

Investigation of the Migration Behavior of Polyisobutylene with Various Molecular Weights in Ethylene/ α -Olefin Copolymer Blown Stretch Films for Improved Cling Properties

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ABSTRACT: High retention forces are the basic requirements on stretch films for agricultural or pallet wrapping of goods and significantly influenced by cling properties (autohesion) that are essential for a reliable load stability during transportation and storage. Low molecular weight polyisobutylene (PIB) has tacky properties and is immiscible with polyethylene. Blended with ethylene/ α -olefin copolymers in coextruded stretch films, PIB can migrate to the film surfaces and cause cling properties. Cling and adhesion forces were investigated using the mechanical cling test, atomic force, and scanning electron microscopy and infrared spectroscopy. The molecular weight of the PIB as well as density and crystallinity of the matrix material have strong influences on migration kinetics and therefore, on the cling forces. Cling forces increase with increasing aging time, having a maximum after 2 weeks of production. The following slight decrease of the cling force might be correlated with a beginning degradation process of the UV sensitive PIB. Polyisobutylene with higher molecular weight diffuses slower through a linear low density polyethylene (LLDPE) matrix than lower molecular weight PIB, but can cause higher cling forces on the film surfaces. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40239.

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INTRODUCTION

Stretch films based on polyethylene play great roles in the packaging industry. Major applications are palletized safety goods wrapping and agricultural silage bundling for product protection and stability during transportation and storage. When transporting goods, the stretch film has to compensate forces of 0.8 G in driving direction and transverse 0.5 G next to the vibration level, which makes it more than just a commodity product.¹ The requirements on the film are steadily growing with respect to a cost efficient and sustainable use of materials (down gauging) and processing. In addition to this, property improvements are always requested. In contrast to other palletized packaging solution, e.g., shrink hoods, stretch films provide many benefits like easy and

flexible handling, manageable costs and favorable mechanical properties.²

Autohesion and shear rate between two superimposed films are responsible for high retention forces after prestretch. The autohesion, i.e., adhesion on itself, is also described as the cling property. The highest level of autohesion corresponds to the cling force. Conventional ethylene/ α -olefin copolymers with long chain branches (LCB) are the most common materials used in the adhesive layer of stretch films. Linear low density polyethylene (LLDPE) stretch films with octene comonomer types seem to be most suitable for stretch film applications, since they provide appropriate mechanical properties like high elongation at break and tear resistance in dependence on processing parameters and machine direction.³ Primary mechanical

adhesion due to molecular chain entanglements and van-der-Waals forces cause bonding between two films of nonpolar polyethylene. Furthermore, ethylene/octene-1 copolymers and appropriate processing conditions cause good mechanical performance with minor necking of the stretched film. Otherwise a high prestretch of the film increases the orientation of the molecular side chains on the film surface in the stretching direction, which makes it more difficult for them to interact with each other. Therefore, cling forces and ultimately the retention forces could decrease, depending on the prestretching level. A blending with low molecular weight polyisobutylene (PIB) can improve the cling force without being dependent on the prestretching level.⁴ PIB as the oldest olefin polymerize has tacky properties that vary with its molecular weight. The polymerized middle chain length PIB with $\text{CH}_2\text{-C}_3\text{H}_6$ groups is chemically inert and can act as a secondary plasticizer or tackifier, respectively, when added to a polyethylene matrix. Due to the incompatibility of PIB with polyethylene, two phases exist and the PIB is distributed in the amorphous phase and can migrate to the film surfaces, where it causes cling properties to change over time. The diffusion rate of the dispersed PIB particles in the polymer matrix contributes significantly to the cling force level and depends on many parameters.⁵

The 2nd Fick's law of diffusion determines a diffusion coefficient to estimate the migration kinetics over the time that is given by Eq. (1),⁷

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (1)$$

wherein $c = c(x, t)$ provides the solution of a concentration of a dissolved substance in the medium under consideration at any time t . D is the diffusion coefficient. Certainly a quantitative statement cannot be done since uniform diffusion constant is missing. In addition to this, these assumptions are primarily valid for mono layer films, which make it even more complicated to characterize the migration kinetics in coextruded film structures. Indeed, the migration kinetics of low molecular components or solvents, respectively, strongly depends on the morphology of the polymer matrix, crystallinity, glass transition temperatures and molecular weight distribution.⁴

McNally and Small et al. [4, 5, 8–11] did quite extensive investigation in the field of autohesive stretch films. One of their main emphases is different polyethylene stretch films blended with PIB for cling film applications. Cling performance was characterized by measuring the peel force with the T-Peel test according to ASTM D 1876,⁶ peeling with angles of $2 \times 90^\circ$. Improved cling properties with increased concentration of low molecular PIB in LLDPE with octene comonomer blended with LDPE in blown and cast films could be observed. Blown stretch films show slightly higher cling forces than cast films, which contradicts the assumption that a lower crystallinity supports the migration of the PIB from the bulk to the film surface.⁷ The molecular weight of the used PIB has a major influence on the amount of migrated components to the film surface, where it causes the cling. Lower molecular weight PIB seemed to migrate faster to the film surface, reaching maximum cling

forces earlier, but with lower levels at all. Cling forces increase with aging time at 25°C, showing significantly higher cling strengths if stored at higher temperatures up to 45°C. In both cases a maximum of the cling force could be expected after approximately two weeks of aging.^{7–9} Conditioning the stretch film at -40°C results in steady cling forces. Summarizing the literature results, it can be stated that the main factors influencing migration kinetics of the PIB through a polyethylene matrix and therefore, the autohesion properties, are the molecular structure or co-monomer type, crystallinity, density, and orientation of the matrix material as well as molecular weight and concentration of cling additives like PIB.^{3–5,8–11} Additionally, the storage conditions of the investigated stretch films have a direct impact on the cling properties and should therefore be strongly considered in further investigations.^{4,5}

This study is focused on the influence of PIB with different molecular weight as well as the polymer matrix, in order to achieve improved cling properties of stretch films. Furthermore, it was investigated whether a blend of low and high molecular weight PIB could accelerate the migration kinetics and therefore, achieve maximum cling forces sooner than with single components.

EXPERIMENTAL

Materials and Film Processing

A summary of the materials used in this study can be taken from Table I. We intended to investigate the influence of the matrix material and of the molecular weight of the cling additive and of the use of processing agents on the cling properties. Therefore, we chose matrix materials with different densities because of their different molecular architecture. We used an LDPE from LyondellBasell (#4, Lupolen 3020 F) and different LLDPE ethylene/ α -olefin copolymers (hexene and octene comonomer) from DOW (#1–#3, Dowlex 2042 E, Dowlex SL 2103 G and Affinity EG 8100 G).

Furthermore, we used PIB compounds of PIB with different molecular weight to investigate their influence on the cling properties and to investigate their influence on PIB migration / ageing. The PIB masterbatch was compounded with 50 wt % LDPE (#4, Lupolen 3020 F) as a carrier resin. The PIB with the lowest molecular weight (#5, PIB_{LMW}) had a molar mass M_n of 1300 and a polydispersity index M_w/M_n of 1.65. The medium molecular weight PIB (#6, PIB_{MMW}) had a M_n of 2100 and an M_w/M_n ratio of 1.85. The highest molecular weight PIB (#7, PIB_{HMW}) had a M_n of 4200 and an M_w/M_n ratio of 1.80. For deeper analysis of the migration behavior we mixed PIBs of different molecular weight. We speculated that this could accelerate the migration process. Therefore, blends of low and medium molecular weight PIB were produced, having mixing ratios of 1 : 3, 1 : 1, and 3 : 1.

The use of processing agents is relatively often necessary in industrial practice. Therefore, the influence of a usual anti-block additive and a slip agent on the cling properties was investigated. The anti-block masterbatch (#8, ME 50004) was compounded with LDPE and a CaCO_3 content of 72.5 wt %. The average agglomerated oversize (topcut) of the CaCO_3 was $\sim 8 \mu\text{m}$.

Table I. Summary of Matrix Materials, Cling Additives, and Processing Agents Used in this Study

No.	Material type	Producer	Comonomer type	Density (g/cm ³)	MFI (g/10 min)	Molecular weight M_n
Matrix materials						
1	LLDPE (Dowlex 2042 E)	DOW	Octene	0.930	1.0	-
2	LLDPE (Dowlex SL 2103 G)	DOW	Octene	0.917	0.7	-
3	LLDPE (Affinity EG 8100 G)	DOW	Octene	0.870	1.0	-
4	LDPE (Lupolen 3020 F)	LyondellBasell	-	0.928	0.9	-
Cling additives						
5	PIB (Indopol H 300)	Ineos	-	0.904	173 ^a	1300
6	PIB (Indopol H 2100)	Ineos	-	0.906	242 ^a	2100
7	PIB (Indopol H 6000)	Ineos	-	0.918	306 ^a	4200
Processing agents						
8	Antiblock (ME 50004)	Multibase	LDPE	1.74	9.0	-
9	Slip agent (PB F15)	Schulmann	LDPE	0.98	12.0	-

^aViscosity index: ASTM-D2270 (mm²/s).

The slip agent (#9, PB F15) was compounded with 65 wt % chalk (CaCO₃ based) in an LDPE carrier resin, which had a topcut of ~3 μm.

The coextruded films were produced on a Dr. Collin lab extruder system. Each of the three used extruder (one separate extruder for each layer of the final film) had a conventional single compression screw and an *L/D* ratio of 24 : 1. The blending of each composition for each layer have been done manually in front of the extrusion by weighting and gravimetrically dosed to the appropriate extruder. The homogenous melt was led together in a pancake die system and blown up immediately. Processing conditions and parameters can be taken from

Table II. Processing Conditions of Coextruded Blown Films

Extruder parameters	Maddock mix and shear elements 100 rpm screw speed Temperature profile : (40)–140–160–180–190–210°C
Die head parameters	Temperature profile: 210–210–210–210°C Die gap: 0.8 mm
Tube formation	Time of solidification 1.8 s Blow-up ratio 1 : 2.2 Draw-down ratio 1 : 18

Table III and were almost kept constant, at least concerning the cooling of the bubble and the draw down ratio.

The investigated stretch films have a three-layer structure with a total thickness of 20 μm. Details about the blend compositions of the used stretch film types are listed in Table II. Generally, the core layer (Layer B) was produced with a thickness of 10 μm, while each skin layer (Layer A and C) had a

Table III. Blend Composition of the Stretch Films Used in this Study Without PIB and Processing Agents

Material type	Type 1 Material (wt %)	Type 2 Material (wt %)	Type 3 Material (wt %)
Layer A (5 μm)			
#1 Dowlex 2042 E			100.0
#2 Dowlex SL 2103 G	75.0	100.0	
#3 Affinity EG 8100 G	25.0		
Layer B (10 μm)			
#1 Dowlex 2042 E			100.0
#2 Dowlex SL 2103 G	75.0	100.0	
#3 Affinity EG 8100 G	25.0		
Layer C (5 μm)			
#1 Dowlex 2042 E	80.0	80.0	80.0
#4 Lupolen 3020 F	20.0	20.0	20.0

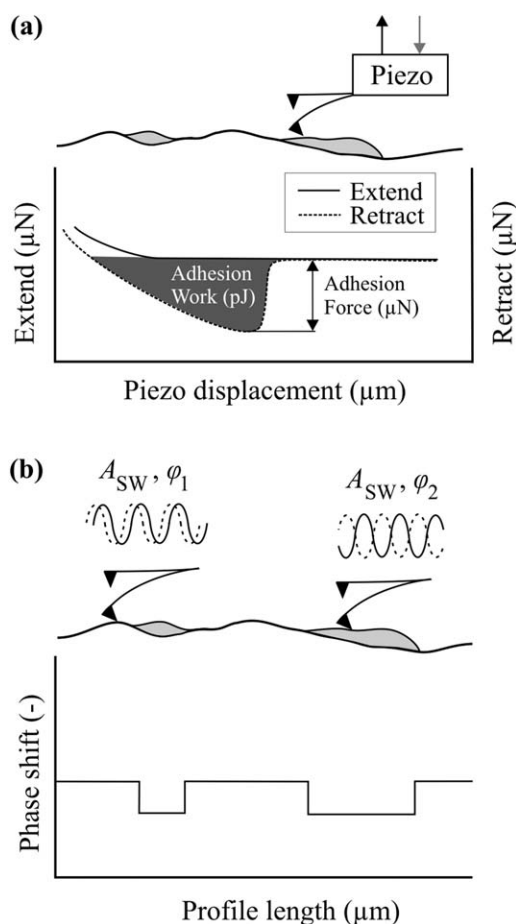


Figure 1. Schematic of atomic force microscope tapping mode detecting adhesion work/force (a) and recording phase shifts (b).

thickness of 5 μm . To investigate the PIB migration, the inner skin layer (Layer A) and the core layer (Layer B) were blended separately with 10 wt % of each of the PIB masterbatches (#5-#7, Indopol H 300, Indopol H 2100, and Indopol H 6000). The different densities of the chosen LLDPE/octene-1 copolymers might be correlated with different concentration and distribution of octene-1 comonomers and therefore chain branching and furthermore crystallinity. The different blended matrices without PIB in core and skin layer were defined as Type 1 with an average density (a.d.) of 0.905 g/cm^3 , Type 2 with an a.d. of 0.917 g/cm^3 , and Type 3 with an a.d. of 0.930 g/cm^3 . The supposed slight variation of the density within the layers due to migration kinetics of the PIB has not been considered in this study.

Atomic Force Microscopy Tapping Mode (tm-AFM)

Atomic force microscopy (AFM) has become a useful method to evaluate adhesion forces, among others, even at small length scales. While bringing the cantilever and the film surface in close contact, the deflection of the spring as a result of the interaction with the surface and the adhesion mechanics can be measured [Figure 1(a)] during a point-by-point analysis of a given measuring field, driven by a piezoelectric driver. With the help of the known spring constant of the cantilever the

deflection-distance (retract) and force-distance (extend) curves can be calculated, representing the adhesion level.¹² The atomic force microscope used in this study was a JPK nanowizard II®. The spring constant k_c of the cantilever was 39.92 N/m and 42.58 N/m. The tip was glass bead and had a radius r_{Tip} of 2.2 or 2.5 μm , respectively. The initial force of the cantilever that was pressed into the film surface had a rel. setpoint of 1 μN and was kept constant for all series. The adhesion force results in the snap-off effect and the difference between maximum deflection of the cantilever and the initial level.

Next to the identification of adhesion forces on the film surface it is possible to characterize different material phases in the border layer via tapping mode AFM. During the screening of the sample's surface it is additionally possible to record phase shifts φ between stimulation and oscillation due to external forces. The constant value of the amplitude A_{SW} generates a short contact between cantilever and film surface in each cycle. In dependence on the morphology of the material, different shifts can be recorded that represent divergent material phases [Figure 1(b)]. The phase contrast is the result of the difference between phase shift φ_1 and phase shift φ_2 . The size of each measured surface was $10 \times 10 \mu\text{m}^2$.

Scanning Electron Microscopy (SEM)

The surfaces of the blown films, which were interspersed with migrated PIB, were observed by scanning electron microscopy (SEM) using a Quanta 3D FEG (FEI, USA) scanning electron microscope at an operating voltage of 5 kV. The films were fixed with carbon tapes at the edges on a standard SEM carrier and their surfaces sputtered with platinum (20–30 nm), to ensure electron conductivity.

Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR Spectroscopy)

Infrared spectroscopy measurements were performed using a Thermo Nicolet® Avatar 360 Fourier transform infrared spectroscopy (FTIR) device. As experimental setup the Nicolet Smart attenuated total reflectance (ATR) module “Golden Gate” with single bounce diamond was mounted. To provide the essential constant pressure, bringing the diamond and the film material in intimate contact, the stamp pressing the film on the diamond surface was tightened with a defined torque moment of 0.5 Nm by a torque wrench.

Cling Test

To measure the cling force between two stretch films, the cling test according to ASTM D 5458^{13,14} was used. One film sample $10 \times 10 \text{ inch}^2$ is fixed on a 20° slope with the outside layer up, whereby the produced machine direction is parallel to direction of loading. The angle makes it necessary to take also the shear rate into account. A $1 \times 7 \text{ inch}^2$ film stripe is cut of separately in machine direction (MD) and fixed onto its back, free of air pockets and imperfections in the interface [Figure 2(a)]. The tests were performed with a Zwicky tensile-testing machine (Zwick/Roell, Germany), using a load cell of 50 N. A strap is connected to the specimen and preloaded with 0.05 N. The cling properties of the film were recorded by measuring the force of at least 6 specimens that is necessary to peel the bonded films up to the cling line (marked

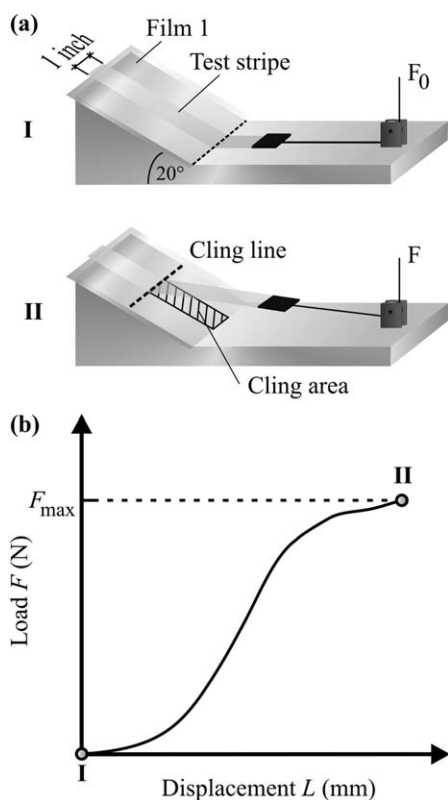


Figure 2. Schematic of the cling test according to ASTM-D 5458 (a) with registration of the force-displacement curve (b).

horizontal line on top face) with a testing speed of 100 mm/min [Figure 2(a)]. The maximum force F_{\max} that is recorded at the cling line is the cling force [Point II in Figure 2(b)]. The first tests were done immediately after production (Day 0). Subsequently, the film samples were conditioned up to 4 weeks at 30°C and a rel. humidity of ~50% and taken off directly before measuring.

RESULTS AND DISCUSSION

Investigation of the Surface Morphology of the Stretch Films

The adhesion properties of coextruded LLDPE/ α -olefin copolymer stretch films blended with different molecular weight polyisobutylenes (PIB) have been investigated.

A study of the surface morphology should give an indication of the presence of polyisobutylene, which could have been caused by migration. The tapping mode of the AFM can give sensitive indications about different material moduli or stiffness, respectively, representing different material phases. Taking into account an optimal reproducibility of the softer PIB phase, measurement conditions were set at constant amplitude of the cantilever for all samples. Otherwise, it would lead to deformations of the PIB phase due to the penetration of the cantilever. Therefore, the chosen parameter setting can consequently lead to the typical artifacts at harder particles on the surface and the observed shadows. The particles are not accurately depicted in phase contrast and appear as a separated phase. However, these particles and the crystalline superstructure have not that relevance to the evaluation of the migration kinetics of the PIB. The main issue is the constant parameter setting for the

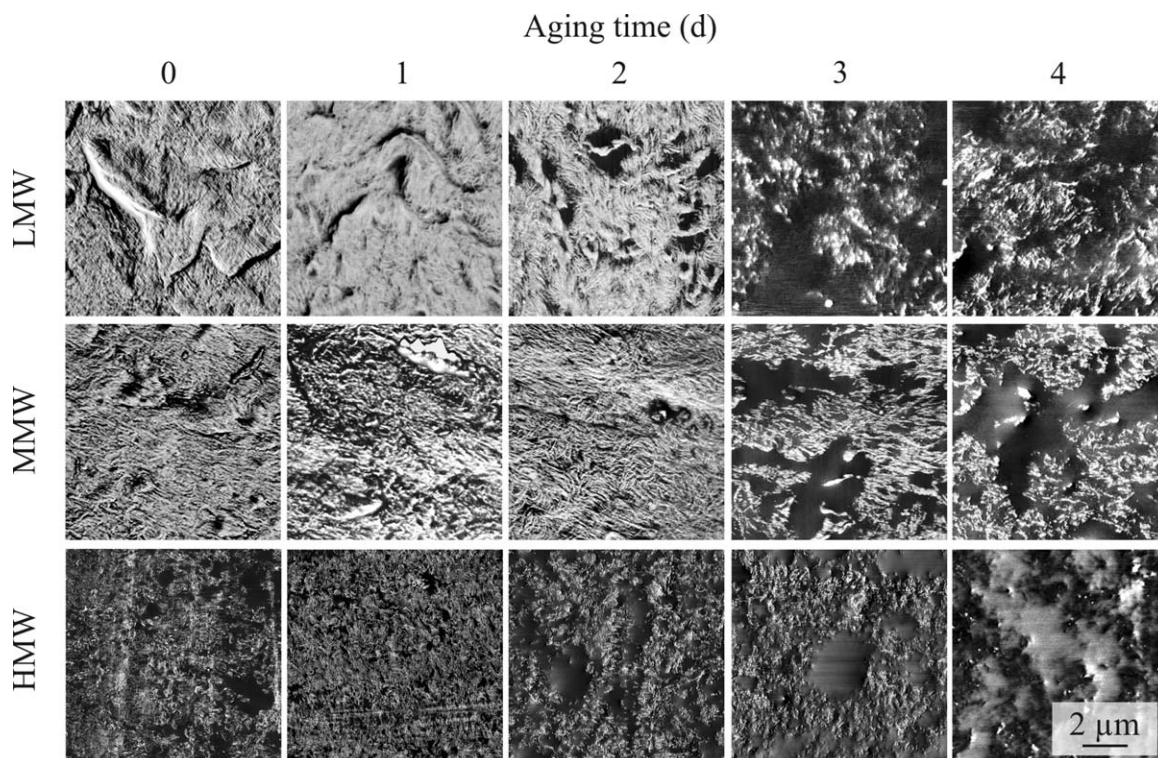


Figure 3. AFM images of the tapping mode phase contrast for PIB_{LMW} , PIB_{MMW} , and PIB_{HMW} in type 2 matrix (a.d. of 0.917g/cm³) as a function of aging time.

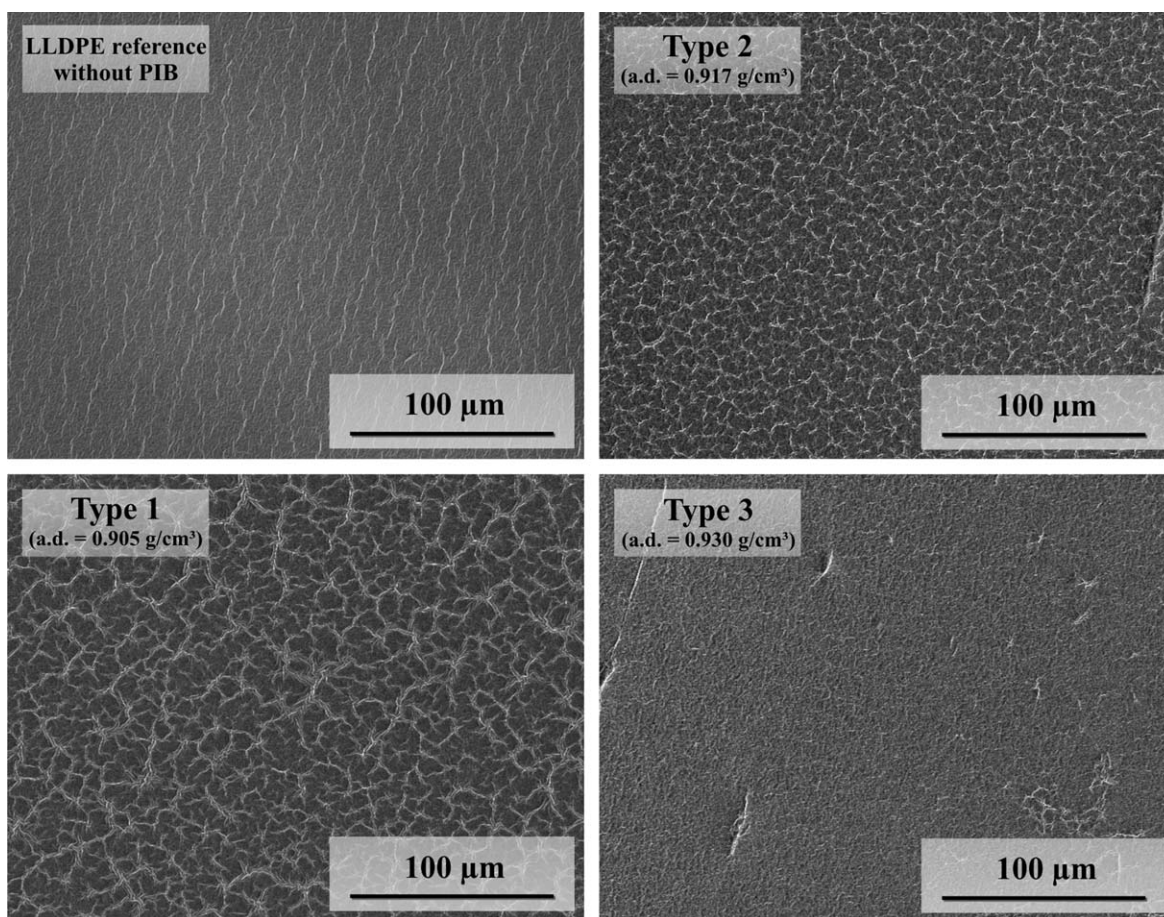


Figure 4. SEM images for each type of matrix material blended with PIB_{HMW}.

reproducibility of the AFM images. Material phases with lower moduli are thereby generally represented by darker optical speckles, stiffer ones by lighter tones.¹⁵ The AFM images below show the development of the phase contrast on film surface for the single PIB blended stretch films of Type 2 as a function of aging time (Figure 3). A morphological change through the migration of the PIB in the first two days was not apparent for each kind of PIB. After the first 2 days a morphological change was visible for the PIB_{LMW} and two different phases are obviously present at the film surfaces, whereby phase 1 (light gray scale) is still predominant. After 3 days a phase contrast is also visible for PIB_{MMW} and PIB_{HMW}. In dependence of aging time an increase of Phase 2 (dark continuous gray scale) occurred, which may have been caused by the migration of the PIB. After 4 days of aging the surface morphology has obviously changed through the migration of the PIB in all three cases.

To get further evidence for the PIB migration to the surface of the blown films, the surface of the stretch films of Type 1 (a.d. = 0.905 g/cm³), Type 2 (a.d. = 0.917 g/cm³), and Type 3 (a.d. = 0.930 g/cm³) blended with PIB_{HMW} after 2 days of aging time was investigated and compared with a LLDPE reference surface without PIB. The PIB phase could be identified as lighter gray-colored phase of the SEM images of Figure 4 since more secondary electrons are emitted on edges and asperities, e.g., caused by fluctuated PIB migration. The darker phase

might be dominated by the PE matrix, whereas magnification and resolution were chosen with regard to a nondestructive recording. The asperities on the LLDPE reference might result from thickness profile variations due to the extrusion on a pilot plant. It could be observed that the migrated PIB forms a kind of network at the surface of the film. This may lead to a relatively homogeneous cling behavior. The formation of this network is most extensive for the film Type 1, which is the film with the lowest matrix density. For film Type 2 (the medium matrix density), also a second phase—the migrated PIB—could be observed. However, the PIB network in case of Type 2 has not been formed as strongly as the PIB network in case of Type 1. The observed content of the migrated PIB for film Type 2 is weaker than for film Type 1. For film Type 3, no distinctive PIB migration could be observed after 2 days of aging time.

Cling Force Versus Adhesion Force

The migration of the PIB to the film surface is obviously responsible for the cling and was characterized with the mechanical cling test according to ASTM D 5458 and the almost nondestructive atomic force microscopy (AFM). Last one is a very sensitive method, which can detect adhesion forces even on small length scales. The disadvantage of the AFM method is the time-consuming measurement and sensitivity to vibrations that can cause measurement uncertainties compared to the user friendly and more practical mechanical

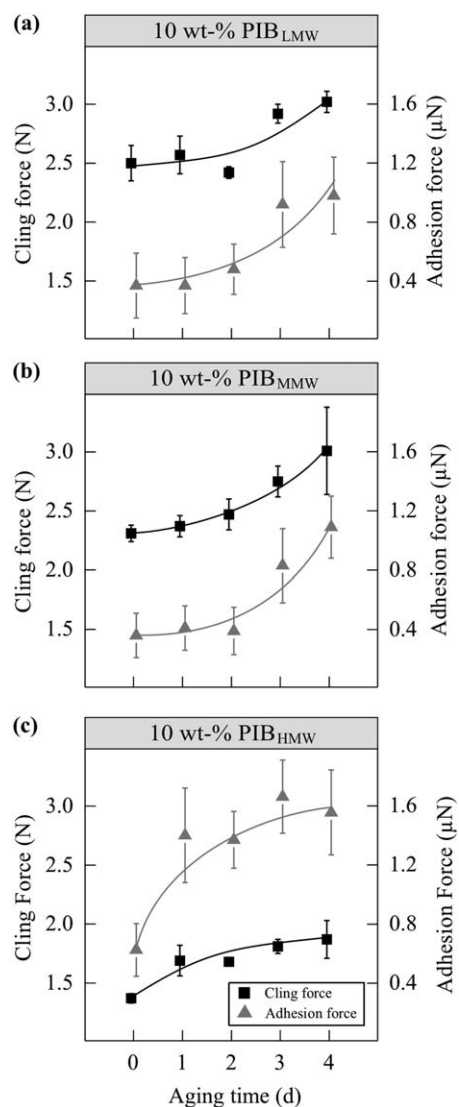


Figure 5. Comparison of measured cling forces and adhesion forces of coextruded LLDPE films (type 1) with 10 wt % low molecular weight PIB (a), medium molecular weight (b), and high molecular weight PIB (c) as a function of aging time for the first four days after production.

cling test. The major difference concerning adhesion is that with AFM it is measured in a direct way, whereas it is concluded indirectly from the results of the cling test. A

comparison of both methods was done by measuring the cling force and the adhesion force of the same stretch films blended with the lower molecular weight PIB [Figure 5(a)] the medium molecular weight [Figure 5(b)] and the higher molecular weight PIB [Figure 5(c)] in dependence on the aging time. Due to the high complexity of preparation and measurement with AFM, only the first 4 days were considered and compared with the cling measurements.

An increase of the autohesion properties within the first four days of aging could be observed with both methods. The dependence of the cling force and the adhesion force on the aging time showed a slight increase for the PIB_{LMW} and PIB_{MMW} grades and a distinct increase for the PIB_{HMW} within the first two days in matrix Type 1. PIB_{LMW} blended stretch film generates slightly higher cling forces with average 2.5 N than the PIB_{MMW} with average 2.3 N from the first day on. It might be suggested that the migration kinetics of the lower molecular weight PIB seems to be faster immediately after the production. A steep increase of the cling and adhesion force occurred after 2 days of production. Equilibrium of both PIB molecular weights was reached after 4 days with a cling force of ~3 N [Figure 5(a,b)]. The cling force level of the highest molecular weight PIB is about 1 N lower than both of the lower molecular weight cling additives [Figure 5(c)]. It might suggest that the higher molecular weight and viscosity are not suited for sufficient cling properties. Contrary to the cling force, the adhesion force is slightly higher for the PIB_{HMW}, which might be correlated with the new cantilever and spring constant that had to be used for investigations of the migration kinetics of the highest PIB H-6000 to get uniform or comparable results within one series. For a better confirmability of the results of Figure 5, the individual values are presented in Table IV.

In general, the rise of all fit curves follows the same trend, even if the level of the standard deviation is higher for the more sensitive but from adhesion point of view more reliable AFM measurement. As a consequence, the mechanical cling force testing is quite appropriate to characterize the autohesion properties of PIB blended stretch films. Furthermore, the uniform testing conditions are easier to realize for the more practical cling test. Therefore, the cling test has been exclusively used for any following investigation in this case.

Table IV. Summary of Cling Force and Adhesion Force with Standard Deviations for the Different Molecular Weight PIB Mixed in Type 1 in Dependence of Aging Time

Aging time (d)	LMW				MMW				HMW			
	Cling force		Adhesion force		Cling force		Adhesion force		Cling force		Adhesion force	
	(N)	s	μN	s	(N)	s	μN	s	(N)	s	μN	s
0	2.5	0.15	0.37	0.22	2.31	0.07	0.36	0.15	1.37	0.04	0.62	0.18
1	2.57	0.16	0.37	0.19	2.37	0.09	0.41	0.15	1.69	0.13	1.40	0.32
2	2.42	0.05	0.48	0.17	2.47	0.13	0.39	0.16	1.68	0.03	1.37	0.19
3	3.05	0.08	1.05	0.29	3.25	0.13	0.93	0.2	1.81	0.06	1.66	0.25
4	3.5	0.09	1.07	0.26	3.8	0.17	1.23	0.18	1.87	0.16	1.56	0.29

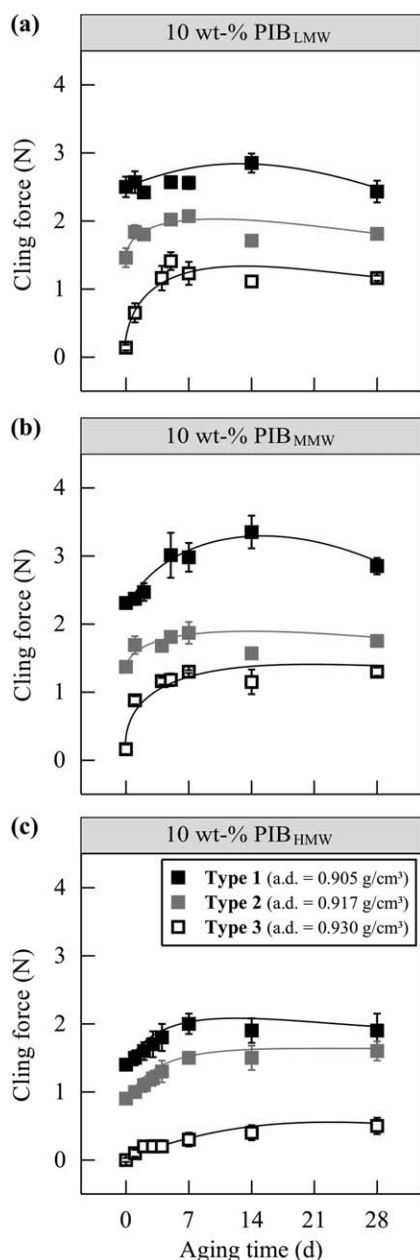


Figure 6. Cling forces of coextruded LLDPE films for Type 1 (a.d. = 0.905 g/cm³), Type 2 (a.d. = 0.917 g/cm³), and Type 3 (a.d. = 0.930 g/cm³) with 10 wt % low molecular weight PIB (a), medium molecular weight (b), and high molecular weight PIB (c) as a function of aging time.

Influence of Aging Time on Cling Properties

Figure 6 shows the cling force development as function of aging time up to 4 weeks after production for all three kinds of PIB and all types of polyolefin matrix. Type 1 and 2 already indicated migration behavior immediately after production, whereas Type 3 hardly showed any cling reaction within the first day. However, after 7 days, the cling force has reached a relatively constant value for all the investigated matrix and PIB types.

Furthermore, the data of Figure 6 reveal that PIB_{LMW} leads to the same and/or slightly higher cling force values than PIB_{MMW}.

However, the level of cling force of PIB_{LMW} and PIB_{MMW} is distinctly higher than that of PIB_{HMW}. Thus, to get high cling forces after a short period of time, PIB_{LMW} and/or PIB_{MMW} has to be preferred.

McNally and Small^{4,5,8–11} investigated the effect of extrusion processing parameters as well as polyisobutylene concentration on the properties of polyethylene stretch and cling films, using a blown film and cast a film-extrusion system and storage conditions of 25, 35, and 45°C for up to 28 days. Although McNally and Small have used with the T-Peel test a different test method to study the cling behavior, the observed increase of the cling force with increasing aging time is in good accordance with the results presented here.

The ATR-IR results, which are plotted in Figure 7, evidence the migration of PIB in case of PIB_{MMW} with increasing aging time and are therefore in good accord with the results of the cling properties presented in Figure 6. The relative transmittance of

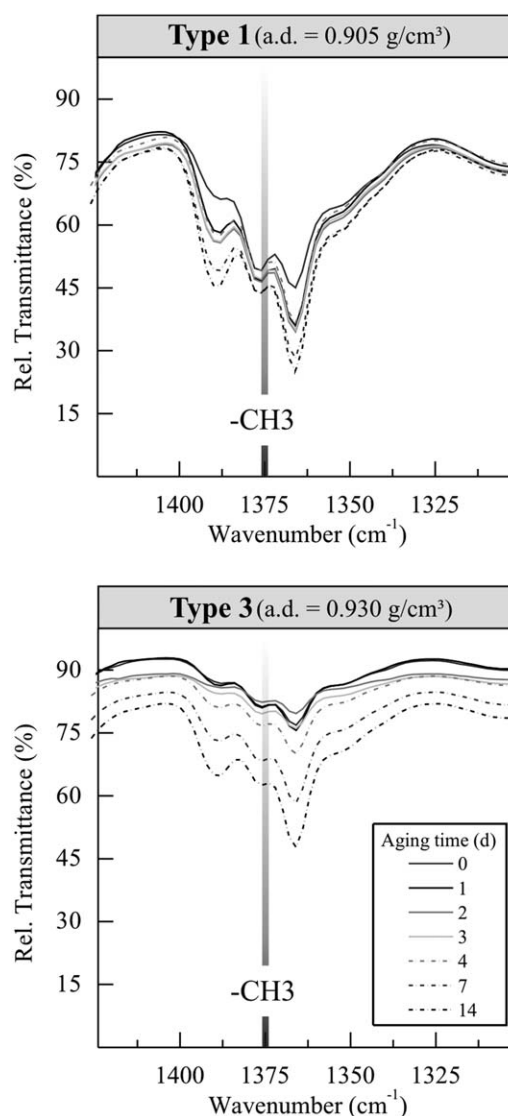


Figure 7. ATR-IR spectras for Type 1 (a.d. = 0.905 g/cm³) and 3 (a.d. = 0.917 g/cm³) blended with PIB_{MMW} in dependence of aging time.

Table V. Summary of Matrix Materials, Cling Additives, and Processing Agents Used in this Study

Aging time (d)	Relative transmittance at 1375 cm ⁻¹ (%)								
	Type 1			Type 2			Type 3		
	PIB _{LMW}	PIB _{MMW}	PIB _{HMW}	PIB _{LMW}	PIB _{MMW}	PIB _{HMW}	PIB _{LMW}	PIB _{MMW}	PIB _{HMW}
0	69.9	51.82	79.9	56.9	60.5	76.4	77.3	81.6	89.4
1	51.8	49.14	-	50.5	51.6	-	57.6	81.7	-
2	50.4	48.55	-	53.5	50.6	-	60.4	82.6	-
3	49.3	49.15	-	47.6	48.6	-	52.6	80.1	-
4	55.2	51.09	51.8	49.9	51.7	65.3	69.7	77.1	79.5
7	48.4	45.70	-	48.0	48.4	-	50.1	68.9	-
14	53.1	45.36	-	47.8	49.5	-	50.1	63.0	-

the CH₃-band, which is characteristic for PIB, decreases with increasing aging time for film Type 1 and film Type 2, both blended with PIB_{MMW}. In other words, the absorbance of the CH₃-band increases with increasing aging time, which clearly indicates an increase of PIB at the film surface with increasing aging time. Thus, the data of Figure 7 reveal that using matrix Type 1, more PIB comes out the film surface than using matrix Type 3. For a better conformability of the results of Figure 7, we presented the individual values in Table V. The trend of the relative transmittance in dependence on aging time for PIB_{LMW} and PIB_{HMW} is in good accord to PIB_{MMW}. In other words, a migration of PIB to the film surface can be suggested, however the kinetics of migration and the absolute migration level depends on PIB type and on matrix material.

Influence of Anti-Block and Slip-Agent Additives on Cling Properties

To characterize the PIB migration to the film surface or the cling force, respectively over a longer period of time, films were conditioned up to four weeks at 30°C in quite accordance with trials of McNally and Small et al.^{4,5} Aging analysis have been done every 24 h for the first week and weekly from the beginning of week two. The references in Figure 8 are the same as mentioned above. The progressive increase of the cling force during the first 4 days turned into a degressive run within the first week, having a maximum after 14 days for PIB_{LMW} and PIB_{MMW}. Stretch films with the lower molecular weight PIB have maximum cling forces of ~3.1 N [Figure 8(a)]. Having no further additives besides the PIB in the film, the higher molecular weight PIB has reached higher cling forces after two weeks of about 3.5 N [Figure 8(b)]. However, a following drop of the cling force occurred, which was much higher for the PIB_{MMW} and fell even below the level of PIB_{LMW} that kept quite constant after reaching maximum cling forces of about 3 N.

Taking into account of further anti-block and slip agent, the PIB_{MMW} seems to be more influenced by their presence. Stretch films with PIB_{MMW} remain about 10–20% below the cling force level of PIB_{LMW} blended stretch films. A balanced average cling force level of 3 N seems to be reached by aging of 4 weeks for PIB_{LMW}. In contrast, the investigated stretch films with PIB_{MMW} achieved maximum cling forces within the first 2 weeks of

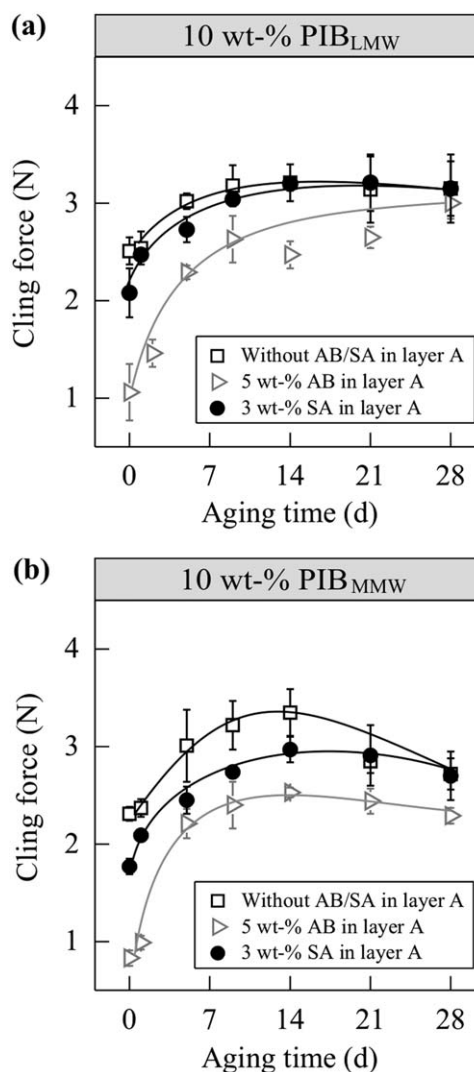


Figure 8. Influence of antiblock (AB) and slip agent (SA) in core and inner skin layer of Type 1 (a.d. = 0.905 g/cm³) on the cling force of stretch films with (a) 10 wt % low molecular weight polyisobuthylene (PIB) and (b) 10 wt % high molecular weight PIB as a function of aging time compared with the PIB blended reference without further additives.

production, with subsequent decrease in cling force afterwards. It can be assumed that the anti-block, which might be dispersed in the amorphous phase, acts as a migration barrier because of the high density of CaCO_3 and particle sizes up to $8 \mu\text{m}$. The slip agent seems to cause a similar barrier effect. However, density, particle size ($3 \mu\text{m}$) and concentration are smaller here, which is consistent with higher cling forces and obviously easier migration of the PIB.

Independent of the PIB, the matrix polyethylene and additives that were used, a further increase of the cling force could not be detected after 2 weeks of production, which is in quite accordance with McNally and Small et al.⁵

Influence of Migration of PIB on the Film Surface Roughness

The interface of a film composite plays an important role for the interaction of an adhesive and an adherence (in this case autoadhesive) in relation to the adhesion mechanism. The surface topography of the adherence or adhesive determines the contact or interaction area and therefore significantly influences the degree of interactions. The probability of weak-boundary forces like van-der-Waals forces or hydrogen bonds increases with the size of the real contact area. This, in turn, can be positively influenced by electrostatic interactions.¹⁶ Figure 9 shows $10 \times 10 \mu\text{m}^2$ surface topographies of Type 2 films filled with PIB_{HMW} as a function of aging time, which could be recovered as topography contrast from the AFM measurement (see also paragraph Investigation of the Surface Morphology). It should be noted that the thickness profile regulation is limited to the facilities of a pilot plant. Furthermore, superstructures of the polyethylene (lamellae, crystallites) and inhomogeneities may affect the roughness in the same way. To obtain a fine roughness profile that is ready to be evaluated, a profile filter has to be used. It might be said that the necessary measurement area after DIN EN ISO 4287¹⁷ could not be reached through which a sensefull wavelength was chosen close to a single measured length. Therefore, the recorded primary profile was edited with a cut-off filter λ_c [DIN EN ISO 4287] by the freeware *Gwyddion*, through which processing or material inhomogeneities and superstructures have been made trivial and a comparison between the different matrix types could be done.

The estimated roughness as a function of the aging time is plotted in Figure 10. For all three types of matrix material the roughness of the film surfaces decreases with increasing aging time to a quite low level. For Type 1 and 2 nearly the same constant roughness level on the nanoscale is reached after 1 week [Figure 10(a)]. It might be suggested that the valleys of the rough surface are smoothed due to migration of the PIB. This assumption is supported by the biggest drop of the fitting curve after 2 days of production, which would be quite consistent with the previous results from cling force and adhesion force measurements. The roughness of film Type 3 has a similar progression to the roughness of Type 1 and 2 up to 14 days of aging. For higher aging time the roughness increases again. We speculated that the increase of the roughness for larger aging times of Type 3 is due to the punctual occurrence of the migrated PIB_{HMW} on the film surface. In accordance to the results of Figure 4, it is well known that PIB_{HMW} migrates very slow and incomplete through matrix Type 3.

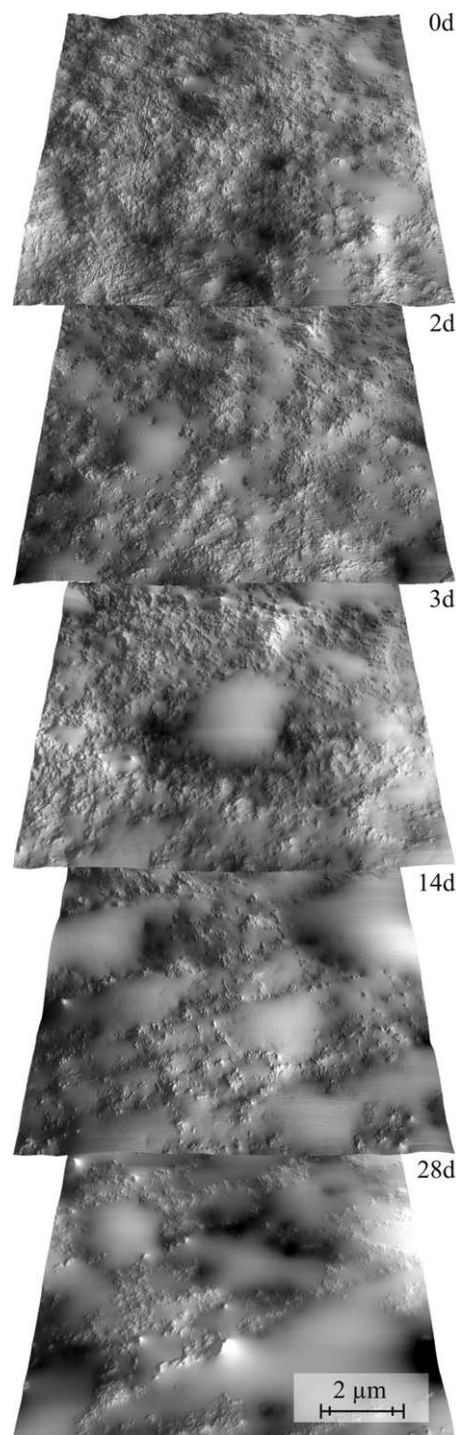


Figure 9. AFM topographic contrast images of Type 2 (a.d. = 0.917 g/cm^3) blended with PIB_{HMW} in dependence of aging time.

Figure 10(b) shows the development of the surface roughness in dependence of the aging time for the first 4 days after the production for all kinds of PIB in Type 2 in comparison to an unfilled Type 2 surface. Last one was measured for the first and the fourth day and stayed constant as supposed. Filled with the highest molecular weight PIB, nearly the same initial roughness value could be measured, which might be correlated with an insufficient migration of the PIB immediately after production

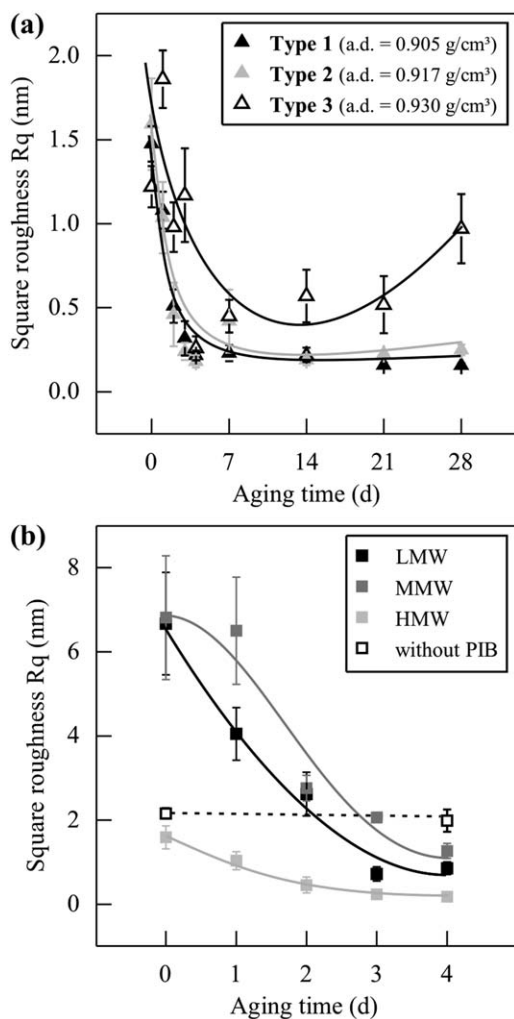


Figure 10. Calculated square roughness from AFM topographic contrast height images in dependence of aging time for matrix densities Type 1 (a.d. = 0.905 g/cm³), Type 2 (a.d. = 0.917 g/cm³), and Type 3 (a.d. = 0.930 g/cm³), blended with PIB_{HMW} (a) and Rq for Type 2 (a.d. = 0.917 g/cm³) filled with PIB_{LMW}, PIB_{MMW}, PIB_{HMW}, and the LDPE surface without any PIB (b).

that could have an influence on the surface roughness. The 3D topographic image from Figure 9 for the first day supports this issue. With increasing aging time a continuous smoothing of the film surface could be observed. The square roughness of PIB_{LMW} and PIB_{MMW} are still above the level of the unfilled sample right at the beginning of aging, which could be accompanied by an initial broad distribution of the obvious faster migrated PIB segments. After Day 4 of aging a lower and constant roughness has been reached that is accompanied with a quite homogenous covering of the film surfaces with PIB and correlates with the stable cling forces from Figure 6.

Influence of the Density of the Polyethylene Matrix and of Polyisobutylene with Different Molecular Weights on the Cling Properties

The previous results could show that stretch films blended with lower molecular weight PIB seems to have advantages, if a

reliable use is needed directly after production. On the other hand medium molecular weight PIB causes higher cling forces at a later stage of aging. Disadvantageous is the decrease of the cling force after a certain time from technical as well as from economical point of view.

The following trials were done to combine the advantages of both grades through blending both PIB with certain amounts. Figure 11 represents the cling performance of different systems with various concentrations of PIB_{LMW} and PIB_{MMW} in all types of LLDPE that differ mainly in their density and once in comonomer type as a function of aging time. The given densities are calculated in dependence on the respective concentration of

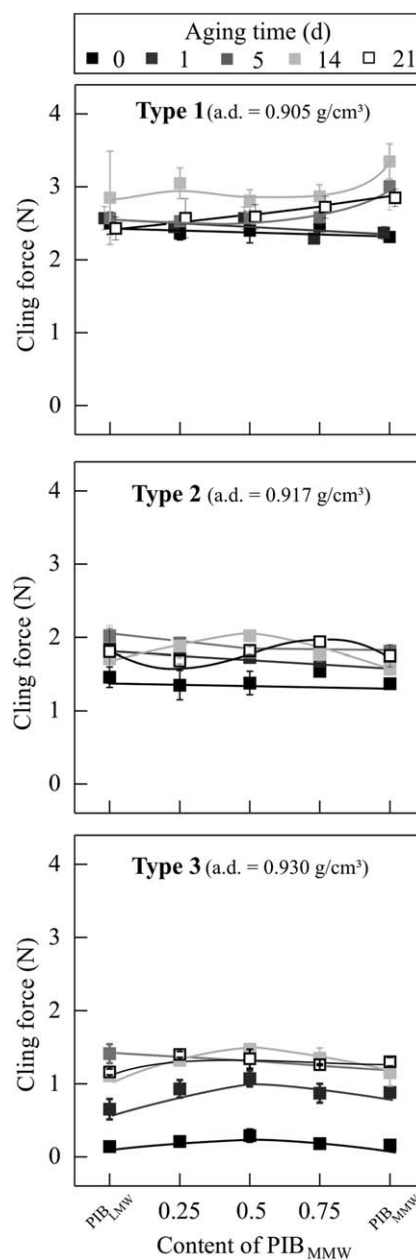


Figure 11. Cling force of single and blended polyisobutylene stretch films in dependence on matrix density for type 1 (a.d. = 0.905 g/cm³), type 2 (a.d. = 0.917 g/cm³), and type 3 (a.d. = 0.930 g/cm³) and aging time.

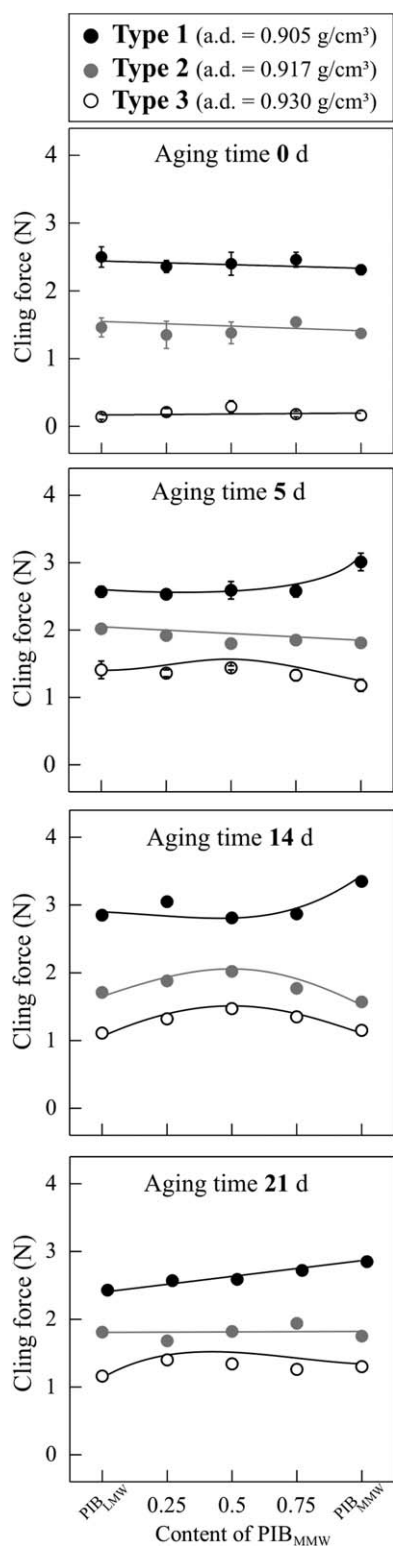


Figure 12. Cling force of single and blended polyisobutylene stretch films in dependence on the concentration of PIB_{MMW} for different matrix density for Type 1 (a.d. = 0.905 g/cm³), Type 2 (a.d. = 0.917 g/cm³), and Type 3 (a.d. = 0.930 g/cm³) with consideration of the aging time.

LLDPE ethylene/ α -olefin copolymers of the inner skin and core layer. The PIB composition is related to the amount of PIB_{MMW} on the total PIB concentration of 10 wt %, starting

with 0 wt %, which means 100 wt % PIB_{LMW}. Stretch films blended with Dowlex C8 (#2) and Affinity C8 (#3) have the lowest mixing density of 0.905 g/cm³ (type 1) at a blend ratio of ~3 : 1. In dependence of the aging time the stretch films had cling forces of about 2.5 N immediately after production. It might indicate the presence of a high concentration of PIB on the film surface and high migration kinetics, respectively, but which could not be confirmed by the AFM phase contrast measurements. Pure PIB_{MMW} in contrast seems to have the opportunity to migrate in the same way, but probably not in that concentration to reach even better cling forces. With continuing aging an increase of the PIB_{MMW} content resulted in higher cling forces, while it has almost no influence on the PIB_{LMW} content. It might be suggested that the concentration of PIB_{LMW} on the film surface is saturated very soon or small amounts of PIB_{LMW} are already enough, taking into account that the shear rate at a testing angle of 20° might not be neglected. Furthermore, with increasing densities of the matrix material, cling forces of 3 N and more have not been reached anymore, independent on the aging time and molecular weight of the PIB. Considering the highest density of 0.930 g/cm³ for the Dowlex C8 (#1), the migration kinetics are time dependent and obviously insufficient for generating reliable cling properties within the first days after production. With increasing aging, the migration of the PIB to the film surface seemed to take place, having maximum values of about 1.5 N. Surprisingly, both the PIB_{LMW} and PIB_{MMW} generates the same cling forces against the assumption that higher molecular weight components could have worse migration kinetics, but compensate or even pass the maximum cling levels of low molecular weight PIB after the first week of production.

Although higher densities of the matrix material seemed to aggravate the migration kinetics of the single molecular weight PIB, it could be observed that blending both PIBs resulted in higher cling forces, at least for increasing densities. An indication could already be observed for samples with pure Dowlex 2103G ($\rho = 0.917$ g/cm³) after a conditioning of two weeks. The favorite blend ratio is 1 : 1 in this case. Stretch films with the highest density benefit even more from this composition, having higher cling forces of about 20% above the cling forces of the single PIB components. It might be suggested that the faster migrating PIB_{LMW} catch the slower migrating PIB_{MMW} up and take it to the film surface sooner. Figure 12 underlines this assumption, showing the cling force as a function of the PIB concentration and aging time for the three kinds of matrix LLDPE. The lower the density of core and inner skin layer was, the easier the higher molecular weight PIB could migrate. Higher densities make it more difficult to migrate in a certain time. After 2 weeks of production, the blending of the same ratio PIB in core and inner skin layer caused higher cling forces. It might be suggested, that entanglements can temporary act as cross-links, which accelerate the transport of the higher molecular weight PIB through the matrix to the surface. It might suggest in this case that using blends of PIB with different molecular weight can accelerate the migration kinetics of higher molecular weight PIB and bring out maximum cling forces at an earlier stage than with either single component. A deeper investigation of the molecular weight

distribution of each PIB, especially the influence of short chain segments on the migration kinetics, should be taken more into consideration.

Nevertheless, the choice of the matrix material has a major effect on the cling properties. Stretch films with lower densities and probably less crystallinity are almost 1 N above the maximum cling forces of higher density stretch films, whereas at the end the whole performance is decisive.

CONCLUSIONS

The influence of different material parameters on the cling properties of multilayer stretch films blended with low molecular weight polyisobutylene in terms of optimized packaging performance has been analyzed. Furthermore, the qualification to characterize low adhesive systems with the mechanical cling test and atomic force microscopy (AFM), next to ATR-IR and scanning electron microscopy was investigated. The LLDPE matrix materials with octene comonomers used in this study have differed substantially in their density and degree of crystallization. The adhesion properties were measured with AFM and the cling test in unstretched condition. Although a stationary level of the cling force is not reached during the cling test due to increasing shear rates and elastic plastic deformations, the cling test is quite appropriate to characterize the adhesion level of stretch films compared with small scale adhesion measurements of sensitive AFM.

The density and therefore the concentration of comonomer content of the used matrix material, where the inert PIB is embedded, has a significant influence on the migration kinetics and therefore the cling forces. Stretch films with densities of LLDPE matrices around 0.90 g/cm^3 allows diffusion of the PIB immediately after film extrusion, which cause sufficient cling forces on the film surface. With increasing density of the bulk material, the migration kinetics of the PIB is restricted to the film surface. At very high densities cling forces could be determined only after a few days with almost insufficient cling forces until high molecular PIB show hardly any cling even after 4 weeks of production. In dependence of the aging time the migration kinetics of the PIB in an appropriate matrix morphology increases until a maximum cling force is reached after ~ 2 weeks of production. An additional mixing with anti-block and slip additives hinders the migration kinetics initially. It might be assumed that CaCO_3 acts as a migration barrier in

dependence of its density and particle size. To confirm this assumption further investigations are needed.

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