding strongly suggests that heat seal strength during heat sealing process is, at least partially, controlled by the flow properties. Similar findings have been observed by other researchers.5,6

Correspondence to: H.-H. Shih.

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 Table I
 Sample Designations

	mPE	LDPE
mPE mPE/LDPE LDPE	100 70	30 100

Basis: weight percent.

Other studies have been conducted to understand why mPE has the higher hot tack at lower sealing temperatures and how it affects the hot tack of its blends. In one, the higher hot tack of mPE film at lower temperatures is attributed to its unique molecular structure and melting behaviors.⁷ A small amount of mPE can enhance the hot tack, especially at lower sealing temperatures.^{8,9} In addition, a small amount of mPE blended with better miscibility polyolefins may lead to lower heat initiation temperatures.¹⁰ It has been found that the processibility of mPE can be enhanced by the addition of a small amount of LDPE. However, how the small amount of LDPE affects the hot tack is seldom discussed.

In this study, mPE was first dry blended with 30 wt % of LDPE. The mPE, LDPE, and their blend were blown into films. Hot tack of those films were measured. Thermal and optical properties of LDPE, mPE, and mPE/LDPE blend were further investigated. Finally, the correlations between chain structures, morphology, and hot tack are discussed.

EXPERIMENTAL

LDPE, mPE, and mPE/LDPE blends, as shown in Table I, were used in this study. These three materials were processed into 40- μ m thick film with an extrusion blown film process. The hot tack [both in machine direction (MD) and transverse direction (TD)] of films were determined with a hot tack tester (Brugger Munchen Inc.). Two films with 15-mm width were placed between two chrome plates and pressed at different temperatures and 2.0 kg/m² load for 0.5 s. The hot tack was measured immediately after the bonded film was cooled for 0.5 s.

Differential scanning calroimetry (DSC) was used to measure the thermal properties of films made of LDPE, mPE, and mPE/LDPE blend. A film about 5-mg weight was placed in the chamber, and the testing temperature range was room temperature to 175° C at an increasing rate of 10° C/min. Then, it was cooled to room temperature at the 10° C/min rate. In addition, the optical and transmission properties of the three films were measured.

A parallel plates rheometer (Paar Physica Company) was used to measure the storage and loss modulus moduli of polyethylenes at various temperatures. A sample disk about 1.5-mm thick and 25 mm in diameter was placed in the chamber. The samples were heated to 170°C and remained at that temperature for 5 min to ensure the samples were completely melted. Then, the storage and loss modulus were measured from 170°C to 50°C at 2°C/min cooling rate and 1 Hz.

RESULTS AND DISCUSSION

Hot Tack of mPE/LDPE Blend

30 wt % of low-density polyethylene was added to the mPE and blown into film. Results of hot tack measurements are listed in Table II. As expected, the films made of mPE has higher hot tack than LDPE film. It is surprising that the mPE/LDPE film has the highest hot tack values among three. This may result from the following: film thickness, melting behaviors, and flow ability. To discard the effect of film thickness, the hot tack of two films with different thickness were measured.

Effect of Film Thickness on Hot Tack

Two films with respective 23 and 31 μ m thicknesses were made to investigate how the film thickness affects the hot tack. Results are listed in Table III. Films with different thicknesses have the same hot tack value at five sealing temperatures, indicating the hot tack is independent

Table II	Hot Tack of Polyethylenes at Vario	us
Testing T	emperatures	

Torrestore		Hot Tack (g)	
Temperature (°C)	mPE	mPE/LDPE	LDPE
100	$<\!\!50$	<50	$<\!\!50$
105	200	250	50
110	225	275	50
115	175	250	$<\!50$

m	Hot Tack (g)		
Temperature (°C)	31 mm	23 mm	
113	<30	$<\!\!30$	
115	50	50	
118	175	175	
120	150	150	
125	125	125	

Table III Effect of Film Thickness on Hot Tack

of the film thickness. Thus, hot tack should be controlled by morphology and flow properties.

Thermal Properties of mPE/LDPE Blend

Melting behaviors of the three films were detected by DSC. The thermograms of three materials are plotted in Figures 1 to 3. The mPE has a bit higher heat of fusion than mPE/LDPE; however, it has a much higher value than LDPE. LDPE has a narrower melting peak; whereas, mPE has a broader one. Furthermore, a broader melting peak can also be observed in the mPE/LDPE blend, probably because the blend has a large portion of mPE.

Regarding crystallization behaviors, LDPE has the lowest crystallization temperature and narrower exotherms. A much broader peak is observed for mPE; moreover, the mPE/LDPE blend obviously, has two, crystallization peaks. The higher and lower one correspond to the crystallization temperature of mPE and LDPE, respectively. In addition, LDPE has the lowest heat of

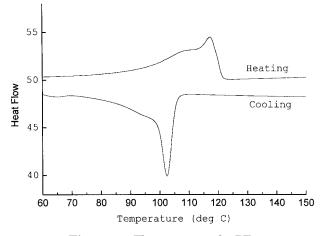


Figure 1 Thermagram of mPE.

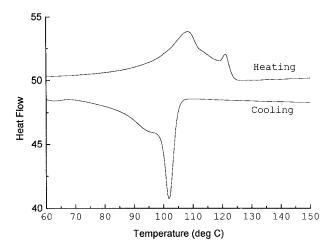


Figure 2 Thermagram of mPE/LDPE.

fusion (78 J/g); whereas, the mPE/LDPE and mPE have similar values (89 and 91 J/g, respectively). In other words, the respective crystallinity of LDPE, mPE/LDPE, and LDPE are 26.6, 30.4 and 31.0.¹¹

Optical Property of mPE/LDPE Blend

The haze and transmission of the three films are listed in Table IV. A high transmission and low haze were reported in mPE/LDPE blend. As described before, the mPE/LDPE has a bit lower heat of fusion than mPE, but it has much a higher value than LDPE. It was found that the higher portion of amorphous region or smaller crystal size will induce a lower haze. Moreover, as stated before, mPE/LDPE and mPE have similar thermal properties (heat of fusion and melting behav-

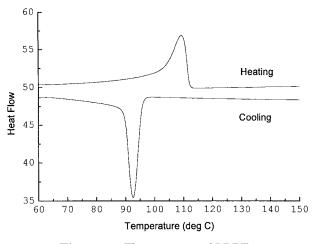


Figure 3 Thermagram of LDPE.

	Haze	Transmission (%)
mPE	17	93
mPE/LDPE	4.1	91
LDPE	8	88

Table IV	Haze and Light Transmission of	
Polyethyle	enes	

iors). Here, we can conclude that the lower haze of
mPE/LDPE should result from the smaller crystal
size in this blend.

Correlations among Chain Structure, Morphology, and Hot Tack

A possible bond formation and fracture mechanism was proposed to clarify why the film made of mPE/LDPE blend has higher hot tack than mPE. The films were subjected to heat (such as, bonded at 105°C), the crystals portion with melting points lower than the sealing temperatures melted. Molten and amorphous portion of polyethylene molecular provides the required wetting. Here, those polyethylene moleculars in both films penetrate each other, forming the required joints.²⁻⁴ Thus, the films are bonded together, completing the bond formation stage.

After two films are bonded together and cooled down for 0.5 s, the hot tack testing proceeds. The film is only partial melted, indicating some solid portion (i.e., unmelted crystal corresponding to the higher melting peaks) still exists. This solid portion can against the external load to prevent the joints from fracture. The resistance to bond fracture represents the hot tack. If the sealing temperature is at or near its crystallization temperature, the molten polyethylene molecular is recrystallized. This induces some additional crystallinity beyond the residual crystallinity, leading to a much higher storage modulus. In other words, the resistance to external force becomes stronger; that is, even at higher hot tack, partial melt still exists.

Table V illustrates the residual crystallinity of polyethylenes at various sealing temperatures. Among the three, LDPE has the lowest residual crystallinity at sealing temperatures; for example, 105°C, and the bonding temperature (105° C) is about 10°C to 13°C higher than the respective crystallization onset and peak temperature of

The state of the s	Residual Crystallinity		
Temperature (°C)	LDPE	mPE/LDPE	mPE
80	26.6	30.4	31.4
85	26.3	30.0	30.4
90	25.9	29.4	29.7
95	24.9	28.0	28.0
100	23.5	26.3	27.3
105	21.2	23.2	23.5
110	17.4	17.7	17.4
115	12.6	10.6	3.8
120	7.2	5.5	0
125	0.7	2.0	
130	0	0	

LDPE. In contrast to the mPE and mPE/LDPE, the bonding temperature is quite close to the crystallization onset, and peak temperatures are 105 and 103°C. Those two factors show that the LDPE has the lowest hot tack. However, the concept of residual crystallinity and crystallization temperature is not enough to explain why mPE/LDPE film has higher hot tack than mPE. There should be some other effects controlling the hot tack.

Morphology and wetting may be other important issues. When the extruded mPE/LDPE blend melt is cooled below about 105°C, the molecular structure corresponding to mPE portion becomes crystallized. This is supported by the thermagrams of mPE, shown in Figure 1. As the temper-

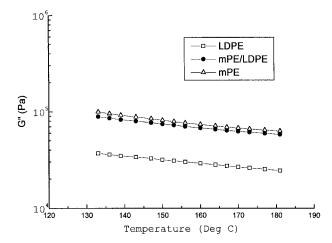


Figure 4 Loss moduli of polyethylenes at various temperatures.

Table VResidual Crystallinity ofPolyethylenes at Various Testing Temperatures

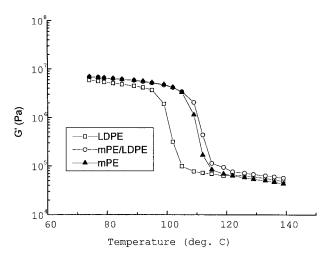


Figure 5 Storage moduli of polyethylenes at various temperatures.

ature lowers, the crystal size of mPE grows larger. When the temperature is cooled to 92°C, LDPE becomes crystallized. The interference of two different crystallization limits the growth of two crystal sizes (Figure 2). Smaller crystal sizes with two different melting points are observed. A smaller crystal size results in better light transmission and less light reflectance (low haze). This is why the mPE/LDPE blend has higher transmission and lower haze (Table II). However, without the interference of LDPE, the mPE crystal will grow larger than the mPE/LDPE (higher haze). Here, as two mPE/LDPE blend films are joined at the temperatures near their crystallization temperatures (such as, 105°C), respectively. The smaller crystal size mPE/LDPE may be melted more quickly than the large crystal size, leading to a much higher flow portion. In addition, the mPE/LDPE has a lower loss modulus; that is, lower viscosity (Figure 4) than mPE, indicating better wetting. These coupling interactions indicate why mPE and mPE/LDPE have higher hot tack. As the sealing temperature increases to 130°C, the residual crystallinity of mPE/LDPE is higher than mPE. This leads to a much larger drop in hot tack in mPE film. This is supported by the viscoelastic responses of mPE and mPE/ LDPE where the mPE/LDPE has higher storage modulus than mPE at the sealing temperature region (Fig. 5).

LDPE has the lowest molten viscosity of three films. However, the lowest residual crystallinity and the recrystallization temperatures of LDPE were also observed, thus explaining why LDPE has lower hot tack than mPE and the mPE/LDPE blend.

CONCLUSIONS

The hot tack, according to the above discussion, is controlled by molecular aspects in the bond formation and fracture stages. During the bond formation stage, the higher flowability of molecular and the large amount of the molten polymers will more molecular interdiffusion. induce The smaller crystal size will be melted faster and more completely, resulting in a more molten polymer portion. Therefore, two films can be bonded much more completely. To provide more resistance to the external forces at the bond fracture stage, the films must have a higher portion of residual crystallinity. In addition, the hot tack will be enhanced, if the hot tack testing conditions are close to the recrystallization temperatures of the polymers.

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REFERENCES

- Kim, Y. S.; Chung, C. I.; Lai, S. Y.; Hyum, K. S. J Appl Polym Sci 1996, 59, 125.
- Meka, P.; Stehling, F. C. J Appl Polym Sci 1994, 51, 89.
- Meka, P.; Stehling, F. C. J Appl Polym Sci 1994, 51, 105.
- Meka, P.; Stehling, F. C. J Appl Polym Sci 1994, 51, 121.
- 5. Ellul, M. D.; Gent, A. N. J Polym Sci 1984, 22, 1953.
- Shih, H. H.; Hamed, G. R. J Adhesion 1997, 61, 231.
- Sanden, D. V.; Halle, R. W. in ANTEC 1992, pp. 154.
- Sanden, D. V.; Halle, R. W. in ANTEC 1993, pp. 46.
- 9. Halle, R. W. in TAPPI, Polymer Laminations, and Coating Conferences, 1995, pp. 561.
- Patel, R. M.; Saavedra, P.; deGroot, J.; Hinton, C.; Guerra, R. in ANTEC 1997, pp. 1950.
- Nagode, J. B.; Roland, C. M. Polymer 1991, 32, 505.