

Effect of Polymorphism of Isotactic Polybutene-1 on Peel Behavior of Polyethylene/Polybutene-1 Peel Systems

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ABSTRACT: The effect of polymorphism of isotactic polybutene-1 (iPB-1) on the peel behavior of the specific peel system low-density polyethylene/polybutene-1 (LDPE/iPB-1) was investigated using wide-angle X-ray scattering, calorimetry, and the T-peel test. Melt-crystallization of iPB-1, initially, yields tetragonal form II crystals which transform as a function of time to trigonal form I crystals. The kinetics of transformation at ambient temperature follows an exponential function, and is completed after about 50–75 h. The presence of LDPE in the peel system does not affect the transformation kinetics. The structure of the crystalline phase of iPB-1 controls the peel force which decreases by about 25% during the crystal–crystal transformation in a blend with

20 m% iPB-1. The reduction of the peel force depends linearly on the mass fraction of iPB-1 crystals in the peel system which further evidences the correlation between the crystal–crystal transformation of iPB-1 and the peel-characteristics of LDPE/iPB-1 blends. Isothermal reorganization of crystals of LDPE is excluded as reason for the change of the peel-performance of LDPE/iPB-1 blends, since it is 5 to 10 times faster than the decrease of the peel force, and crystal–crystal transformation of iPB-1, respectively. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3111–3118, 2008

Key words: isotactic polybutene-1; polymorphism; phase transition; peel force

INTRODUCTION

Isotactic polybutene-1 (iPB-1) belongs to the class of flexible, linear polymers and is able to crystallize by chain-folding and formation of lamellae/spherulites.^{1,2} The degree of crystallinity is typically about 50–70%.^{3,4} iPB-1 is polymorphic, i.e., the crystalline phase can adopt different structures. Crystal polymorphs include forms I, II, and III and forms I' and II'. The formation of the different polymorphs is controlled by the selected thermodynamic pathway of crystallization or specific condition of preparation/processing, respectively.^{5–9}

Crystallization from solution allows formation of modifications I', II, and III, being controlled by dissolution and crystallization temperatures.¹⁰ Melt-crystallization, at ambient pressure, triggers formation of form II crystals.^{11,12} In the presence of special nucleating agents, melt-crystallization can also lead to form III crystals.^{8,9} Furthermore, melt-crystallization

at elevated pressure higher than about 100 MPa,^{7,10} on defined substrates⁹ or of a strained melt results in formation of form I' crystals. Finally, crystallization during polymerization causes formation of form I' and form III crystals.^{10,13}

Forms I and I' have identical crystal structures. The prime in the notation of form I' indicates that these crystals were formed directly, during polymerization, from the melt or solution. Form I, in contrast, is formed via form II, by a crystal–crystal transformation. The unit cell of form I, and I', is trigonal with the molecules adopting a 3₁ helix. The different path of formation of form I and I' crystals yields differences regarding the crystal perfection, and, consequently, the less perfect modification I' exhibits a lower temperature of melting.^{7,10,14} Form II and II', similarly, have identical crystal structures, with the prime, in case of form II', pointing to formation of crystals from the melt at elevated pressure, leading again to less perfect crystals with a lower temperature of melting than form II crystals.¹⁴ The unit cell of forms II and II' is tetragonal, and the conformation of the molecules is characterized by a 11₃ helix. Form III is orthorhombic with the chains showing a 4₁ helical conformation.^{15,16}

The different crystal modifications can be interconverted by annealing at well-defined temperatures.^{10,17} In the present study we focus on the trans-

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formation from form II crystals to form I crystals at ambient temperature. Melt-crystallization at ambient pressure yields primary formation of tetragonal form II crystals, which convert at ambient temperature to stable trigonal form I crystals.^{3,12,16,18–23} The crystal-crystal transformation occurs via nucleation at crystal sites which locally are under stress, despite the exact mechanism at molecular scale is not fully identified.¹⁶ The kinetics of the phase transformation depends on one side on the chemical structure of the macromolecule, i.e., on the molecular weight, tacticity, or presence of comonomers, and on the physical superstructure which is controlled by the condition of processing/primary solidification.^{3,4,23} As for the effect of condition of primary crystallization, it was found that the transformation rate is increased with decreasing temperature of primary formation of form II crystals.²⁴ Since a decrease of the crystallization temperature yields smaller crystals, it can be assumed that the phase-transformation rate increases due to an increase of possible sites of nucleation. On the other side, the kinetics of the crystal-form II to crystal-form I transformation is a function of the thermodynamic variables temperature and pressure/deformation,^{7,20} and depends additionally on the presence of additives, i.e., of a second component.²² The phase transformation is possible between about 248 K, which is the glass transition temperature, and about 333 K. The maximum rate of transformation is observed near ambient temperature, between 293 and 313 K.³ Quantitative calorimetric analysis of the transformation rate of a specific PB-1 with a molecular weight of 525,000 g mol⁻¹ and a fraction of isotactic pentades of close to 83%, which initially was melt-crystallized at 323 K, revealed that the transformation at 293 K is completed after about 300 h.³ Pressure and mechanical deformation, in general, increase the rate of phase transformation since the nucleation density within the crystals gets increased. Additives also were found to accelerate the transformation by providing surfaces which support the development of the stable form I structure of PB-1. Research, for evaluation of the effect of the presence of a second component on the transition kinetics, employed low molecular weight compounds including biphenyl, stearic acid, dioctyl phthalate, or 1-naphthylacetamide, polymers, including isotactic polypropylene (iPP) or high-density polyethylene (HDPE), and nanofillers.^{22,25,26} Blending of iPB-1 with iPP, for instance, was found to accelerate the rate of the transition from form II to form I crystals of iPB-1.²⁵ For pure iPB-1, at ambient temperature, full conversion of form II to form I was achieved after aging for at least 6 days, whereas in blends with 25 m% iPP, the transition was completed after 3 days. The increase of the transformation rate was addressed to similar helical conformation of

macromolecules in the monoclinic α -structure of iPP and form I structure of iPB-1.

In the present study, we attempt to establish a relation between the form II and form I crystal-crystal phase transformation of iPB-1 in presence of LDPE and mechanical properties. This research is not only of academic but also of practical importance since the immiscible polymer system iPB-1/LDPE is used as peel system in packaging, including food and household packaging or packaging for OI-cutlery in the medical sector.^{27,28} Peel systems are based on the breakdown of the interface between the LDPE-matrix and the dispersed iPB-1-peel component. A sealing area is produced by application of heat between two peel films. Because of the dispersed iPB-1 particles in the sealing area, zones of different adhesive strength are formed. The interface between iPB-1 particles and the LDPE-matrix acts as predetermined point of failure on mechanical loading.

It is expected that the crystal structure of iPB-1 has direct impact on the peel-properties of the system iPB-1/LDPE. Form I crystals of iPB-1 exhibit about 5% higher density than form II crystals, which can lead to internal stress when volume changes are inhibited due to the presence of a second component. Furthermore, it was found that the crystal-crystal transformation of iPB-1 is accompanied by an increase of the modulus of elasticity, strength, or hardness.

Summarizing the scope of our research we intend (a) to evaluate the effect of LDPE on the kinetics of the form II to form I crystal-crystal transformation of iPB-1, and (b) to relate the transformation kinetics to peel-relevant mechanical properties of the specific peel system.

EXPERIMENTAL

Materials

The LDPE and iPB-1 of the present study are commercial polymers, provided by Basell Polyolefins (Germany). The LDPE used is Lupolen 2420F, which is designed for film production including blow-molding. The density is 0.923 g cm⁻³ and the melt-flow index, determined at 503 K with a load of 2.16 kg, is 0.73 g (10 min)⁻¹. The melting temperature of LDPE is about 384 K, and the crystallinity is about 38%. The iPB-1 of the present study is PB 8640M, a statistical copolymer with low amount of ethylene, for primary use as minority blend component for blown-film extrusion. The melt-flow index, determined at 503 K with a load of 2.16 kg, is 1 g (10 min)⁻¹. The melting temperature of iPB-1 is about 386 K. The polymers were blended in a single-

screw extruder (Collin), using mixing and shear elements, and processed to films of thickness of 50 μm by blow-molding. The maximum concentration of iPB-1 in the low-density polyethylene/polybutene-1 (LDPE/iPB-1) blends was 20 m%, which is considered as an upper limit for the use as peel system. Films were sealed at a temperature of 413 K, for a period of time of 2 s, and subsequently the sealed films were cooled to ambient temperature.

Instrumentation

Microscopy

The phase structure of selected blends was analyzed by transmission electron microscopy (TEM) using a LEO 912 microscope (ZEISS, Germany), operated at 120 kV. Thin sections of thickness of about 80 nm were prepared using an Ultracut E (Reichard, Germany) microtome, and subsequently stained with RuO_4 . The samples were oriented such that the images show the structure of the MD-ND and TD-ND cross-sections, with MD being the machine direction, i.e., the direction of extrusion, TD being the transverse, i.e., circumferential direction, and ND being the direction of the normal of the surface of the blown-film.

Wide-angle X-scattering

Wide-angle X-scattering (WAXS) data, for analysis of the crystal-crystal phase transformation of iPB-1, were recorded using an URD 63 diffractometer (Seifert-FPM, Germany), using Ni-filtered $\text{Cu K}\alpha$ radiation and a scintillation counter for registration. The measurements were performed in transmission mode with the sample oriented in MD.

Temperature-modulated differential scanning calorimetry

Isothermal reorganization of the structure of LDPE was followed by temperature-modulated differential scanning calorimetry (TMDSC) using a heat-flux type differential scanning calorimeter DSC 820 from Mettler-Toledo (Switzerland). The instrument was operated in conjunction with the liquid nitrogen accessory. The furnace was purged with nitrogen gas at a flow rate of 80 mL min^{-1} . Calibration of temperature and heat-flow rate were done according to standard procedures, published elsewhere,²⁹ using metals as calibrants. Samples with a mass of about 5 mg were encapsulated in 20 μL aluminum pans. Temperature-modulation was done using a sawtooth-type temperature-profile with a programmed amplitude and period of modulation of 1 K and 240 s, respectively.³⁰ The modulated heat-flow-rate raw data

were processed to an apparent specific heat capacity, using the instrument software.

T-peel test

For investigation of the peel properties, the T-peel test was applied. A schematic of the T-peel test including sample geometry or direction of loading respective to sample orientation, respectively, is described elsewhere.^{31,32} The sample width was 15 mm. For the test, a Zwicki (Zwick, Germany) tensile-testing machine was used. The initial distance between the clamps and the rate of testing were 50 mm and 100 mm min^{-1} , respectively. The recorded data, force as a function of elongation, were used to determine the peel force, which is defined as an average force between 20 and 80% of the elongation at break.

RESULTS AND INITIAL DISCUSSION

Figure 1 shows TEM images of LDPE/iPB-1 blends with 6 m% (left, images a6 and b6) and 15 m% iPB-1 (right, images a15 and b15). The images show the structure of the MD-ND (top, images a6 and a15) and TD-ND cross-sections (bottom, images b6 and b15). MD and TD in the top and bottom images, respectively, are indicated by the orientation of iPB-1 domains. The images were taken to get an overview about the phase structure, and to confirm immiscibility of the blend components at microscopic level. Note that immiscibility, and, consequently, phase separation is required to achieve acceptable peel-properties. The TEM images clearly show separation of LDPE and iPB-1, with the bright areas representing the iPB-1 phase. The iPB-1 domains are non-spherical due to the specific condition of processing. The TEM micrographs suggest plate-like geometry of the iPB-1 domains, with the smallest dimension oriented parallel to ND, i.e., initially particle-like objects are elongated in circumferential and, even more, in longitudinal direction of the blown film. Note that the structure of phases at molecular level is not analyzed, i.e., partial miscibility of the different components cannot be excluded. Imaging at higher magnification, which is not shown since it is subject of a separate study about the fine-structure of LDPE/iPB-1 blown films, reveals typical lamellar morphology of both, LDPE and iPB-1 crystals.³³

Figure 2 shows WAXS data, intensity as a function of the scattering angle 2θ , of the blend LDPE/iPB-1 with 20 m% iPB-1, measured 2 h (thin line), and 240 h (thick line) after sealing at 413 K, and subsequent aging at ambient temperature. The data show, as expected, separate crystallization of LDPE and iPB-1. Crystallization of LDPE is indicated by the

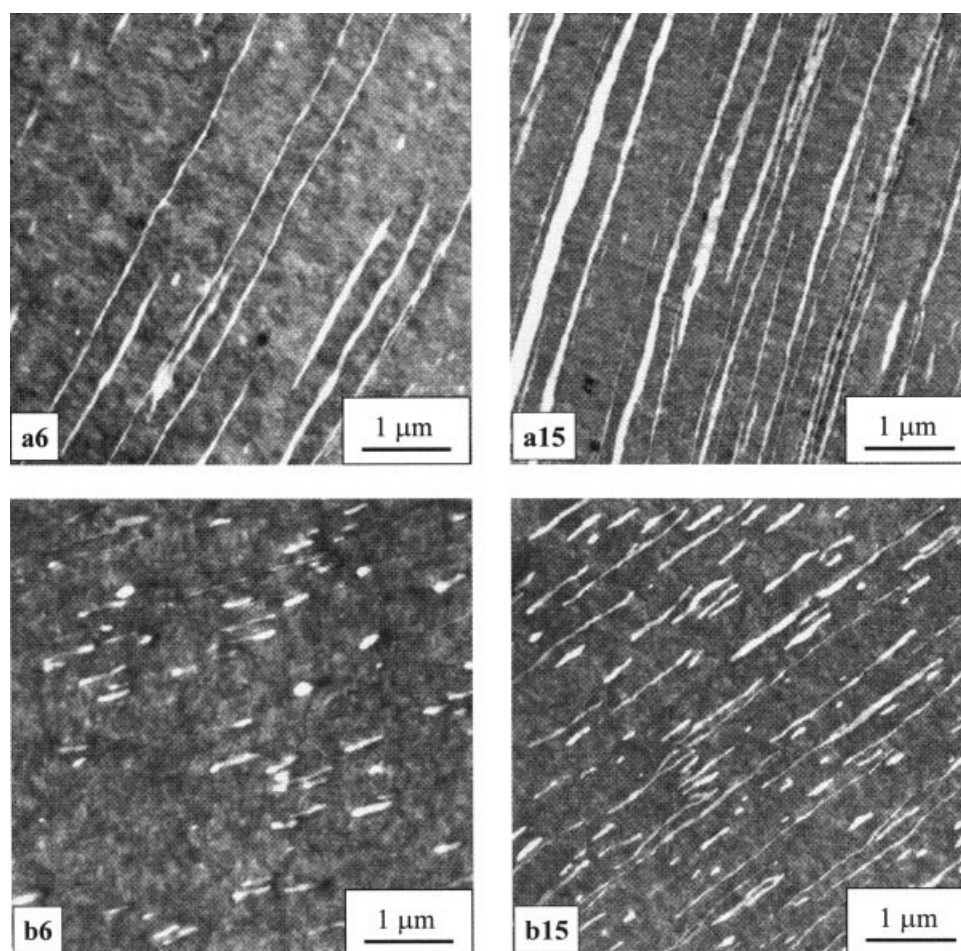


Figure 1 TEM images of LDPE/iPB-1 blends with 6 m% iPB-1 (left column, images a6 and b6), and 15 m% iPB-1 (right column, images a15 and b15). The top images (a6 and a15) show the phase structure of the MD-ND cross-section and the bottom images (b6 and b15) show the phase structure of the TD-ND cross-section.

scattering maxima at 21.4° and 23.7° 2θ , which are indexed by 110 and 200, respectively. Further peaks are observed at about 10.0° , 11.8° , 17.4° , 18.3° , and 20.2° 2θ , which originate from form I and form II crystals of iPB-1. The 110, 300, and 220 interferences at 10.0° , 17.4° , and 20.2° 2θ are due to scattering from trigonal form I crystals, and the 200 and 213 peaks at 11.8° and 18.3° 2θ are caused by tetragonal form II crystals. Further interference maxima from iPB-1 crystals are not detected in the analyzed angular range, likely caused by the low concentration of iPB-1 of only 20 m% in the blend with LDPE.

The WAXS diagrams of Figure 2 are examples of a larger set of measurements for quantification of the kinetics of the form II–form I crystal–crystal transformation of iPB-1 in presence of LDPE, after a specific history of sealing. For evaluation of the transition kinetics, the evolution of the relative intensities of the scattering maxima at 10.0° and 11.8° 2θ was analyzed as a function of time. The interference maxima at 17.4° , 18.3° , and 20.5° 2θ were not considered for analysis due to their low intensity or superposition

with maxima of different crystal modifications. Figure 3 shows, with the open squares, the decrease of the relative intensity of the 200 reflection of tetragonal form II crystals of iPB-1 as a function of time during isothermal annealing at ambient temperature. Simultaneously, the relative intensity of the 110 reflection of trigonal form I crystals increases, which is shown in Figure 3 with the filled squares. The solid lines represent a fit of the data, using exponential functions with a single characteristic time. The reduction/increase of the relative concentrations of form II/form I crystals can be quantified with characteristic times of 14.9 and 12.8 h, respectively. The minor difference between the characteristic times is addressed to the limited number of data points. The form II–form I crystal–crystal transformation of the specific iPB-1 is faster than expected. Former, independent research about the transition kinetics suggests completion of the phase transformation after 100 to 200 h.^{3,4,18} The phase transformation of the particular iPB-1 of the present study, obviously, is completed already after about 50 h. The faster

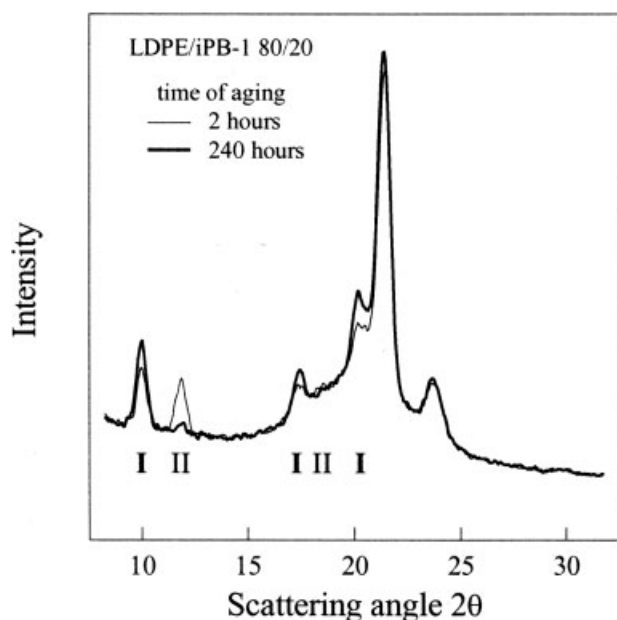


Figure 2 WAXS of a blend of LDPE with 20 m% iPB-1, after sealing at 413 K and subsequent aging for periods of 2 h (thin line) and 240 h (thick line). The scattering maxima from form I and form II crystals of iPB-1 are indicated.

kinetics of phase transformation is addressed to the molecular characteristics of the specific iPB-1 of this work, since we can rule out an accelerating effect of

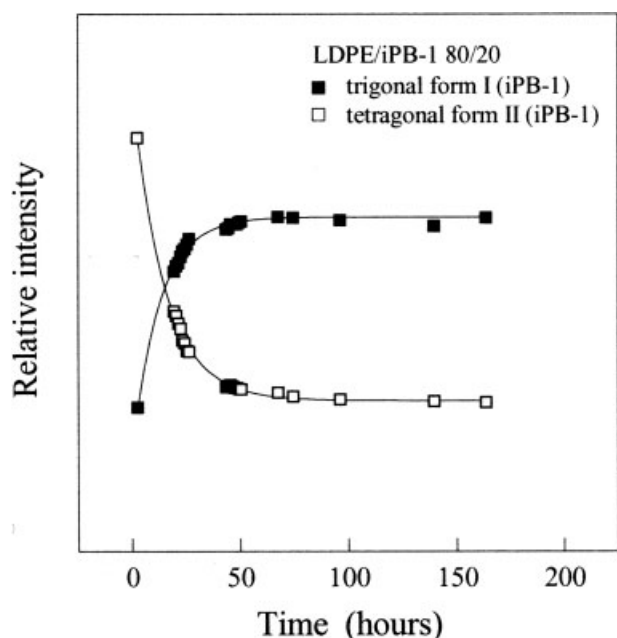


Figure 3 Relative intensity of WAXS maxima at 11.8° (open squares) and 10.0° 2θ (filled squares), representing the relative concentration of tetragonal form II and trigonal form I crystals of iPB-1 in a blend with 80 m% LDPE, respectively. The solid lines were obtained by fitting the experimental data using an exponential function.

the presence of LDPE. Figure 4 shows a comparison of the kinetics of the phase transformation of iPB-1 crystals in pure, nonblended iPB-1 (stars), and iPB-1 in the blend with 80 m% LDPE (filled squares). The evolution of the relative intensity of the trigonal form I interference at 10.0° 2θ with time is almost identical in these preparations, despite we were not able to ensure identical thermomechanical history. The nonblended iPB-1 was prepared initially by injection-molding, whereas the blend was prepared by blow-molding and subsequent sealing at 413 K.

The primary intention of the present work is the establishment of a correlation between the crystal structure of iPB-1 and peel-relevant mechanical properties of the polymer system LDPE/iPB-1. A measure of the peel-characteristics is the peel force, as it is determined by a standard peel test. Figure 5 is a plot of the peel force, i.e., of the average force between 20 and 80% of elongation at break in the T-peel test, as a function of the time of annealing at ambient temperature. The thermomechanical history of the sample is identical with that of the sample which was investigated regarding the phase/crystal structure, necessary for a direct comparison of structural and mechanical data. The solid line in Figure 5 is a fit of the experimental data, using an identical function as was used to simulate the data of Figures 3 and 4. The characteristic time is 14.9 h, i.e., it is in

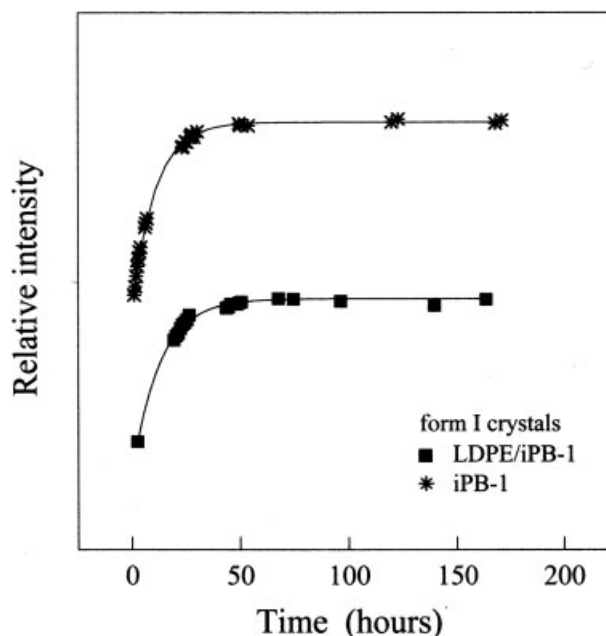


Figure 4 Relative intensity of the WAXS maximum at 10.0° 2θ , representing the relative concentration of trigonal form I crystals of iPB-1. The stars were obtained on pure, nonblended iPB-1, and the filled squares were obtained on iPB-1, blended with 80 m% LDPE. The solid lines were obtained by fitting the experimental data using exponential functions.

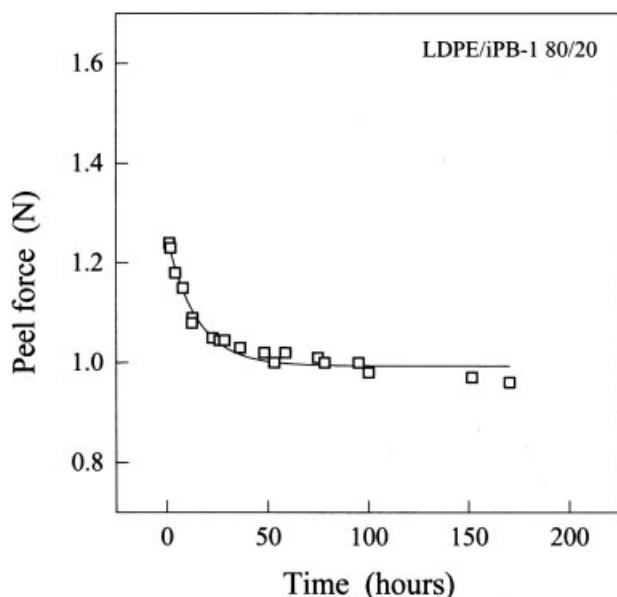


Figure 5 Peel force of the polymer blend LDPE/iPB-1 with 20 m% iPB-1 as a function of time of annealing at ambient temperature, after sealing at 413 K.

excellent accord with the characteristic time of the crystal-crystal transformation of iPB-1. A parallel investigation about the mechanical properties of nonsealed LDPE/iPB-1 blends as a function of time reveals an exponential increase of the modulus of elasticity with a similar characteristic time. This result confirms the correlation between phase transition and mechanical properties of iPB-1. However, the tensile strength of nonsealed films does not show any time-dependency.

Figure 6 shows the effect of the concentration of iPB-1 in the polymer system LDPE/iPB-1 on the reduction of the peel force during annealing. Raw data were reduced to a normalized difference of peel forces (ΔF_{peel}^n) according to eq. (1):

$$\Delta F_{\text{peel}}^n = \frac{F_{\text{peel}}^{2\text{h}} - F_{\text{peel}}^{240\text{h}}}{F_{\text{peel}}^{240\text{h}}} \times 100\% \quad (1)$$

In Eq. (1), $F_{\text{peel}}^{2\text{h}}$ and $F_{\text{peel}}^{240\text{h}}$ are the peel forces, which were measured 2 h and 240 h after sealing at 413 K, respectively. In case of the blend with 20 m% iPB-1, for example, ΔF_{peel}^n is 25% [$\approx (1.2 - 0.95)/0.95 \times 100\%$]. It increases linearly with the concentration of iPB-1 in the polymer system LDPE/iPB-1. In other words, if the fraction of iPB-1 crystals in the polymer system LDPE/iPB-1 increases, then the reduction of the peel-force on annealing is larger. In addition, the increase of ΔF_{peel}^n with increasing concentration of iPB-1 seems linear, with an approximate slope of unity, i.e., if the fraction of iPB-1 crystals is duplicated, then the decrease of the peel force versus annealing time is twofold.

Primary crystallization in semicrystalline polymers may be followed by secondary crystallization and/or reorganization of the crystalline phase, depending on the prior history of crystallization.³⁴ These processes are thermodynamically irreversible, and yield a state of increased thermodynamic stability of the global structure. In case of LDPE, irreversible secondary crystallization and/or reorganization is expected to occur even at ambient temperature, immediately after prior cooling of the melt.^{35,36} The continued isothermal change of structure of LDPE at ambient temperature, among others, can be caused by branching of the macromolecule, which requires an ethylene-sequence-length-selection process during crystallization, being controlled by temperature. Secondary crystallization and/or reorganization, in general, affect the mechanical properties, including a loss of ductility and increase of brittleness. In addition, these aging-processes of LDPE may also be responsible for the decrease of the peel force on annealing of the particular peel system LDPE/iPB-1. To ultimately address the main reason for the decrease of the peel force of the peel system LDPE/iPB-1 on annealing at ambient temperature, which either is the crystal-crystal transformation of iPB-1 or the classical secondary crystallization/reorganization of LDPE, the kinetics of the latter process was determined by TMDSC. The temperature-profile of the sealing process, i.e., heating to 413 K, followed by cooling, was simulated in the calorimeter, and subsequently the kinetics of irreversible structural changes of LDPE was analyzed, by recording the heat-flow rate due to latent heat effects. Instrumental

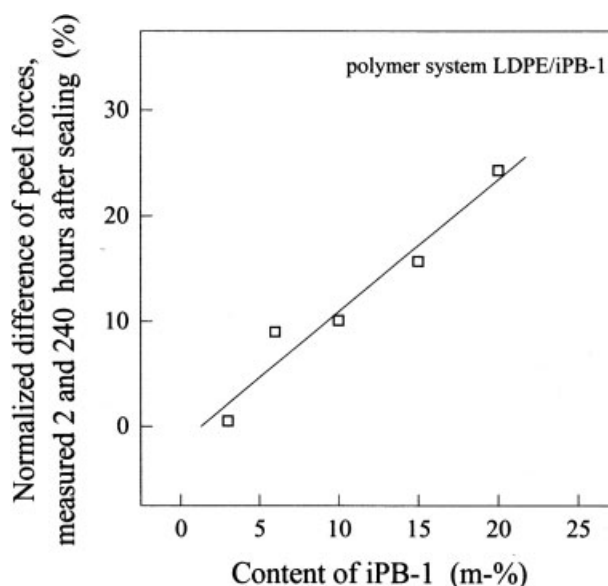


Figure 6 Normalized difference of peel forces, measured 2 h and 240 h after sealing at 413 K, as a function of the concentration of iPB-1 in the polymer system LDPE/iPB-1. Normalization is by the final peel force.

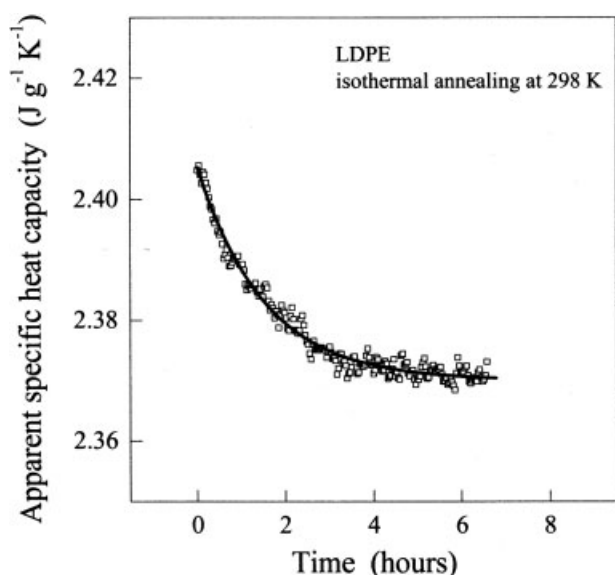


Figure 7 Apparent specific heat capacity of LDPE as a function of time of annealing at ambient temperature. The sample, initially, was heated to 413 K, and subsequently melt-crystallized at 10 K min^{-1} .

long-term drift, which is a major disadvantage of standard DSC since it is superimposing the sample-caused heat-flow rate, is effectively removed by temperature modulation with a frequency faster than the long-term drift of the instrument.³⁶ The selection of the amplitude of temperature modulation of 1 K allows equilibration of the structure, i.e., repeated destabilization of the structure in each heating and cooling segment is avoided. The modulated heat-flow-rate-raw data, collected during quasi-isothermal temperature-modulation, typically, are recalculated to an apparent specific heat capacity, using standard equations.³⁰ Figure 7 shows the apparent specific heat capacity of LDPE as a function of time during isothermal annealing at 298 K. The apparent specific heat capacity decreases due to irreversible changes of structure, which, based on the calorimetric data, cannot be addressed further. Most important, in the context of this work, is the completion of these irreversible processes after about 5 to 10 h. This result is expected since it is in accord with former research about the annealing behavior of linear low-density polyethylene (LLDPE).³⁵ The calculated characteristic time, extracted from an exponential fit, is about 1.5 h, indicating that irreversible crystallization/reorganization of LDPE is distinctly faster than (a) the crystal-crystal transformation of iPB-1, and (b) the change of the peel-characteristics.

FINAL DISCUSSION AND CONCLUSIONS

The peel-characteristics of sealed LDPE/iPB-1 films, with a typical concentration of iPB-1 of less than

20 m%, changes distinctly within about 50 h after the sealing-process. A measure of the peel-characteristics is the peel force which decreases as a function of time after the sealing process by about 20–30% in case of a preparation with 20 m% iPB-1. This decrease of the peel force can be considered as an advantage if the sealed films need to be reopened with rather low force. From point-of-view of total strength of the sealed films, i.e., during the period before wanted destruction of the sealed joint, the decrease of the peel force is disadvantageous. Therefore, the decrease of the peel force of the specific peel system LDPE/iPB-1, immediately after sealing, needs to be controlled, which only is possible if the structural reason behind is analyzed.

Sealing involves localized melting of two films which, mechanically, are in close contact in a localized area, and which adhere as a result of the specific thermomechanical treatment. The sealing process of this particular polymer system is performed at a temperature of 413 K, for a period of a few seconds. The selected sealing-temperature of 413 K is considerably higher than the temperature of melting, which is close to 390 K, and which results in sufficient mobility of macromolecules for optimum welding.^{37,38} Subsequent cooling allows recrystallization of the liquid in a restricted environment. The restriction is due to nonmelted material in close proximity of the sealed joint, which probably nucleates the crystallization, and furthermore due to mechanical restraint which allows partial preservation of preferred orientation of macromolecules, evident in the initially blow-molded films. The cooling process from the temperature of sealing of 413 K to ambient temperature results in formation of separate crystals of LDPE and iPB-1. Separate crystallization is evidenced with the X-ray data of Figure 2, however, is expected since the components LDPE and iPB-1 are thermodynamically immiscible and separated as a result of the initial processing history.

The observed decrease of the peel force in blends of LDPE and iPB-1 within a few days after sealing, and under isothermal condition, can be due to several reasons, which are connected to the crystalline phase of either LDPE or iPB-1. Relaxation of the amorphous phases of LDPE or iPB-1 we do not favor as a major cause for the distinct change of mechanical properties, since the glass transition temperature is considerably lower than the temperature of analysis, which probably allows fast relaxation of nonstable structural states. Regarding the crystalline phase of LDPE, it may be possible that the particular history of cooling after sealing, and/or the molecular architecture prevent completion of the crystallization process before reaching ambient temperature. In this case, the crystallization would continue isothermally, taper off, and reach a final value. The approach of metastable equi-

librium was monitored by TMDSC, which suggests completion of continued crystallization of LDPE within 5 to 10 h (Fig. 7). Despite the analysis of irreversible annealing of LDPE crystals was performed in absence of iPB-1, we assume negligible effect of presence of iPB-1 in LDPE/iPB-1 blends, since the components are separated. The X-ray data of Figure 2, qualitatively, confirm continuation of crystallization/reorganization of LDPE in blends with iPB-1, by observation of a slight increase of the intensities of the 110 and 200 reflections. Regarding the crystalline phase of iPB-1, based on the performed experiments, we have no indication of isothermal reorganization and continued primary formation of tetragonal form II crystals from the liquid. Instead, we see transformation of tetragonal form II crystals to stable trigonal form I crystals. The crystal-crystal transformation is completed after about 50 to 75 h, and is independent of the presence of LDPE (Figs. 3 and 4), confirming absence of phase interactions.

The decrease of the peel force of sealed LDPE/iPB-1 films as a function of time, after sealing, must therefore be addressed to either secondary crystallization/reorganization of LDPE crystals or the crystal-crystal transformation of iPB-1 crystals. Inspection of the kinetics of these two processes favors crystal-crystal transformation of iPB-1 as main reason for the observed change of the mechanical characteristics. The peel force of the LDPE/iPB-1 blend and the crystal-crystal transformation of iPB-1 in the LDPE/iPB-1 blend approach constancy, or are completed, respectively, about 50 h after sealing. The annealing of LDPE crystals, in contrast, is finished after about 5 to 10 h, i.e., annealing of LDPE crystals is 5 to 10 times faster than the crystal-crystal transformation of iPB-1. The correlation between the iPB-1-crystal-crystal transformation and the time-dependence of the peel-behavior in LDPE/iPB-1 blends is strongly supported by a linear dependence of the reduction of the peel force on the fraction of iPB-1 crystals (Fig. 6).

The form II-form I crystal-crystal transformation of iPB-1 is connected with an increase of the density of the crystalline phase from 0.90 to 0.95 g cm⁻³, i.e., the iPB-1 crystals reduce their specific volume by about 5%. The volume-reduction may directly be transferred to the surrounding amorphous iPB-1 phase, due to molecular coupling at the crystal-amorphous interface. The TEM micrographs of Figure 1 shows plate-like iPB-1 domains, which are embedded in a matrix of LDPE. The linkage between the LDPE-matrix and the iPB-1 domains, in contrast, is of noncovalent nature. Therefore, we may speculate that the volume-reduction cannot be as easily transferred to the LDPE-matrix, as is possible between iPB-1 crystals and iPB-1 amorphous structure. If this is true then the interfacial strength between the LDPE matrix and the iPB-1 particles

would be reduced, and, consequently the peel force, required to destruct the sealed joint, is lowered.

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References

1. Wunderlich, B. *Macromolecular Physics, Vol. 1: Crystal Structure, Morphology, Defects*; Academic Press: New York, 1973.
2. Hsu, T. C.; Geil, P. H. *Polym Commun* 1990, 31, 105.
3. Alfonso, G. C.; Azzurri, F.; Castellano, M. *J Therm Anal Cal* 2001, 66, 197.
4. Azzurri, F.; Flores, A.; Alfonso, G. C.; Balta Calleja, F. J. *Macromolecules* 2002, 35, 9069.
5. Natta, G.; Corradini, P.; Bassi, I. W. *Nuovo Cim Suppl* 1960, 15, 52.
6. Petraccone, V.; Pirozzi, B.; Frasci, A.; Corradini, P. *Eur Polym J* 1976, 12, 323.
7. Nakafuku, C.; Miyaki, T. *Polymer* 1983, 24, 141.
8. Kopp, S.; Wittmann, J. C.; Lotz, B. *Polymer* 1994, 35, 908.
9. Kopp, S.; Wittmann, J. C.; Lotz, B. *Polymer* 1994, 35, 916.
10. Tosaka, M.; Kamijo, T.; Tsuji, M.; Kohjiya, S.; Ogawa, T.; Isoda, S.; Kobayashi, T. *Macromolecules* 2000, 33, 9966.
11. Danusso, F.; Gianotti, G. *Makromol Chem* 1965, 88, 149.
12. Boor, J. Jr.; Mitchell, J. C. *J Polym Sci Part A: Gen Pap* 1963, 1, 59.
13. Rakus, J. P.; Mason, C. D. *J Polym Sci Part B: Polym Lett* 1966, 4, 467.
14. Kalay, G.; Kalay, C. R. *J Appl Polym Sci* 2003, 88, 814.
15. Holland, V. F.; Miller, R. L. *J Appl Phys* 1964, 35, 3241.
16. Kopp, S.; Wittmann, J. C.; Lotz, B. *J Mater Sci* 1994, 29, 6159.
17. Kaszonyiova, M.; Rybnikar, F.; Geil, P. H. *J Macromol Sci Phys* 2006, 44, 377.
18. Marigo, A.; Marega, C.; Cecchin, G.; Collina, G.; Ferrara, G. *Eur Polym J* 2000, 36, 131.
19. Fujiwara, Y. *Polym Bull* 1985, 13, 253.
20. Hong, K. B.; Spruiell, J. E. *J Appl Polym Sci* 1985, 30, 3163.
21. Goldbach, G. *Angew Chem* 1972, 11, 337.
22. Boor, J. Jr.; Mitchell, J. C. *J Polym Sci* 1962, 62, 70.
23. Schaffhauser, R. *J Polym Sci Part B: Polym Lett* 1967, 5, 839.
24. Armendaud, A.; Abenoza, M. *Raman Spectrosc Proc Int Conf* 1982, 8, 589.
25. Shieh, Y. T.; Lee, M. S.; Chen, S. A. *Polymer* 2001, 42, 4439.
26. Wanjale, S. D.; Jog, J. P. *Polymer* 2006, 47, 6414.
27. Aithani, D.; Lockhart, H.; Auras, R.; Tanprasert, K. *J Plast Film Sheeting* 2006, 22, 247.
28. Hwo, C. C. *J Plast Film Sheeting* 1987, 3, 245.
29. Wunderlich, B. *Thermal Analysis of Polymeric Materials*; Springer: Berlin, 2005.
30. Androsch R. *J Therm Anal Cal* 2004, 77, 1037.
31. ASTM D 1876. *Standard Test Method for Peel Resistance of Adhesives (T-Peel Test)*: MN, 2001.
32. Grellmann, W.; Seidler, S. *Polymer Testing*; Hanser: Munich, 2007.
33. Nase, M.; Zankel, A.; Langer, B.; Baumann, H. J.; Grellmann, W. In *Proceedings of International Conference Scanning 2007*; Monterey, USA, 2007; p 50.
34. Wunderlich, B. *Macromolecular Physics, Vol. 2: Crystal Nucleation, Growth, Annealing*; Academic Press: New York, 1976.
35. Androsch, R.; Wunderlich, B. *Macromolecules* 1999, 32, 7238.
36. Androsch, R.; Wunderlich, B. In *Macromolecular Engineering: Precise Synthesis, Materials Properties, Applications, Vol. 3*; Matyjaszewski, K.; Gnanou, Y.; Leibler, L., Eds.; Wiley-VCH: Weinheim, 2007.
37. Bonten, C.; Schmachtenberg, E. *Polym Eng Sci* 2001, 41, 475.
38. Wool, R. P.; Yuan, B. L.; McGarel, O. J. *Polym Eng Sci* 1989, 29, 1340.