TOMAS BATA UNIVERSITY IN ZLÍN
FACULTY OF TECHNOLOGY
Department of Polymer Engineering

Lenka Chvátalová

CONTROLLING INNOVATIVE POLYOLEFIN PROPERTIES BY STRUCTURAL TRANSFORMATIONS

Řízení vlastností netradičních polyolefinů strukturními transformacemi

Doctoral Thesis

Programme	Chemistry and Materials Technology
Course	Technology of Macromolecular Substances
Supervisor	doc. Ing. Roman Čermák, Ph.D.
Consultant	prof. RNDr. Miroslav Raab, CSc.
Year	2011

ABSTRACT

This Doctoral Thesis is focused on the property-modification of common isotactic poly(propylene) and innovative isotactic poly(1-butene) and the structural evolution in these polymers during modification and processing is characterized on the molecular, super-molecular, and microscopic levels.

Special attention is devoted to the modification of isotactic poly(propylene) by a specific β-nucleating agent. The interrelations between the specific β-nucleator, the thermal history, and the molecular weight of poly(propylene) were investigated.

In this Thesis, the influence of the transformation of the super-molecular structure of isotactic poly(1-butene) on macroscopic properties was studied and it presents evidence and an explanation of the effect of annealing temperature on the kinetics of phase transformation and the evolution of the mechanical properties in isotactic poly(1-butene) parts.

The work further focuses on the possibilities of controlling the surface hydrophylicity or hydrophobicity of poly(1-butene), using plasma treatment.

From a practical application point-of-view, the study brings to light and presents important new knowledge about the photodegradation behaviour of isotactic poly(1-butene).

Keywords

Poly(propylene), poly(1-butene), polymorphism, specific nucleation, morphology, phase transformation, degradation, plasma.

ABSTRAKT

Předkládaná doktorská práce se zabývá modifikací vlastností tradičního izotaktického poly(propylenu) a méně běžného izotaktického poly(1-butenu). Vývoj struktury polymeru během modifikace a zpracování je charakterizován jak na úrovni molekulární, tak i nadmolekulární.

Zvláštní pozornost je kladena na úpravu vlastností izotaktického poly(propylenu) užitím specifického β-nukleačního činidla. Jsou pozorovány souvislosti mezi β-nukleačního činidla, tepelnou historií a molekulovou hmotností poly(propylenu).

V práci je studován vliv transformace nadmolekulární struktury izotaktického poly(1-butenu) na výsledné vlastnosti. Je popisován a vysvětlován vliv temperační teploty na kinetiku fázové transformace a vývoj mechanických vlastností poly(1-butenu).

Práce se dále zabývá možností řízení povrchové hydrofility nebo hydrofobity poly(1-butenu) působením plazmatu.

Z pohledu praktických aplikací práce přináší nové důležité poznatky o fotodegradačním chování izotaktického poly(1-butenu).

Klíčová slova

Poly(propylen), poly(1-buten), polymorfizmus, specifická nukleace, morfologie, fázová transformace, degradace, plazmat.

I would like to take this opportunity to express my cordial gratitude to my supervisor Roman Čermák for his encouragement, guidance and inspiration during my Ph.D.

I am also grateful to Miroslav Raab for his effort during the research and most fruitful discussions.

It is my pleasure to pay a tribute also to all colleagues from the Department of Polymer Engineering for their help and friendly environment.

Special thanks are directed to my family and friends for their love, prayers and support.

CONTENT

PAPERS I - IV

INTRODUCTION

During last decades polymeric materials turned to be highly important for many industries, frequently substituting conventional materials as glass or metals. This is a consequence of a wide variety of polymers that can be produced with properties fitting a broad area of applications. Additionally, their processing is relatively simple and economically competitive.

Polymeric materials with identical chemical composition may exhibit different properties like toughness, elasticity, transparency, or permeability. These properties are dependent on the supermolecular structure, which is, in turn, determined by the processing conditions.

Among these polymorphic materials belong polyolefins that comprise the largest portion of the world’s commercial polymers [1, 2]. Isotactic poly(propylene) represents the most important segment of all commodity plastics as well exhibits pronounced polymorphisms and morphologies depending on mechanical treatment and thermal history through which material pass during its processing. Similarly, presence of only minute amount of special additive, e.g. *N,N’*-dicyclohexylnaphthalene-2,6-dicarboxamide, induces controlled specific nucleation into required structure [3–5].

The crystallizion behaviour of further member of polyolefin family – isotactic poly(1-butene) – is significantly different and more complicated. Isotactic poly(1-butene) is a polymorphic material occurring in five crystallographic modifications [6, 7]. Poly(1-butene) upon solidification from the melt crystallizes into tetragonal phase II. However, this phase is metastable and during several days transforms into more stable trigonal phase I. Resulting polymer is stiff with satisfying properties [6, 8]. It is expected that kinetics of phase transformation and evolution of mechanical properties will be influenced by annealing conditions. Supermolecular structure and polymorphism of poly(1-butene) influence not only the macroscopic properties, but also the degradation behaviour. It can be supposed that the degradation process is similar to isotactic poly(propylene) due to the presence of tertiary carbon on the backbone. Chemical composition, molecular structure, and roughness of a polymer surface critically influence surface wettability. Low wettability of poly(1-butene) brings considerable problems in many practical applications. To enhance wettability and hydrophilicity of poly(1-butene) plasma treatment is a very effective way [9, 10].

In this context, the study of the interrelations between processing, supermolecular structure and resulting macroscopic properties of polymers has become a topic of major scientific importance. The present study is focused on the detail description of these interrelations in isotactic poly(propylene) and isotactic poly(1-butene).

STATE OF THE ART

1 BETA-NUCLEATED ISOTACTIC POLY(PROPYLENE)

Isotactic poly(propylene) (PP) has become one of the most commonly used thermoplastic compatible with many processing techniques [11]. It is an important commodity material offering a combination of outstanding physical, chemical, mechanical, thermal and electrical properties not found in any other thermoplastics. Its price/performance ratio is very attractive. Therefore poly(propylene) is one of the fastest growing classes of commodity thermoplastics.

Poly(propylene) is prepared by polymerization of propylene in the presence of a catalyst under carefully controlled heat and pressure [12, 13]. The molecular structure of poly(propylene) is illustrated in Figure 1.1.

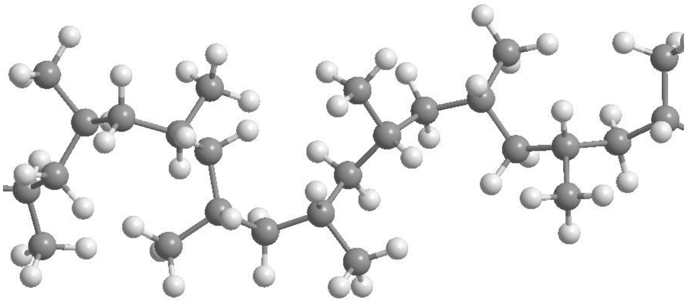

Figure 1.1 Molecular structure of poly(propylene)

An important concept in understanding the link between the structure of poly(propylene) and its properties is tacticity. The relative orientation of each methyl group relate to methyl groups of neighbouring monomeric unit has a strong effect on the finished polymer's ability to form crystals, because each methyl group occupies space and constrains backbone bending [13]. The methyl branching implies an asymmetrical carbon C^* (tertiary carbon) in the propylene group (CH_2-C^*HCH_3), therefore poly(propylene) exhibits three typical stereo-configurations: isotactic, syndiotactic and atactic [13–16]. From commercial point of view predominantly isotactic poly(propylene) is used.

Isotactic poly(propylene) can exist in different morphological phases, depending on the crystallization conditions, such as pressure, temperature, and cooling rate. Different phases can coexist, and one crystalline phase can change into another as conditions change [17].

The monoclinic α-phase of poly(propylene) is predominant and most common in melt-crystallized or solution-crystalllized samples (α-PP) [4, 5, 18–20]. A second polymorph was designated as a β-phase [5, 17, 19, 22–24]. Morrow and Newman found the third one, a triclinic γ-phase [25]. The γ-phase can be observed in low molecular weight PP or in PP crystallized at elevated pressure above 200 MPa [20, 26]. In addition, a quenched crystal phase, called the mesophase or smectic phase, was observed [5, 18]. It can be prepared by rapid quenching from the melt [27, 28].

1.1 Beta-Phase of Isotactic Poly(propylene)

The β-phase of isotactic poly(propylene) (β-PP) is less common and with more disorder than the α-phase. The β-phase was identified in 1959 by Keith and co-workers [17] and for many years has been referred to have a hexagonal crystalline structure [29]. More recently, the crystal structure of β-modification of PP was established as trigonal by Lotz et al. [30] and some other authors (Figure 1.2) [31].

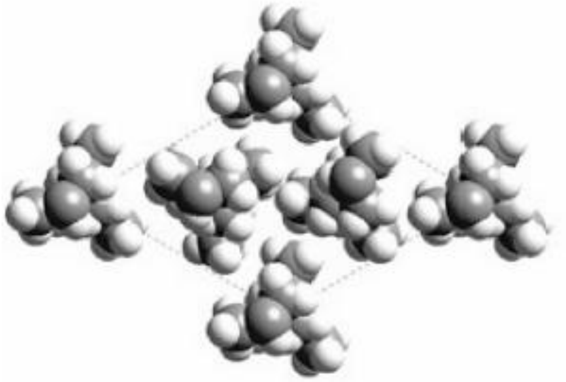

Figure 1.2 Structural model of β-PP as determined by electron crystallography [31]

Almost pure β-phase can be obtained with the aid of specific nucleating agents [32]. Crystallization in a temperature gradient is also an efficient way to produce oriented PP samples with predominant β-phase [4].

It was demonstrated that wide-angle X-ray scattering, differential scanning calorimetry or microhardness technique can be successfully used to evaluate the amount of α- and β-phases within a PP sample [33]. The proportions of the β-phase (*k-value*) in the samples can be calculated from X-ray diffractograms according to Turner-Jones [20] as follows:

$$k-value = \frac{H_b}{H_{a1}+H_{a2}+H_{a3}+H_b}$$

where H_{a1}, H_{a2}, H_{a3} are the intensities of α-diffraction peaks corresponding to angles 2θ = 14.2°, 17.0° and 18.8°, respectively, and H_b is the intensity of the β peak at 2θ = 16.2°. The *k-value* indicates the relative content of the β-phase in the sample.

Studies on β-nucleated PP revealed that the formation of pure β-phase has an upper ($T(\beta\alpha)$ = 140 °C) and a lower ($T(\alpha\beta)$ = 100–110 °C) temperature limits. Between these two temperatures the growth rate of β-spherulites is up to 70 % faster than that of α-spherulites and therefore, formation of the β-phase is preferred. The β-phase is metastable relative to the α-phase (T_m = 150 °C versus 180 °C), it has lower density (921 kg/m^3 [24]) and is unstable upon stretching, which produces a transition to α-PP or to the smectic phase depending on whether the sample is processed above or below 60 °C [5, 34]. The most reliable value of the equilibrium melting point of the β-phase is $T_m^0(\beta)$ = 148±4 °C, which was obtained with pure β-phase when the disturbance of βα-recrystallization was eliminated [5].

2.2.1 Specific β-Nucleating Agents

Specific β-nucleating agents can be added to PP for the preparation of the β-phase. The most widespread high active β-nucleating agent are γ-quinacridone red pigment, δ-quinacridone, calcium salts of suberic or pimelic acid, and calcium-phtalat [17, 35].

Several works dealing with a poly(propylene) nucleated by commercial β-nucleating agent *N,N'*-dicyclohexylnaphthalene-2,6-dicarboxamide (NJ STAR NU 100) (Figure 1.3) can be found [31, 35–40]. Accorging to Varga and Menyhard [38] (i) this organic substance can initiate also the formation of certain amount of α crystallites, (ii) it is a crystalline material which can dissolved in PP melt and (iii) the nucleating activity of NU 100 is exhibited only by solid crystalline particles. Nevertheless, this observation is in contradiction with Kotek et. al [35], considering the amount of 0.03 wt.% of NU 100 as a critical nucleant concentration. Moreover, it can be supposed that PP molecular characteristics as molecular weight can influence the sensitivity to specific nucleation. Čermák et. al [40, 41] comprehensively studied the effect of processing parameters on the morphology and properties of injection-moulded parts of β-nucleated PP.

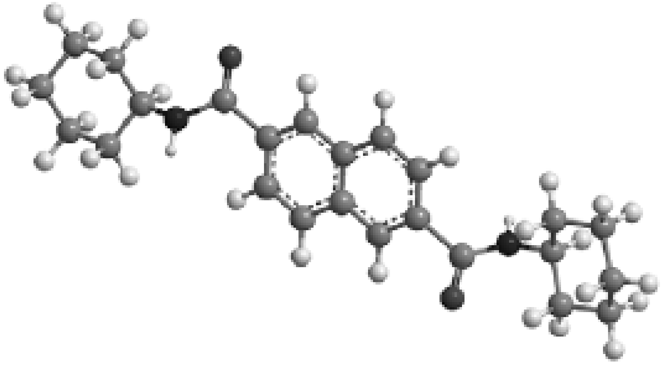

Figure 1.3 Molecular structure of β-nucleating agent NJ STAR NU 100; N,N'-dicyclohexylnaphthalene-2,6-dicarboxamide

2.2.2 Properties of β-Nucleated Poly(propylene)

Some properties of β-PP differ significantly from those of α-PP. In comparison with α-PP, β-PP possesses lower crystal density, melting temperature and lower fusion enthalpy**.** The chemical resistance of β-PP seems to be lower than that of α-PP [42]. On the other hand, intensive studies of degradation behaviour of PP confirm that poly(propylene) containing predominantly β-modification within the crystalline portion of the material is significantly less sensitive to UV-irradiation as compared to common poly(propylene) (α-PP) [35, 39, 42–47]. β-PP compared with α-PP has a lower E-modulus and yield stress but higher ultimate tensile strength and strain. The improvement in the latter might be related to the βα-transition occurring during the necking which leads to the formation of the α-phase of enhanced strength (strain-hardening) [5].

2.2.3 Application of β-Nucleated Poly(propylene)

The application of β-PP is favoured in some fields, based on its high impact resistance and toughness. The β-phase of isotactic poly(propylene) is used for industrial pipeline construction, dielectric capacitors (with roughened surface), paper like films, biaxially drawn microporous film (gas exchange membranes) and porous fibres with improved moisture adsorption [17, 37].

2 ISOTACTIC POLY(1-BUTENE)

Isotactic poly(1-butene) (PB-1) is one of the members of the polyolefin family which exhibits advantages over the other polyolefins in toughness, tear strength, flexibility, creep, stress cracking resistance, impact resistance, abrasion resistance and high temperature resistance. However, even after more than 40 years from its discovery, and despite its potentials, PB-1 is still a relatively new material that is being produced in limited quantities and has not yet found a large commercial success as compared to the other polyolefins. This is probably due to both the relatively high monomer cost, possibly coupled with difficulties in polymerization technology, and the special crystallization behaviour of the polymer [48].

2.1 Molecular Structure of Poly(1-butene)

Poly(1-butene) exists in different extents of tacticity: isotactic, syndiotactic, and atactic. The stereochemical configuration of successive monomer units in polyolefins such as poly(1-butene) can strongly affect the physical and mechanical properties of the polymers [49]. The tacticity of poly(1-butene) is strongly dependent on the catalyst system used, polymerization temperature, and reaction diluents [50]. The molecular structure of poly(1-butene) is illustrated in Figure 2.1.

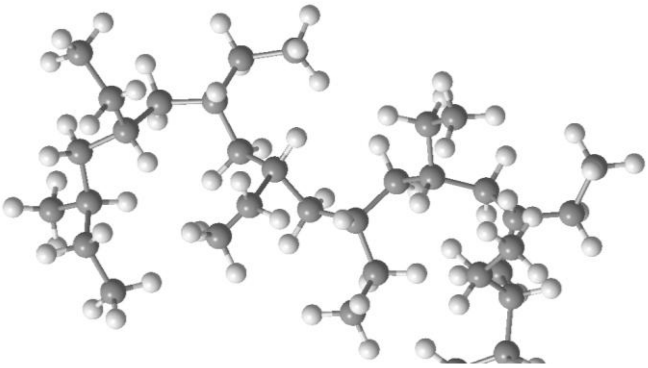

Figure 2.1 Molecular structure of poly(1-butene)

Natta and coworkers first synthesized poly(1-butene) in 1954 using two-component catalyst systems containing organoaluminium compounds and transition metal salts and halides. Subsequent modifications to the original Ziegler–Natta catalytic systems by other researchers helped to improve the degree of isotacticity [46]. Di Lorenzo et al. [51] revealed that isotactic poly(1-butene), similarly to other semi-crystalline polymers, is characterized by a three-phase structure, composed of crystalline, mobile amorphous and rigid amorphous fractions. On the other hand, the synthesis of syndiotactic poly(1-butene) was achieved only recently due to the discovery of the homogeneous metallocene catalytic systems [52]. Nevertheless, from commercial point of view isotactic poly(1-butene) is still the most important.

2.2 Supermolecular Structure of Isotactic Poly(1-butene)

For macroscopic behaviour of stereoregular PB-1 is important that isotactic and syndiotactic poly(1-butene) are semi-crystalline materials. Analogous to the other polyolefins with assymmetric monomer units also isotactic and syndiotactic poly(1-butene) exhibit polymorphic crystallization behaviour. Five different crystalline modifications have been reported, which are referred to as I, II, III, I’, and II’ [6–8, 53–58]. Natta et al. [6] were the first to discover that poly(1-butene) assumes an 11_3 helical conformation with a tetragonal unit cell when crystallizing from the melt. This crystalline structure is known as a phase II and upon ageing at room temperature is gradually transformed into the trigonal phase I. The phase III has been observed in films of poly(1-butene) precipitated from certain solvents [7]. Nakafuku and Miyaki [8] studied the effect of pressure on the crystallization behaviour of isotactic poly(1-butene). Above 200 MPa phases I’ and II’ are crystallized from the melt. The phase I’ is stable, however, the phase II’ is metastable at atmospheric pressure and transforms into the phase I’ on standing at room temperature. These phases show the same X-ray diffraction pattern as phases I and II but have a much lower melting temperature (phase I′, I – 96 versus 125 °C).

The as-polymerized samples prepared with the Ziegler-type catalysts contain phases I and III. Melt crystallization usually leads to the formation of the phase II. However, when PB-1 is melt-crystallized under high hydrostatic pressure (over 100 MPa) formation of the phase I has been reported. Formation of the phase III has also been reported when PB-1 is melt-crystallized with a specific nucleating agent. In the case of crystallization from a dilute amyl acetate solution, all three phases can be obtained by controlling dissolution and crystallization temperatures. When the phases I and III were formed directly from the melt or from the amyl acetate solution, they transform into the phase II by annealing at 90–100 °C through a melting-recrystallization process [59].

2.2.1 Structural Transformations of Isotactic Poly(1-butene)

The transformation of the phase II into the phase I is an interesting phenomenon which takes place after crystallization of PB-1 from the melt. The phase II is unstable and at room temperature and atmospheric pressure transforms into a stable 3_1 helix conformation with trigonal unit cells – phase I. This transformation takes about one week under normal conditions and is reflected in important changes in the physical-mechanical properties. During the transformation density, hardness, rigidity, stiffness and tensile strength increase to values characteristic for the phase I [60]. Moreover, the melting point increases from 120 to 135 °C [8]. The relatively constant values for ultimate tensile strength and elongation indicate that stretching or orientation accelerates the phase transformation [6]. The kinetics of this transformation is known to be also influenced by pressure [8], and temperature [52] (Figure 2.2). Apparently, the process is not accompanied by changes in the overall morphology and crystallinity; also, a small but significant increase of the degree of crystallinity of about 5 % has been reported for samples quenched from the melt [61].

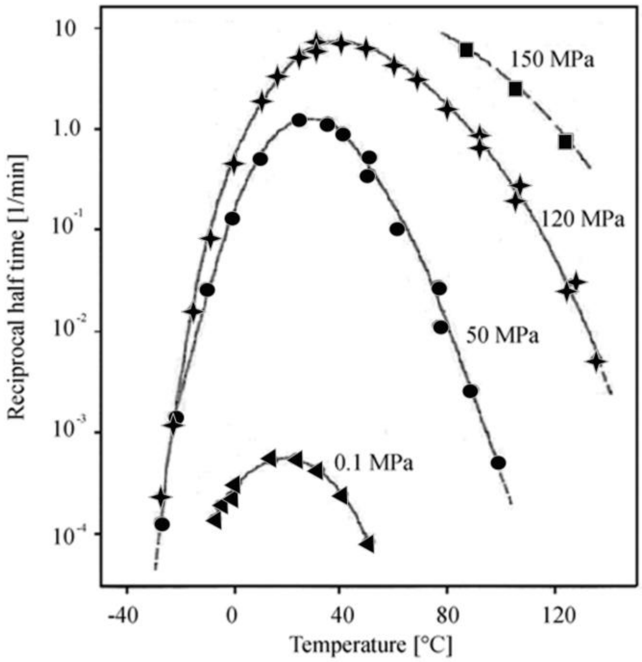

Figure 2.2 Dependence of phase transformation of PB-1 on ambient temperature and pressure [61]

At atmospheric pressure (0.1 MPa) the maximum rate of transformation occurs around 20 °C but drops significantly by increasing or decreasing the temperature. If ageing is performed at lower or higher temperatures than 20 °C only the time to achieve final properties is prolonged: the final performance of the material itself is not affected. It can be shortened from days to only a few minutes by application of hydrostatic pressure of up to 200 MPa using a suitable autoclave [61]. Also it can be accelerated by addition of ethylene, propylene, etc., comonomers in the structure but it is hindered by 4-methyl-1-pentene. It has also been suggested that molar mass is another variable affecting the kinetics of the transformation [62]; a faster rate of transformation has been reported for oligomers of M_w lower than 4000 g/mol. This slow process is not advantageous for industrial applications and it is probably the main factor that has hindered the commercial relevance of this polymer [63–65].

Kinetics of structural transformation has been thoroughly investigated by means of various techniques, such as infrared spectroscopy, thermal analysis, e.g. differential scanning calorimetry [61, 63–65] or by X-ray diffraction, as shown in Figure 2.3 [65].

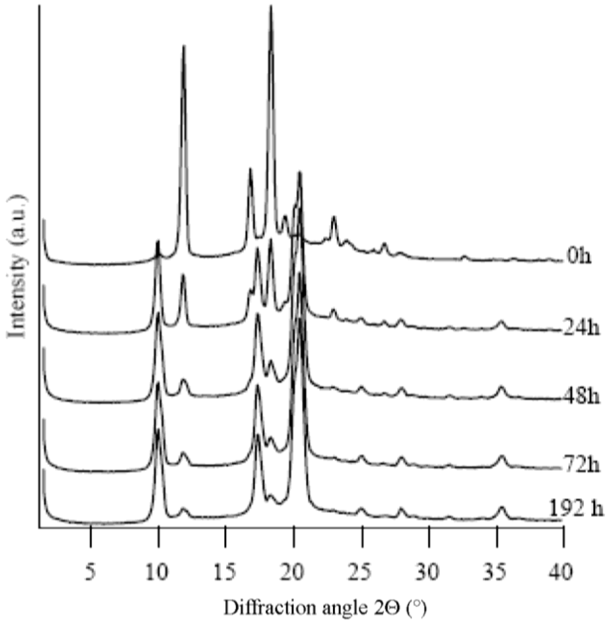

Figure 2.3 WAXD patterns of sample PB 0300M at different ageing times [65]

Also microindentation hardness allows to easily distinguish between the kinetically favoured phase II and the thermodynamically stable phase I of PB-1. The measured microhardness values of the phase I are shown to be notably higher than those of the phase II due to the higher chain packing density of the former [66].

Despite the extensive investigation on the kinetics of PB-1 polymorphic transformation, its mechanism is not fully understood yet. The information and clarification of the influence of annealing temperature on kinetics of phase transformation and evolution of mechanical properties in poly(1-butene) is industrially vital but still missing. This lack of knowledge can contribute to the delay in commercialization of poly(1-butene).

2.2.2 Properties of Isotactic Poly(1-butene)

Isotactic poly(1-butene) is a semi-crystalline polymer with high isotacticity and consequently high crystallinity. In analogy to others thermoplastics PB-1 shows viscoelastic behaviour, i.e. its mechanical properties depend not only on stress and temperature but also on time [61].

Table 2.1 Properties of PB-1, PP, PE-HD and PMP [67, 68]

Property of material	PB-1	PP	PE-HD	PMP
Flexural elastic modulus [MPa]	450	1000–1700	400–1100	800–1200
Tensile strength at yield [MPa]	20	30–43	26–33	23–28
Tensile strength at break [MPa]	35	29–30	18–33	17–20
Elongation at break [%]	300	500–900	12–700	10–25
Notched impact strength	20	21–320	43–750	100–200

The Table 2.1 gives a comparison of typical average values of mechanical properties of PB-1, PP, high density poly(ethylene) (PE-HD) and poly(4-methyl-1-pentene) (PMP) [67, 68].

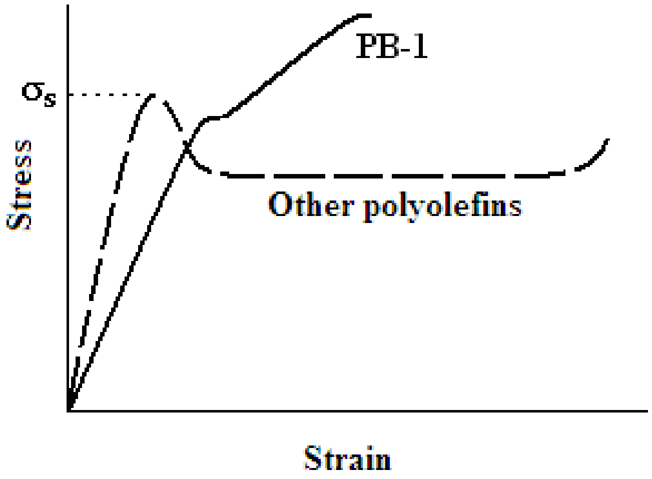

Figure 2.5 Tensile behaviour of PB-1 vs. other polyolefins [61]

Poly(1-butene) possesses a unique tensile behaviour which is based mainly on chain entanglements. Upon loading no necking behaviour of PB-1 appears [69]. However, the conditions of specimen preparation and the way of measurement may be responsible for the suppresion of yielding (Figure 2.5) [61].

Isotactic poly(1-butene) possesses excellent impact toughness. The IZOD notched impact strength (ISO 180) of PB-1 is classified as “no break” at room temperature. Due to a glass transition temperature of PB-1 located at approx. -16 °C the material retains its flexibility even at temperatures below freezing point which strongly facilitates installation of pipes during cold seasons [61].

Isotactic poly(1-butene) shows very good wet abrasion resistance in wet sand/slurry environment. In this case it is comparable with ultra high molecular weight poly(ethylene) which is well known for its outstanding abrasion and wear resistance. Contrary, in dry conditions PB-1 behaves similarly to conventional polyolefins [61].

On the other hand, significant problems can appear when applying surface coating, sticking or printing because poly(1-butene) is non-polar, hydrophobic polymer with poor adhesion and wettability. In this context, many application of this polymer require modification of the surface and adhesive properties. With the aim of improving the low wettability and adhesive properties of polymers such as poly(propylene), poly(ethylene), poly(styrene) etc., plasma treatment has been widely used in recent decades [70–73]. It is very efective method when only outermost atomic layers of the polymer are modified [74]. Generally, surface wettability of polymers can be influenced by several factors: (i) chemical composition, (ii) morphology and roughness, and (iii) molecular structure at the polymer surface, with emphasis on conformation and orientation of functional groups, and chemical bonding [75–78]. To improve the surface properties it is important to understand the interrelations between these factors and wettability. Nevertheless, published studies dealing with plasma-modified poly(1-butene) are very scarce, Shen Chou et. al used radio frequency plasma polymerisation to treat glass fibres to improve the interfacial adhesion between PB-1 and glass fibre [79].

Transparency and translucency of isotactic poly(1-butene) depend upon its crystallographic form. The unstable phase II of PB-1 is colourless, transparent, soft and easily deformed. In contrast, the stable phase I is translucent or opaque with a refractive index in a region of 1.52 to 1.53 [80], rigid and resistant to mechanical deformation. However, this transition to the phase I often yields finished products with undesirable shape changes and changes in optical properties [81].

From the commercial point of view good electrical insulation properties of PB-1 are important [71]. Products, e.g. pipes made from PB-1 exhibit excellent sound dampening properties thanks to their high elasticity and low density (950–960 kg/m^3) [82].

2.2.3 Photodegradation of Isotactic Poly(1-butene)

The knowledge of the relationships between supermolecular structure and properties of PB-1 is important for the estimation of the lifetime of the polymer. Durability of polymers can be strongly affected by the environment and especially by photodegradation processes. The degradability of semi-crystalline polymers is significantly influenced by their morphology.

As generally accepted, degradation reaction of semi-crystalline polymers proceed predominantly in amorphous regions. However, physical factors, such as the size, arrangement and distribution of crystalline regions, affect the degradation process as well. Photodegradation kinetics in polymer systems basically depends on oxygen permeability through the material [83]. The rate of oxidation drops with decreasing oxygen diffusin, following the increase of crystallinity and molecular orientation.

On the other hand, the crystallinity and the molecular orientation determine the mobility of the radicals and therefore reduce the rate of termination, allowing an increase in the propagation of chemical reactions leading to molecular scission; this effect is opposite to that caused by reduced oxygen mobility. Which of these two effects will predominate depends on the oxidation conditions, including the type of degradation, temperature and oxygen concentration [39, 84]. The situation is more complicated in the case of polymorhpic polymers because the rate of photooxidation is dependent on the type of phase [85, 86].

Two types of processes occur during polymer photodegradation: (i) primary photochemical reactions due to the absorbed radiation, resulting in the formation of free radicals or non-radicals rearrangement; and (ii) secondary reactions in which radicals formed initiate a number of reactions which are independent of the light [83, 87].

Degradation behaviour of PB-1 is not still fully described. However, it is supposed to be similar to isotactic poly(propylene) due to the presence of tertiary carbon on the backbone. Photodegradation of plastic materials is caused mainly by UV-light with wavelength of 290–400 nm. Because neat poly(propylene) and also poly(1-butene) contain only C-C and C-H bonds they do not absorb the light above the wavelength 200 nm, and thus they are not highly sensitive to the UV-light. However, chromophors which are developed during polymerization or thermal processing of commertial polymers cause the photolysis. Chromophores are sensitive to the photolysis by the light above the wavelength 300 nm. The fact that photodegradation of polymers occurs even above 300 nm indicates the presence of some kind of chromophoric groups in these polymers [87].

Specified by-products of the free radical oxidation of most polymers are hydroperoxides [88]. The mechanism of radical oxidation in poly(1-butene) is still unknown, nevertheless, the similar mechanism as in the case of poly(propylene) is suggested, where resulting hydroperoxides are predominantly tertiary (≈ 90 %), the remainder being essentially secondary ones [89].

2.2.4 Application of Isotactic Poly(1-butene)

The main areas of PB-1 application covered creep resistant applications, such as tanks, hose and tubing, moulded parts, etc. Piping systems made from PB-1 are being used today in a wide range of applications, e.g. domestic and commercial plumbing (hot and cold water supply); floor and wall heating; radiator connections; community and district heating projects and many more. The next groups are film applications – controlled adhesion, sealants, film modifiers, shrink film, etc; compounds and additives; fibre and fabric applications; hot melt adhesives and other applications [90].

REFERENCES

[1] RAAB, M., KOTEK, J. *Vesmír* 2009, 88, 186

[2] CHVÁTALOVÁ, L., VÝCHOPŇOVÁ, J., ČERMÁK, R., RAAB, M. *Plasty a kaučuk*, 2007, 7-8, 202

[3] PHILLIPS, R. A., WOLKOWICZ, M. D. *Structure and Morphology*, In: *Polypropylene Handbook*, Carl Hanser Verlag, Munich 1996, ISBN 3-446-18176-8

[4] VARGA, J. *J. Macromol. Sci.* 2002, 41, 1121

[5] VARGA, J. *Crystallization, melting and supermolecular structure of isotactic polypropylene,* In: KARGER-KOCSIS, J., *Polypropylene: Structure, Blends and Composites,* Chapman & Hall, London 1995, ISBN 0-412-58430-1

[6] NATTA, G., CORRADINI, P., BASSI, I. W. *Nuovo Cimento Suppl.* 1962, 1, 52

[7] BOOR, J., JR., YOUNGMAN, E. A. *J. Polym. Sci.* 1964, B2, 903

[8] NAKAFUKU, C., MIYAKI, T. *Polymer* 1983, 24, 141

[9] WEI, Z., ZHENNAN, Z., XINPING, W. *J. Col. Interf. Sci.* 2009, 333, 346

[10] DORAI, R., KUSHNER, M. J. *J. Phys. D. Appl. Phys.* 2003, 36, 666

[11] BAILEY, M. S., BRAUER, D. *Polypropylene: New Array of Polymer Variations Expand End- use Applications*, Modern Plastics Encyclopedia, reference book (M603.1.5) – McGraw-Hill 1994

[12] ELBER, G. *Trade Journal* – Advanstar Communications 1993, 18, 5

[13] MONASSE, B., HAUDIN, J. M. *Molecular structure of polypropylene homo- and copolymers.* In: KARGER-KOCSIS, J., *Polypropylene: Structure, blends and composites*, Chapman & Hall, London 1995, ISBN 0-412-58430-1

[14] CAPSHEW, C. *Polypropylene: A Commodity Plastic Reaches Record Highs in 1995 Production*, Modern Plastics Encyclopedia 1997, reference book (Vol. 73, No. 12) – McGraw-Hill 1997

[15] GRAVES, V. *Polypropylene: A Commodity Plastic Reaches Record Highs in 1994 Production*, In Modern Plastics Encyclopedia, McGraw-Hill 1996, PB-62

[16] Macrogalleria. [online] Available on: *http://pslc.ws/macrogcss/pp.html* [cit. 2010-05-09]

[17] KARGER-KOCSIS, J. *Polypropylene: An A-Z Reference,* Kluwer Academic Publishers, Dordrecht Netherlands 1999, ISBN 0-412-80200-7

[18] NATTA, G., CORRADINI, P. *Nuovo Cimento, Suppl*. 1960, 15, 40

[19] PADDEN, F. J., KEITH, H. D. *J. Appl. Phys.* 1959, 30, 1479

[20] TURNER-JONES, A., AIZLEWOOD, J. M., BECKETT, D. R. *J. Macromol. Chem.* 1964, 75, 134

[21] VARGA J. *J. Mater. Sci.* 1992, 27, 2557

[22] PADDEN, F. J., KEITH, H. D. *J. Appl. Phys.* 1973, 44, 1217

[23] BRUCKNER, S., MEILLE, S. V. *Nature* 1989, 340, 455

[24] CHEUNG, T., TJONG, S. C., Li, R. K. Y., *Mechanical Behavior of Calcium Carbonate Filled Beta-Crystalline Form Polypropylene Composite, ANTEC 1996*, conference proceedings – Society of Plastics Engineers, 1996

[25] MORROW, D. R., NEWMAN, B. A. *J. Appl. Phys.* 1968, 39, 4944

[26] CHENG, D. Z. S., JANIMAK, J. J., RODRIGUEZ, J. *Crystalline structures of polypropylene homo- and copolymers,* In: KARGER-KOCSIS, J., *Polypropylene: Structure, blends and composites,* Chapman & Hall, London 1995, ISBN 0-412-58430-1

[27] NATTA, G., PERALDO, M., CORRADINI, P. *Rend Accad Naz Lincei* 1959, 26,14

[28] NATTA G. *Makromol. Chem.* 1960, 35, 94

[29] ADDINK, E. J., BIENTEMA, J. *Polymer* 1961, 2, 185

[30] LOTZ, B. *Polymer* 1998, 39, 19, 4561

[31] DORSET, D.L., MCCOURT, M.P., KOPP, S., SCHUMACHER, M., OKIHARA, T., LOTZ, B. *Polymer* 1998, 39, 25, 6331

[32] OBADAL, M., ČERMÁK, R., BARAN, N., STOKLASA, K., ŠIMONÍK, J. *J. Int. Polym. Process* 2004, 19, 35

[33] BALTA CALLEJA F. J., MARTINEZ SALAZAR J, ASANO T. *J. Mater. Sci. Lett.* 1998, 7, 165

[34] VARGA, J. *J. Therm. Anal.* 1989, 35, 1891

[35] KOTEK, J., RAAB, M., BALDRIAN, J., GRELLMANN, W. *J. Appl. Polym. Sci.* 2002, 85, 1174

[36] CHVÁTALOVÁ, L., NAVRÁTILOVÁ, J., ČERMÁK, R., RAAB, M., OBADAL, M. *Macromolecules* 2009, 42, 7413

[37] LIBSTER, D., ASERIN, A., GARTI, N. *Polym. Adv. Tech.* 2007, 18, 685

[38] VARGA, J., MENYHÁRD, D. *Macromolecules* 2007, 40, 2422

[39] OBADAL, M., ČERMÁK, R., RAAB, M., VERNEY, V., COMMEREUC, S., FRAÏSSE, F. *Polym. Degrad. Stabil.* 2005, 88, 532

[40] CERMAK, R., OBADAL, M., PONIZIL, P., POLASKOVA, M., STOKLASA, K., LENGALOVA, A. *Eur. Polym. J.* 2005, 41, 1838

[41] CERMAK, R., OBADAL, M., PONIZIL, P., POLASKOVA, M., STOKLASA, K., HECKOVA, J. *Eur. Polym. J.* 2006, 42, 2185

[42] JACOBY, P., BERSTED, B. H., KISSEL, W. J., SMITH C. E. *J. Polym. Sci. Polym. Phys.* 1986, 24, 461

[43] KOTEK, J., KELNAR, I., BALDRIAN, J., RAAB,M. *Eur. Polym. J.* 2004, 40, 679

[44] OBADAL, M., CERMAK, R., RAAB, M., VERNEY, V., COMMEREUC, S., FRAISSE, F. *Polym. Degrad. Stab.* 2006, 91, 459

[45] ROMANKIEWICZ, A., STERZYNSKI, T., BROSTOW, W. *Polym. Int.* 2004, 53, 2086

[46] VYCHOPNOVA, J., HABROVA, V., OBADAL, M., CERMAK, R., CABLA, R. *J. Therm. Anal. Calorim.* 2006, 86, 687

[47] VYCHOPNOVA, J., CERMAK, R., OBADAL, M., RAAB, M., VERNEY, V., COMMEREUC, S. *Polym. Degrad. Stab.* 2007, 92, 1763

[48] NATTA G, CORRADINI P, DANUSSO F, MANTICA E, MAZZANTI G, PINO P, MORAGLIO G. *J. Am. Chem. Soc.* 1955, 77, 1708

[49] BRANDRUP, J., IMMERGUT, E. H., GRULLKE, E. A. *Polymer handbook*, J. Wiley & Sons, New York 1999, ISBN 0-471-16628-6

[50] HUANG, Q., ZHU, F., WU, Q., LIN, S. *Polym. Internat.* 2001 50, 45

[51] DI LORENZO, M. A., RIGHETTI, M. C. *Polymer* 2008 49, 1323

[52] KALAY, G., KALAY, C. R. *J. Polym. Sci.: Part B: Polym. Phys.* 2002 40, 1828

[53] HOLLAND, V. F., MILLER, R. L. *J. Appl. Phys.* 1964 35, 3241

[54] GOHIL, R. M., MILES, M. J., PETERMANN, J. *J. Macromol. Sci.-Phys.* Ed 1982 B21(2), 189

[55] ARMENIADES, C. D., BAER, E. *J. Macromol. Sci.-Phys.* Ed 1967 B1(2), 309

[56] ANDROSCH, R., DI LORENZO, M. L., SCHICK, CH.,WUNDERLICH, B. *Polymer* 2010, 51, 4639

[57] HONG, W., SPRUIELL, J. E. *J. Appl. Polym. Sci.* 1985, 30, 3163

[58] FUJIWARA, Y. *Polym. Bul.l* 1985, 13, 253

[59] TOSAKA, M., KAMIJO, T., TSUJI, M., KOHJIYA, S., OGAWA, T., ISODA, S., KOBAYASHI T. *Macromolecules* 2000, 33, 9666

[60] MARIGO, A., MAREGA, C., CECCHIN, G., COLLINA, G., FERRARI, G. *Eur. Pol. J.* 2000, 36, 131

[61] Polybutene-1: pipe extrusion guide, *Bassel Polyolefine publication*, provided by commercial representation 2005

[62] FOGLIA, A. J. *Appl. Polym. Symp.* 1969, 11, 1

[63] SCHONHERR, H., HRUSKA, Z., VANCSO, G. J. *Macromolecules* 1998, 31, 3679

[64] NAVANEETHA PANDIYARAJ, J., SELVARAJAN, V., DESHMUKH, R. R., GAO, Ch. *Vacuum* 2009, 83, 332

[65] JUNKAR I., VESEL A., CVELBAR U., MOZETIČ M., STRAND S. *Vacuum* 2010, 84(1), 83

[66] NOVAK, I., POLLAK, V., CHODAK, I. *Plasma Process. Polym.* 2006, 3, 355

[67] TUSJEK, L., NITSCHKE, M., WERNER, C., STANA-KLEINSCHEK, K., RIBITSCH, V. *Coll. Surf. A: Physicochem. Eng. Aspects* 2001, 195, 81

[68] DORAI, R., KUSHNER, M. J. *J. Phys. D. Appl. Phys.* 2003, 36, 666

[69] STROBEL, H. M., STROBEL, M., LYONS, C. S., DUNATOV, C., PERRON, S. J. *J. Adhes. Sci. Technol.* 1991, 5, 119

[70] WEI, Z., ZHENNAN, Z., XINPING, W. *J. Col. Interf. Sci.* 2009, 333, 346

[71] KIM, B. K., KIM, K. S., PARK, C. E., RYU, C. M. *J. Adhes. Sci. Technol.* 2002, 16, 509

[72] SHEN CHOU, SHIH, K.-S., CHEN, S.-H. *Pol. & Pol. Comp.* 2001, 9, 3, 185

[73] MARUYAMA, M., SAKAMOTO, Y. MOZAKI, K., YAMAMOTO, T., KAJIOKA, H., TODA, A. , YAMADA, K. *Polymer* 2010, 51, 5532

[74] ALFONSO, G. C., AZZURRI, F., CASTELLANO, M. *J. Therm. Anal. Calorim.* 2001, 66, 197

[75] CAUSIN, V., MAREGA, M., MARIGO, A., FERRARA, G., IDIYATULLINA, G., MANTINEL, F. *Polymer* 2006, 47, 4773

[76] AZZURRI, F., FLORES, A., ALFONSO, G. C., BALTA CALLEJA F. J., *Macromolecules* 2002, 35, 9069

[77] The Polybutene Piping Systems Association [online] Available on: *www.pbpsa.com/eng/siteplan.asp* [cit. 2008-02-03]

[78] DE ROSA, C., AURIEMMA, F., BORRIELLO, A., CORRADINI, P. *Polymer* 1995, 36, 4723

[79] TURNER, S. *Mechanical Testing of Plastics,* 2nd Ed, Longman Inc. New York 1983, 133

[80] Polymer data file: polybutylene-PB [online] Available on: *www.tangram.co.uk/TI-Polymer-PB.html* [cit. 2007-02-05]

[81] MACK, et al. Transparent and translucent poly(butene-1). United States Patent. 4, 219, 639 [online] Available on: *http://patimg1.uspto.gov* [cit. 2007-11-23]

[82] SCHEMM, F. VAN DE VLIET, F. KÖNNECKE, K., GRASMEDER, J. Polybutene-1 entering the next generation. [online] Available on: *www.pbpsa.com/eng/downloads/conf-plasticpipes2004.pdf* [cit. 2007-12-16]

[83] AUDOUIN, L., LANGOIS, V., VERDU, J., DE BRUIN, J. C. M. *J. Mater. Sci.* 1994, 29, 569

[84] VERNEY, V., MICHEL, M. *Rheol Acta* 1989, 28, 54

[85] AZZURRI, F., FLORES, A., ALFONSO, G. C., BALTÁ CALLEJA, F. J. *Macromolecules* 2002, 35, 9069

[86] BENÍČEK, L., CHVÁTALOVÁ, L., OBADAL, M., ČERMÁK, R., VERNEY, V., COMMEREUC, S. *Polym. Degrad. Stab.* 2011, doi:10.1016/j.polymdegradstab.2011.08.001

[87] RABEK, J. F. *Polymer photodegradation: Mechanism and Experimental Methods:* Springer, 1994, p. 680, ISBN 978-0-412-58480-0

[88] COMMEREUC, S., VAILLANT, D., PHILIPPART, J. L., LACOSTE, J., LEMAIRE, J., CARLSSON, D. J. *Polym. Degrad. Stab.* 1997, 57, 175

[89] LACOSTE, J., VAILLANT, D., CARLSSON, D. J. *J. Polym. Sci. A Polym. Chem.* 1993, 31, 715

[90] Polybutene-1: Versatility, value and opportunity [online] Available on: *www.industriepark-hoechst.com/broschuere-iphunternehmen_en.pdf* [cit. 2007-12-05]

AIMS OF THE DOCTORAL STUDY

Several different grades of β-nucleated isotactic poly(propylene) and isotactic poly(1-butene) were selected for the study. These polymers show a number of attractive properties that distinguish them from the most common polyolefins and offer wide range of applications. A fundamental presumption for their use is a need to understand interrelations between structure, macroscopic properties and processing.

Thus, the main goal of the study is experimental determination of the interrelations between structure, processing, and macroscopic properties of β-PP and PB-1. These factors are studied on the molecular and supermolecular structure levels using various experimental devices and methods such as wide-angle X-ray scattering, differential scanning calorimetry, X-ray photoelectron spectroscopy, atomic force microscopy, contact angle measurement, oscillatory rheometry, and mechanical testing.

Consequently the main attention within this work is particularly dedicated to following points:

- The effect of molecular structure and processing conditions on the efficiency of specific nucleation in isotactic poly(propylene).

- The influence of annealing temperature on the kinetics of phase transformation and evolution of mechanical properties in isotactic poly(1-butene).

- Modification of isotactic poly(1-butene) surface by plasma treatment.

- Characterization of photodegradation of isotactic poly(1-butene).

LIST OF PAPERS

I **Joint Effects of Molecular Structure and Processing History on Specific Nucleation of Isotactic Polypropylene**
Lenka Chvátalová, Jana Navrátilová, Roman Čermák, Miroslav Raab, Martin Obadal
Macromolecules, 2009, 42, 7413–7417.

II **Effect of Annealing Temperature on Phase Composition and Tensile Properties in Isotactic Poly(1-butene)**
Lenka Chvátalová, Lubomír Beníček, Kristýna Berková, Roman Čermák, Martin Obadal, Vincent Verney, Sophie Commereuc
Journal of Applied Polymer Science – DOI 10.1002/app.35360

III **The Effect of Plasma Treatment on Structure and Properties of Poly(1-butene) Surface**
Lenka Chvátalová, Roman Čermák, Aleš Mráček, Ondřej Grulich, Alenka Vesel, Petr Ponížil, Antonín Minařík, Uroš Cvelbar, Lubomír Beníček
Submitted for publication.

IV **Photodegradation of Isotactic Poly(1-butene): Multiscale Characterization**
Lubomír Beníček, Lenka Chvátalová, Martin Obadal, Roman Čermák, Vincent Verney, Sophie Commereuc
Polymer Degradation and Stability, 2011, 96, 1740–1744.
.

SUMMARIES OF PAPERS

In the following, short summaries and the major results of Papers I to IV are presented.

The **Paper I** (Joint Effects of Molecular Structure and Processing History on Specific Nucleation of Isotactic Polypropylene) focuses on the influence of molecular parameters and thermal history on specific nucleation of isotactic poly(propylene). Commercially available isotactic poly(propylene) with broad range of molecular weights, from 240 000 to 1 300 000, was modified by 0, 0.01 and 0.03 wt.% of β-specific nucleation agent *N,N'*-dicyclohexylnaphthalene-2,6-dicarboxamide. Specimens were then compression-moulded at various processing temperatures and times. The interrelation between β-specific nucleation, thermal history, and molecular weight has been investigated by wide-angle X-ray scattering, differential scanning calorimetry, and scanning electron microscopy. Samples with low nucleator concentration showed a dramatic decrease of nucleation activity with increasing molecular weight, and processing time and temperature. This behaviour was ascribed to the temperature-dependent solubility of the nucleator in poly(propyle) melt and a competition between heterogeneous β-nucleation and self-nucleation.

The effect of annealing temperature on the both kinetics of polymorphic changes and mechanical properties within the time in isotactic poly(1-butene) was dealt in the **paper II** (Effect of Annealing Temperature on Phase Composition and Tensile Properties in Isotactic Poly(1-butene)). For these purposes wide-angle X-ray scattering and tensile testing were used. Extruded tapes of PB-1 have been exposed to several annealing temperatures: -22, +5, +22, +40 and +60 °C. The evolution of content of phase I for various annealing temperatures upon time shows predominantly S-shaped trend. Annealing temperature considerably affects the overall rate of transformation in poly(1-butene). On the contrary, the resulting mechanical properties are solely controlled by the polymorphic composition.

The paper III (The Effect of Plasma Treatment on Structure and Properties of Poly(1-butene) Surface) presents the influence of plasma treatment on the poly(1-butene) surface. Several types of plasmas based on air, argon, argon and then allylamine, argon wearing ammonia and argon with octafluorocyclobutane have been used. Modified surface of poly(1-butene) was characterized by contact angle measurements, X-ray photoelectron spectroscopy and atomic force microscopy. The plasma treatment greatly changed the surface chemistry. The polar functional groups generated almost all used types of plasma treatment on the surface of poly(1-butene) sheets cause decrease in contact angle and increase of hydrophilicity. Contradictory effect causes fluorocarbon plasma. Surface morphology and chemical composition of plasma-modified samples remains nearly unchanged upon a given time. The gradual changes in surface hydrophilicity/hydrophobicity of plasma-treated PB-1 samples can be attributed to the variation of the conformation of plasma-introduced functional groups.

In the paper IV (Photodegradation of Isotactic Poly(1-butene): Multiscale Characterization) is studied the effect of photodegradation on the isotactic poly(1-butene). Photodegradation of PB-1 leads to induction of chemical and physical heterogeneities; therefore it is necessary to predict the material durability. For these reasons oscillatory shear rheology is appropriate method for analysis of molecular chain motions, infrared spectroscopy for characterization of evolution of chemical species in PB-1 and finally differential scanning calorimetry for observation of changes in melting and crystallization behaviour and impact on kinetics of phase transformation. Thermal analysis determined significant changes in crystallization behaviour influencing morphology arrangement and resulting thermal properties. Moreover it has been proven that the degradation significantly retards the phase transformation. Rheological measurement has been found as an effective method for determination of early stages of photodegradation of PB-1.

CONTRIBUTIONS TO THE SCIENCE AND PRACTICE

The presented doctoral thesis deals with the modification of novel polyolefins, as β-nucleated isotactic poly(propylene) and isotactic poly(1-butene). The contributions of the current study to the level of scientific knowledge are as follows:

- Examination and understanding of the effect of isotactic poly(propylene) molecular weight on the sensitivity to specific nucleation opened a new insight into the mechanism of specific nucleation process and, at the same time, brings about practical recommendations important for optimizing processing technology.

- An evidence and explanation of the influence of annealing temperature on kinetics of phase transformation and evolution of mechanical properties in isotactic poly(1-butene).

- Modification of the surface properties of isotactic poly(1-butene) using a radio frequency plasma important for several industrial applications.

- Multiscale characterization of photodegradation of isotactic poly(1-butene) is important both from theoretical and practical points of veiw.

Obtained results were already published or have been submitted to publication. Some of them have direct practical importance for application in industry (pipes) and medicine (syringes).

AUTHOR’S PUBLICATIONS

JOURNAL ARTICLES

[a1] CHVÁTALOVÁ, L., NAVRÁTILOVÁ, J., ČERMÁK, R., RAAB, M., OBADAL, M. *Joint Effects of Molecular Structure and Processing History on Specific Nucleation of Isotactic Polypropylene*, Macromolecules, 2009, 42, 7413–7417.

[a2] CHVÁTALOVÁ, L., BENÍČEK, L., BERKOVÁ, K., ČERMÁK, R., OBADAL, M., VERNEY V, COMMEREUC S., *Effect of Annealing Temperature on Phase Composition and Tensile Properties in Isotactic Poly(1-butene),* Journal of Applied Polymer Science – DOI 10.1002/app.35360.

[a3] BENÍČEK, L., CHVÁTALOVÁ, L, OBADAL, M., ČERMÁK, R., VERNEY V, COMMEREUC S. *Photodegradation of isotactic poly(1-butene): Multiscale characterization,* Polymer Degradation and Stability, 2011, 96, 1740–1744.

JOURNAL ARTICLES IN CZECH

[cz1] CHVÁTALOVÁ, L., VÝCHOPŇOVÁ, J., ČERMÁK, R., RAAB, M. *Struktura, vlastnosti a perspektivy netradičních polyolefinů,* Plasty a kaučuk, 2007, 44, 202–208.

[cz2] CHVÁTALOVÁ, L., NAVRÁTILOVÁ, J., ČERMÁK, R., RAAB, M., OBADAL, M. *Vliv molekulární struktury a zpracovatelské historie na specifickou nukleaci izotaktického polypropylenu,* Plasty a kaučuk, 2010, 47, 203–207.

[cz3] BERKOVÁ, K., BENÍČEK, L., ČERMÁK, R., CHVÁTALOVÁ, L. *Vývoj fyzikálních a mechanických vlastností během fázové transformace v poly(1-butenu),* Plasty a kaučuk, 2011, 48, 205–209.

CONFERENCE CONTRIBUTIONS

[c1] CHVÁTALOVÁ, L., VÝCHOPŇOVÁ, J., ČERMÁK, R. *Specific Nucleation of Isotactic Poly(propylene): the Role of Molecular Structure and Processing Conditions*, European Polymer Congress 2007, Portorož, Slovenia, 2007.

[c2] CHVÁTALOVÁ, L., VÝCHOPŇOVÁ, J., ČERMÁK, R., OBADAL, M., VERNEY, V., COMMEREUC, S. *The Effect of Nucleation Specificity on Crystallization of UV-irradiated Poly(propylene)*, European Polymer Congress 2007, Portorož, Slovenia, 2007.

[c3] HNIDÁKOVÁ, D., ČERMÁK, R., CHVÁTALOVÁ, L., VÝCHOPŇOVÁ, J., OBADAL, M. *Structure and Properties of β-poly(propylene) Cast Films*, ANTEC 2007, Cincinnati, USA, 2007.

[c4] CHVÁTALOVÁ, L., VÝCHOPŇOVÁ, J., ČERMÁK, R., MOŠNOVSKÁ, R. *The Effect of Structure and Processing Conditions on Efficiency of Specific Nucleation in Poly(propylene)*, Polymer Processing Society PPS-24, Salerno, Italy, 2008.

[c5] MOŠNOVSKÁ, R., ČERMÁK, R., COMMEREUC, S., CHVÁTALOVÁ, L. *The role of physical factors in photodegradation of polypropylene*, Polymer Processing Society PPS-24, Salerno, Italy, 2008.

[c6] BENÍČEK, L., CHVÁTALOVÁ, L., ČERMÁK, R., VERNEY, V. *Polymorphic Transformation in Polybutene-1: Temperature Influence*, Polymer Processing Society PPS-24, Salerno, Italy, 2008.

[c7] BENÍČEK, L., CHVÁTALOVÁ, L., ČERMÁK, R., VERNEY, V. *Evolution of mechanical properties during polymorphic transformation in polybutene-1*, Biannual Conference on Modification, Degradation and Stabilisation of Polymers, MoDeSt2008, Liege, Belgium, 2008.

[c8] CHVÁTALOVÁ, L., NAVRÁTILOVÁ, J., ČERMÁK R., OBADAL, M. *The role of melt flow index in crystallization of specifically nucleated polypropylene*, Macro 2008, Taipei, Taiwan, 2008.

[c9] CHVÁTALOVÁ, L., VÝCHOPŇOVÁ, J., ČERMÁK, R., OBADAL, M. *The role of molecular parameters of PP in the sensitivity to specific nucleation*, ANTEC 2008, Milwaukee, USA, 2008.

[c10] BENÍČEK, L., CHVÁTALOVÁ, L., ČERMÁK, R., VERNEY, V. *Thermal-induced transformation of structure and properties in polybutene-1,* ANTEC 2008, Milwaukee, USA, 2008.

[c11] CHVÁTALOVÁ, L., NAVRÁTILOVÁ, J., ČERMÁK, R., BENÍČEK, L., *Microhardness of Polypropylene: Influence of β-Nucleating Agent and Molecular Weight*, Polymer Processing Society PPS-25, Goa, India, 2009.

[c12] BENÍČEK, L., ČERMÁK, R., VERNEY, V., COMMEREUC, S., OBADAL, M., CHVÁTALOVÁ, L. *Thermal Behaviour of Photodegraded Poly(1-butene),* Polymer Processing Society PPS-25, Goa, India, 2009.

[c13] CHVÁTALOVÁ, L., ČERMÁK, R., HNIDÁKOVÁ, D. *Microhardness-Structure Correlation of Polypropylene: Influence of β-Nucleating Agent and Processing Conditions,* European Polymer Congress 2009, Graz, Austria, 2009.

[c14] CHVÁTALOVÁ, L., ČERMÁK, R., PONÍŽIL, P., MRÁČEK, A. *Plasma Treatment of Poly(1-butene),* Week of Doctoral Students 2009, Prague, Czech Republic, 2009.

[c15] CHVÁTALOVÁ, L., ČERMÁK, R., MRÁČEK, A., BENÍČEK, L. *Study of Poly(1-butene) Surface Modified by Air Plasma Treatment,* ANTEC 2010, Orlando, Florida, USA, 2010.

[c16] CHVÁTALOVÁ, L., NAVRÁTILOVÁ, J., ČERMÁK, R., RAAB, M., OBADAL, M. *Influence of Molecular Structure and Processing History on Specific Nucleation of Isotactic Polypropylene,* Plastko 2010, Zlín, Czech republic, 2010.

[c17] BENÍČEK, L., CHVÁTALOVÁ, L., MONTÁGOVÁ, K., ČERMÁK, R., OBADAL, M. *Fázová transformace ve vstřikovaném a vytlačovaném polybutenu-1,* Plastko 2010, Zlín, Czech republic, 2010.

[c18] CHVÁTALOVÁ, L., ČERMÁK, R., MRÁČEK, A. *Surface Properties of Plasma-Modified Poly(1-butene)* WSEAS 2010, Corfu, Greece, 2010.

[c19] MONTÁGOVÁ, K., BENÍČEK, L., ČERMÁK, R., CHVÁTALOVÁ, L. *Evolution of physical and mechanical properties during phase transformation in poly(1-butene*), WSEAS 2010, Corfu, Greece, 2010.

CITATIONS

[d1] Horváth, Z., Sajó, I. E., Stoll, K., Menyhárd, A., Varga, J. *The effect of molecular mass on the polymorphism and crystalline structure of isotactic polypropylene.* Polymer Letters, 2010, 4, 101–114. Citation of Paper I.

[d2] Chen, Y.-H., Mao, Y.-M., Li, Z.-M., Hsiao B. S. *Competitive Growth of α- and β-Crystals in β-Nucleated Isotactic Polypropylene under Shear Flow.* Macromolecules, 2010, 43, 6760–6771. Citation of Paper I.

[d3] Yang, Z., Mai, K. *Nonisothermal crystallization and melting behavior of β-nucleated isotactic polypropylene and polyamide 66 blends*. Journal of Applied Polymer Science, 2011, 119, 3566–3573. Citation of Paper I.

[d4] Kobayashi, Y., Otsuki, Y., Kanno, H., Hanamoto, Y., Kanai, T. *Relating scratch resistance to injection molding-induced morphology of polypropylene*. Journal of Applied Polymer Science, 2011, 120, 141–147. Citation of Paper I.

[d5] Kobayashi, Y., Otsuki, Y.,Kanno, H., Sasakawa, T.,Hanamoto, Y., Kanai, T. *Crystallization of polypropylene near the surface in injection-molded plaques: A comparison of morphology and a numerical analysis*. Polymer Engineering and Science, 2011, 51, 7, 1236–1244. Citation of Paper I.

[d6] Beníček, L., Čermák, R., Mlejnek, P., Navrátilová, J. *Photodegradation of polypropylenes with clarifying agent.* Annual Technical Conference - ANTEC, Conference Proceedings, 2011, 3, 2281–2285. Citation of Paper I.

[d7] Hao, X. Q., Zheng, G. Q., Dai, K., Jia, Z. H., Jia, Q., Chen, J. B., Liu, C. T., Shen, C. Y. *Facile preparation of rich β-transcrystallinity in PET fiber/iPP composites*. Express Polymer Letters, 2011, 5, 11, 1017–1026. Citation of Paper I.

CURRICULUM VITAE

Name: Lenka CHVÁTALOVÁ
Date of Birth: 1980, May 15
Address: Tomas Bata University in Zlín, Faculty of Technology
Department of Polymer Engineering, TGM 275, 762 72 Zlín
Czech Republic

E-mail: chvatalova@ft.utb.cz

Education

2006 MSc., Tomas Bata University in Zlín, Faculty of Technology, Programme – *Chemistry and Technology of Materials*

Employment

2010–present Teaching Assistant
Tomas Bata University in Zlín, Faculty of Technology

Stays abroad

Two-months stay at Vienna University of Technology, Austria,
Institute of Material Science and Technology

Three-month stay at Blaise Pascal University in Clermont-Ferrand, France,
Laboratory of Molecular and Macromolecular Photochemistry

Others

2008–present Society of Plastics Engineers – member

PAPER I

“The final publication is available at www.pubs.acs.org/Macromolecules“

Macromolecules
ARTICLE

Macromolecules **2009**, *42*, 7413–7417 **7413**
DOI: 10.1021/ma9005878

Joint Effects of Molecular Structure and Processing History on Specific Nucleation of Isotactic Polypropylene

Lenka Chvátalová,[†] Jana Navrátilová,[†] Roman Čermák,*,[†] Miroslav Raab,[‡] and Martin Obadal[§]

[†]*Faculty of Technology, Department of Polymer Engineering, Tomas Bata University in Zlín, nám. T. G. Masaryka 275, 762 72 Zlín, Czech Republic,* [‡]*Institute of Macromolecular Chemistry, AS CR, v. v. i., Heyrovského nám. 2, 162 06 Prague, Czech Republic, and* [§]*Borealis Polyolefine GmbH, St.-Peter-Strasse 25, 4021 Linz, Austria*

Received March 18, 2009; Revised Manuscript Received August 29, 2009

ABSTRACT: The interrelation between specific β-nucleation, thermal history, and molecular weight of isotactic polypropylene (PP) has been investigated by wide-angle X-ray scattering, differential scanning calorimetry, and scanning electron microscopy. Samples with a broad range of molecular weight (M_w), from 240 000 to 1 300 000, allowed to examine the effect of PP molecular structure on the nucleation sensitivity. *N,N′*-Dicyclohexylnaphthalene-2,6-dicarboxamide (NU 100) was introduced in the concentrations of 0, 0.01, and 0.03 wt % as a β-specific nucleating agent into neat PP. Specimens were then processed via compression molding at various processing temperatures and times. Samples containing 0.01 wt % of NU 100 showed a dramatic decrease of nucleation activity into β-phase with increasing M_w, processing time, and temperature. This effect was ascribed to a partial solubility of nucleator in PP melt and a competition between heterogeneous β-nucleation and self α-nucleation.

Introduction

Controlling supermolecular structure of polymorphic semicrystalline polymers is a smart way of tailoring their properties. In particular, in the case of isotactic polypropylene (PP) several crystallographic phases have been recognized, the monoclinic α and trigonal β having practical relevance. During past decades a considerable amount of knowledge has been collected on the formation and transformation of the β-phase.[1−7] This crystallographic modification of this important commodity polymer shows superior toughness and drawability but slightly lower stiffness as compared to the more common α-phase.[2,8−13] Moreover, PP containing predominantly β-phase within the crystalline portion of the material is significantly less sensitive to UV-irradiation as revealed Kotek et al. and Obadal et al.[14−16] Specific nucleation caused by an addition of β-nucleating agent is an efficient way of introducing the β-phase into the polymer.[2−5] Nucleating agents are generally low molecular mass organic or inorganic substances added to polymers, before or during processing.[17] The commercial β-nucleator *N,N′*-dicyclohexylnaphthalene-2,6-dicarboxamide (NU 100) was used in many studies.[10,14−26] Recently, the action of this nucleator, known under the trade name NJ Star NU 100, has been comprehensively described by Varga and Menyhard.[18]

These authors revealed three important features of this organic substance: *First*, the dual effect of this nucleator has been documented; it can also initiate the formation of certain amount of α crystallites. Nevertheless, the β-phase finally prevails owing to its higher crystallization rate. *Second*, NU 100 is a crystalline material and can dissolve in polypropylene melt. *Third*, the nucleating activity of NU 100 is exhibited only by solid crystalline particles. Individually dissolved molecules do not show any nucleating effect during solidification of PP from the melt. In this context a question arises whether the critical concentration of the nucleator of 0.03 wt % as described by Kotek et al.[19] is generally valid.

One can expect that thermal conditions and processing history can play an important role here. Indeed, the influence of processing parameters on the morphology and properties of injection-molded parts from β-nucleated PP has been described by e.g. Cermak et al.[20,21] However, heterogeneous nucleation reflects a mutual interaction between segments of a polymer chain and a solid inclusion. Obviously, the effect of polymer molecular structure can be expected. The goal of the present study is to examine the effect of PP molecular weight on the sensitivity to specific nucleation. For this purpose, polypropylene samples with a broad range of molecular weights have been chosen. The nucleation has then been followed at various processing conditions and nucleator concentrations. This approach should open a new insight into the mechanism of specific nucleation process and, at the same time, bring about practical instructions important for optimizing processing technology.

Experimental Section

Ten samples of PP homopolymer with various molecular weight supplied by the Borealis group were used as a starting material throughout this study. The molecular characteristics of the samples are summarized in Table 1. The following characteristics are given: weight-average molecular weight (M_w), numeric-average molecular weight (M_n), polydispersity index (PDI), and melt flow index (MFI). The molecular parameters (M_w, M_n, and PDI) were obtained from GPC equipped with a light-scattering detector. The MFI values were measured at 230 °C, 2.16 kg in accordance with ISO 1133.

The specific nucleating agent *N,N′*-dicyclohexylnaphthalene-2,6-dicarboxamide was supplied by Rika Int., Manchester, Great Britain, as NJ Star NU 100. The nucleator concentration was 0, 0.01, and 0.03 wt %. Nucleator was homogenously dispersed into

---

*Corresponding author: e-mail cermak@ft.utb.cz; Ph +420 576 031 323; Fax +420 576 032 733.

© 2009 American Chemical Society

Published on Web 09/17/2009

Table 1. Molecular Characteristics of PP Samples

no.	sample	M_w	M_n	PDI	MFI [g/10 min]
1	BE52	1300000	320000	4.0	0.3
2	HB205TF	830000	300000	2.8	1.0
3	HD601CF	570000	170000	3.5	8.0
4	HE125MO	490000	130000	3.8	12.0
5	HF136MO	410000	170000	2.5	20.0
6	HG455FB	360000	150000	2.4	27.0
7	HK060AE	330000	86000	3.7	125.0
8	HL504FB	290000	85000	3.4	450.0
9	HL508FB	280000	60000	4.9	800.0
10	HL512FB	240000	55000	4.5	1200.0

Table 2. Processing Conditions of Compression Molding

set	pressing temp [°C]	pressing time [min]	cooling temp [°C]	cooling time [min]
1	210	6	60	6
2	200	20	60	6
3	210	20	60	6
4	220	20	60	6

PP pellets using 0.30 wt % of paraffin oil. The mixture was then processed in a Brabender twin-screw extruder. The processing conditions were as follows: screw speed 55 min^{-1}; temperatures of barrel zones 190, 200, and 210 °C. From the prepared materials plates of thickness of ~0.5 mm were compression-molded. Four sets of processing conditions, differing in pressing temperature and time, were applied, as shown in Table 2. After the pressing in the hot press, cooling of the sheets was performed in the cold press set up to the temperature of 60 °C. During 1 min the temperature increased to 72 °C, and within the next 5 min the temperature dropped to 64 °C (~2 °C/min). Subsequently, specimens were examined by wide-angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC).

The amount and composition of the crystalline portion were determined by wide-angle X-ray scattering. An X'Pert PRO, PANalytical diffractometer equipped with Cu Kα and Bragg−Brentano geometry was employed in reflection mode. Crystallinity was calculated as a ratio of the integral intensities diffracted by a crystalline part and total integral intensities. The relative content (K) of the β-phase within the crystalline portion of the material was calculated according to Turner-Jones et al.:[3]

$$K = H_b/(H_{a1}+H_{a2}+H_{a3}+H_b) \qquad (1)$$

where H_{a1}, H_{a2}, and H_{a3} are the intensities of α-diffraction peaks corresponding to angles $2\theta = 14.2°$, $17.0°$, and $18.8°$, respectively, and H_b is the intensity of the β-peak at $2\theta = 16.2°$.

Melting behavior of the specimens was measured by a Perkin-Elmer Pyris 1 differential scanning calorimeter. Cylindrical specimens with a diameter of 4 mm were cut from the prepared plates using a hole-puncher. The specimens with a mass of ~6 mg were inserted into standard aluminum pans and heated from 50 °C up to 190 °C with heating rate of 10 °C/min. The measurements were performed under nitrogen atmosphere (20 mL/s).

Morphology of the specimens was directly documented by a Phillips XL30 ESEM scanning electron microscope (SEM) using secondary electron detector. The compression-molded plates were cryo-fractured under liquid nitrogen; fracture surfaces were then exposed to a permanganic etching (1% KMnO$_4$ in concentrated H$_3$PO$_4$) and finally sputtered with a gold−palladium alloy.

Results and Discussion

Effect of Molecular Weight and Specific Nucleation. The X-ray data have shown that the overall crystallinity was ~65%, and no γ-phase was present at all the specimens. The content of the β-phase however is a function of nucleator content, processing condition, and molecular weight. In Figures 1−4 results for specimens processed under the processing setup 1 are presented. The content of the β-phase in non-nucleated specimens is virtually zero nearly in all samples. Only the material with the highest M_w shows a small β-reflection at $2\theta = 16.2°$ (Figure 1). On the other hand, the material with 0.03 wt % of nucleating agent crystallizes predominantly into the β-phase; the values reach more than 90%. The specimens prepared with 0.01 wt % of nucleator

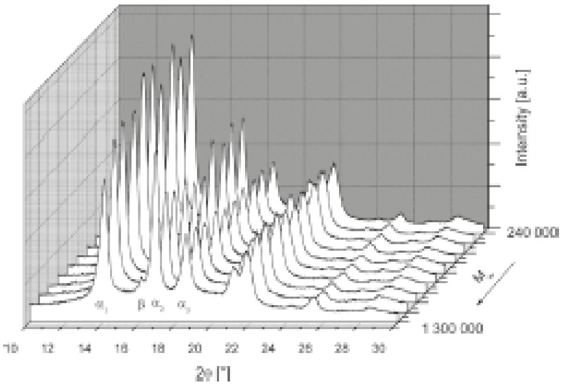

Figure 1. X-ray diffraction patterns of the neat PP specimens compression-molded at temperature of 210 °C for 6 min.

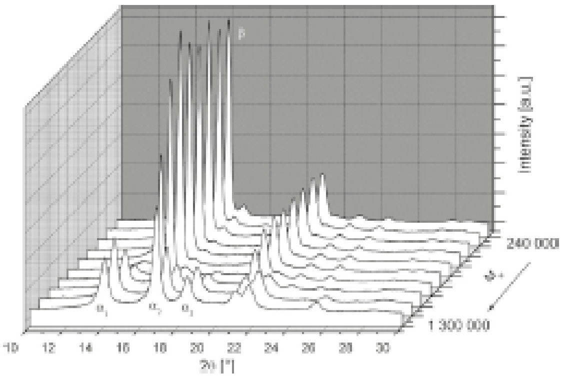

Figure 2. X-ray diffraction patterns of the PP specimens containing 0.01 wt % of nucleator compression-molded at temperature of 210 °C for 6 min.

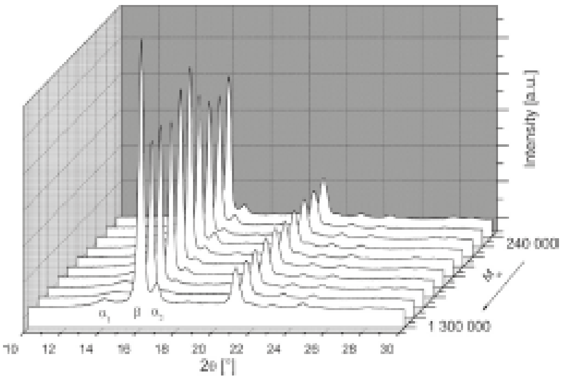

Figure 3. X-ray diffraction patterns of the PP specimens containing 0.03 wt % of nucleator compression-molded at temperature of 210 °C for 6 min.

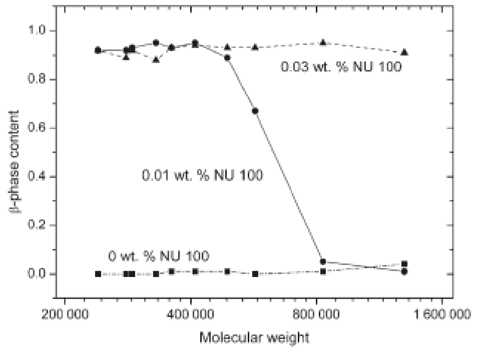

Figure 4. Dependence of β-phase content on M_w of the specimens compression-molded at temperature of 210 °C for 6 min.

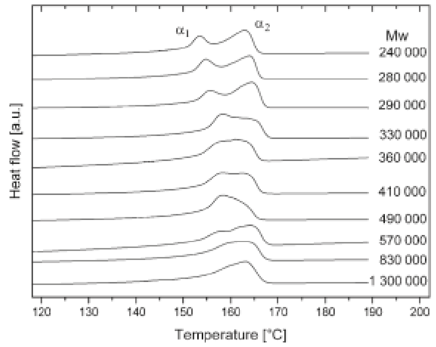

Figure 5. Melting thermograms of the neat specimens compression-molded at temperature of 210 °C for 6 min.

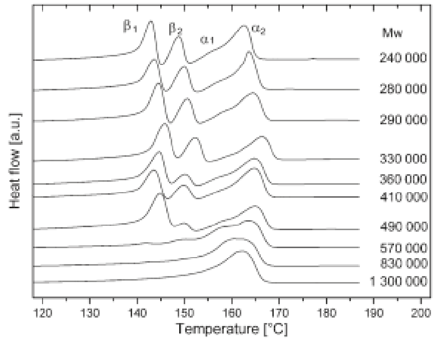

Figure 6. Melting thermograms of the specimens with 0.01 wt % NU 100 compression-molded at temperature of 210 °C for 6 min.

show a strong dependence on molecular weight. A dramatic change of the β-phase content appears between the lowest and highest M_w; in a relatively narrow M_w window the values drop from 0.91 to 0.04.

The effect of molecular weight on the phase structure is also manifested by the DSC thermograms (Figures 5–7). Again, no β-phase was detected for non-nucleated specimens. The effect of molecular weight is expressed in the different shape of the α-melting peaks: twin peak for lower M_w and single maximum for the highest M_w. Rather complicated melting profiles occur with the nucleated specimens. For the lower nucleator concentration (0.01 wt %) the β-melting peak disappears with increasing M_w. In the medium M_w range three different peaks can be observed, indicating $\beta \rightarrow \alpha$ recrystallization.[1,2] Specimens containing the "critical" nucleator concentration (0.03 wt %) show distinct β-melting peaks in the whole M_w range. Nevertheless, a double melting β-peak appears in the lower M_w range. These results correlate well with the WAXS data.

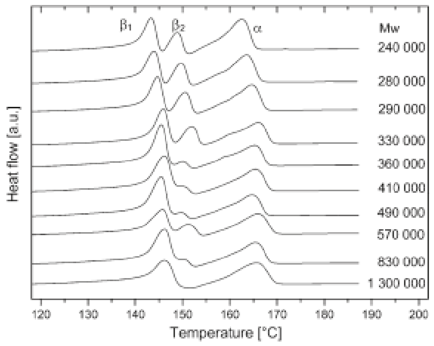

Figure 7. Melting thermograms of the specimens with 0.03 wt % NU 100 compression-molded at temperature of 210 °C for 6 min.

Scanning electron microscopy shows the higher structural level of the morphology, namely the detailed lamellar structure and spherulite shape. The fracture surfaces presented in Figure 8 show a distinct difference between α- and β-lamellar structure: smooth crack surface of material containing predominantly α-phase reflects fine lamellar structure (Figure 8, left). On the other hand, a distinctly rough surface structure of the PP rich in β-phase is a manifestation of thick sheaf-like lamellae (Figure 8, right). Scanning electron microscopy has also shown an interesting encounter of α- and β-structure in one material (Figure 8, middle). This is exactly the specimen exhibiting both α- and β-morphology by X-ray diffraction and DSC. Here electron microscopy shows that α- and β-phases coexist in one specimen but are divided in space at virtually macroscopic level.

Effect of Molecular Weight and Processing. The joint effect of processing conditions (temperature history during compression-molding) and the molecular weight on the β-phase content is presented in Figures 9–12. Here the data for specimens with the lower nucleator content (0.01 wt %) are given. It is shown unambiguously that particularly these materials with low nucleation are very sensitive to the thermal history. The processing temperature (T_p) plays here a crucial role: for low T_p (200 °C) the nucleator concentration 0.01 wt % is sufficient for the virtually complete crystallization into the β-phase. On the other hand, for T_p 220 °C the nucleation activity practically vanishes. For intermediate processing temperature (T_p 210 °C) a transition from high to very low nucleation activity is observed, in dependence on the M_w. At the same time, a distinct effect of processing time is clearly demonstrated. Prolonged processing time (from 6 to 20 min) distinctly limits the nucleation activity.

The distinct effect of processing temperature on the supermolecular structure of nucleated PP is directly documented on SEM micrographs for samples with intermediate molecular weight (Figure 13). Material processed at lower temperature, 200 °C (left), shows complete β-morphology, high processing temperature, 220 °C (right), induced formation of α-spherulites solely, and material processed at 210 °C (middle) shows a coexistence of both crystallographic modifications. Similar morphology variation (caused by nucleator concentration) has been presented in Figure 8.

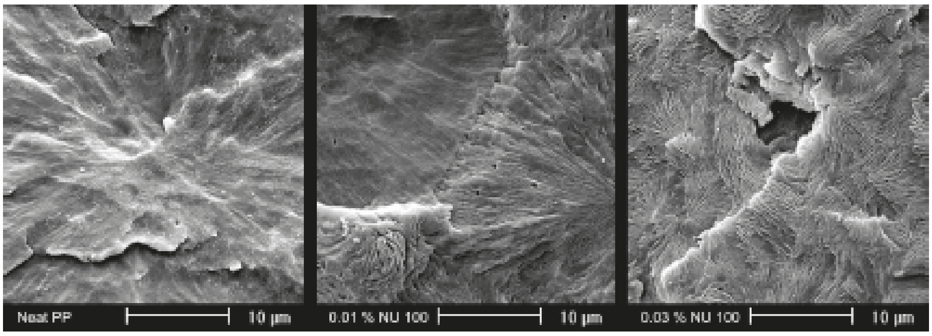

Figure 8. SEM images of PP with M_w 570 000 containing various amounts of nucleator (0, 0.01, and 0.03 wt %) processed under the condition 1 (210 °C, 6 min).

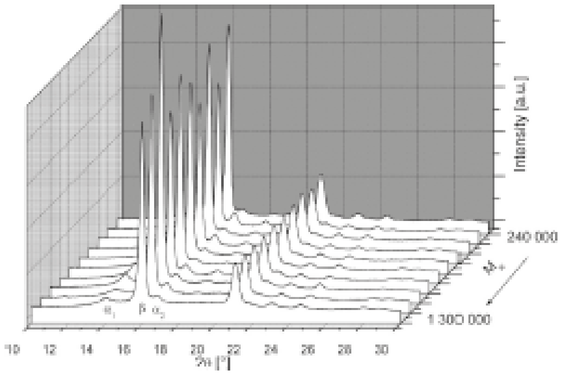

Figure 9. X-ray diffraction patterns of the specimens containing 0.01 wt % NU 100 processed at temperature of 200 °C.

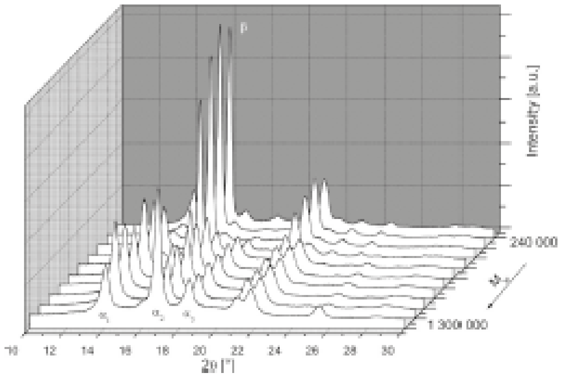

Figure 10. X-ray diffraction patterns of the specimens containing 0.01 wt % NU 100 processed at temperature of 210 °C.

Obviously, the effects of processing temperature and time can be unambiguously ascribed to dissolution of the nucleator in polymer melt, in agreement with the recent concept of Varga and Menyhard.[18] However, the effect of molecular weight has not been reported yet. According to our knowledge, the pronounced effect of the polymer molecular weight on its sensitivity to specific nucleation is presented here for the first time. In addition, the solubility of nucleator itself cannot offer a plausible explanation, as it should decrease with increasing M_w; the presented data show an opposite trend—decreasing nucleation activity with increasing M_w.

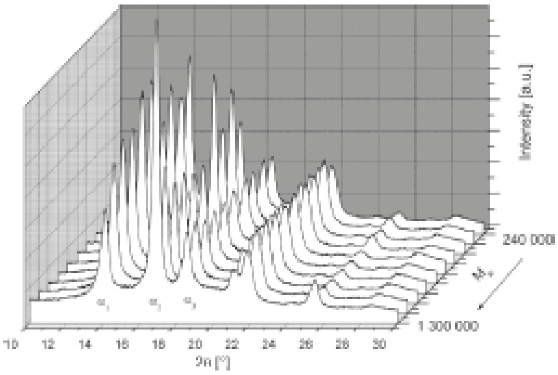

Figure 11. X-ray diffraction patterns of the specimens containing 0.01 wt % NU 100 processed at temperature of 220 °C.

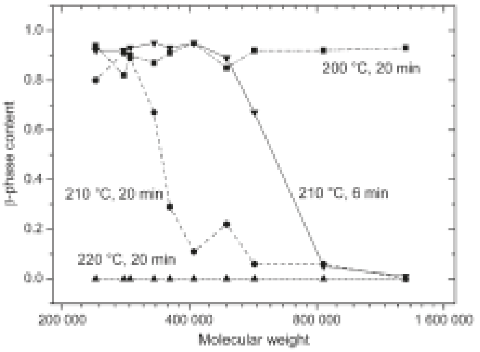

Figure 12. Dependence of β-phase content on M_w of the specimens containing 0.01 wt % NU 100 processed at various temperatures.

An explanation of this effect is not thus straightforward but can be based on the notion of competition between self-nucleation and heterogeneous β-nucleation. Generally, self-nucleation is a process during which the primary nucleation takes place in the melt on its own crystals grown previously. According to Galeski,[27] this nucleation prevails in PP melt. Indeed, the number of the self-nuclei depends on the annealing conditions. In this context, one can expect that also M_w of the polymer can play an important role; the stability of self-nuclei in the melt within annealing at a given temperature should be controlled by the viscosity and diffusion rate of chain segments. Upon annealing, the number of

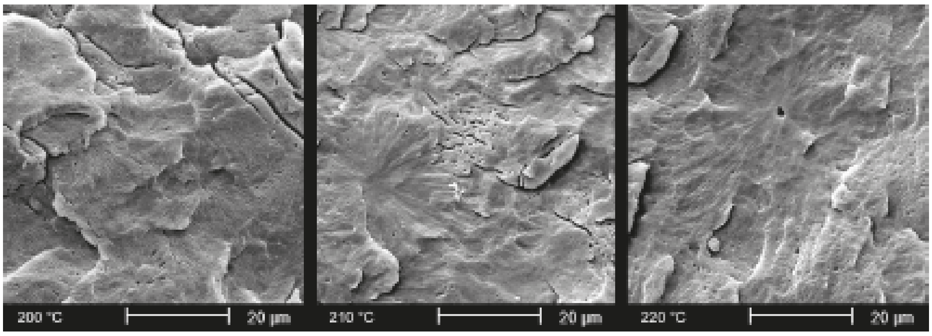

Figure 13. SEM images of PP with M_w 360 000 containing 0.01% NU100 processed under the conditions 2−4 (200, 210, and 220 °C, 20 min).

self-nuclei should be higher in high-M_w systems. Then, the content of the β-form in PP with low amount of β-nucleator should be sensitive to self α-nucleation and decrease with M_w. At this point, it is worth mentioning that some further effects could play an additional role, such as the presence of impurities arising from the catalyst residua or the effect of the length of crystallizing sequences on nucleation and growth rate. A successive study of overall crystallization kinetics would be helpful.

Conclusions

The experimental study has shown combined effects of a specific nucleation, processing parameters, and molecular weight on the resulting morphology of isotactic polypropylene. Samples encompassing a broad range of molecular weight (M_w from 240 000 to 1 300 000) allowed to describe for the first time the effect of molecular structure on nucleation efficiency. For the samples with low nucleator concentration of 0.01 wt % a dramatic decrease of nucleation activity with increasing M_w, and processing time and temperature were documented. This behavior was ascribed to the temperature-dependent solubility of the nucleator in PP melt and a competition between heterogeneous β-nucleation and self-nucleation. The results obtained within this study have important consequences for both polymer physics and plastics technology.

Acknowledgment. The authors kindly acknowledge the support provided by the Czech Science Foundation, GACR (project 106/07/P262), and the Ministry of Education, Youth and Sport of the Czech Republic (project MSM7088352101). Thanks also belong to Dr. Petr Vondráček for the material supplies, Mr. Asbjørn Iveland for his help in electron microscopy, and Dr. Christian Piel and IOS Linz for support in GPC measurements.

References and Notes

(1) Padden, F. J.; Keith, H. D. *J. Appl. Phys.* 1959, *30*, 1479–1484.
(2) Varga, J. *J. Macromol. Sci., Phys.* 2002, *41*, 1121–1171.
(3) Turner-Jones, A.; Aizlewood, J. M.; Beckett, D. R. *Macromol. Chem.* 1964, *75*, 134–154.
(4) Varga, J. In *Polypropylene: Structure, Blends and Composites*; Karger-Kocsis, J., Ed.; Chapman & Hall: London, 1995; Vol. *1*, p 56.
(5) Varga, J. *J. Mater. Sci.* 1992, *27*, 2557–2579.
(6) Lotz, B.; Wittmann, J. C.; Lovinger, A. J. *Polymer.* 1996, *37*, 4979–4992.
(7) Stocker, W.; Schumacher, M.; Graff, S.; Thierry, A.; Wittmann, J. C.; Lotz, B. *Macromolecules* 1998, *31*, 803–814.
(8) Karger-Kocsis, J.; Varga, J. *J. Appl. Polym. Sci.* 1996, *62*, 291–300.
(9) Tordjeman, P.; Robert, C.; Marin, G.; Gerard, P. *Eur. Phys. J. E* 2001, *4*, 459–465.
(10) Grein, C. *Adv. Polym. Sci.* 2005, *188*, 43–104.
(11) Seidler, S.; Koch, T. *J. Macromol. Sci., Part B: Phys.* 2002, *41*, 851–861.
(12) Raab, M.; Kotek, J.; Baldrian, J.; Grellmann, W. *J. Appl. Polym. Sci.* 1998, *69*, 2255–2259.
(13) Obadal, M.; Cermak, R.; Baran, N.; Stoklasa, K.; Simonik, J. *Int. Polym. Process.* 2004, *19*, 35–39.
(14) Kotek, J.; Kelnar, I.; Baldrian, J.; Raab, M. *Eur. Polym. J.* 2004, *40*, 679–684.
(15) Obadal, M.; Cermak, R.; Raab, M.; Verney, V.; Commereuc, S.; Fraisse, F. *Polym. Degrad. Stab.* 2005, *88*, 532–539.
(16) Obadal, M.; Cermak, R.; Raab, M.; Verney, V.; Commereuc, S.; Fraisse, F. *Polym. Degrad. Stab.* 2006, *91*, 459–463.
(17) Romankiewicz, A.; Sterzynski, T.; Brostow, W. *Polym. Int.* 2004, *53*, 2086–2091.
(18) Varga, J.; Menyhard, A. *Macromolecules* 2007, *40*, 2422–2431.
(19) Kotek, J.; Raab, M.; Baldrian, J.; Grellmann, W. *J. Appl. Polym. Sci.* 2002, *85*, 1174–1184.
(20) Cermak, R.; Obadal, M.; Ponizil, P.; Polaskova, M.; Stoklasa, K.; Lengalova, A. *Eur. Polym. J.* 2005, *41*, 1838–1845.
(21) Cermak, R.; Obadal, M.; Ponizil, P.; Polaskova, M.; Stoklasa, K.; Heckova, J. *Eur. Polym. J.* 2006, *42*, 2185–2191.
(22) Vychopnova, J.; Habrova, V.; Obadal, M.; Cermak, R.; Cabla, R. *J. Therm. Anal. Calorim.* 2006, *86*, 687–691.
(23) Vychopnova, J.; Cermak, R.; Obadal, M.; Raab, M.; Verney, V.; Commereuc, S. *Polym. Degrad. Stab.* 2007, *92*, 1763–1768.
(24) Varma-Nair, M.; Agarwal, P. K. *J. Therm. Anal. Calorim.* 2000, *59*, 483–495.
(25) Menyhard, A.; Varga, J.; Molnar, G. *J. Therm. Anal. Calorim.* 2006, *83*, 625–630.
(26) Nezbedova, E.; Pospisil, V.; Bohaty, P.; Vlach, B. *Macromol. Symp.* 2001, *170*, 349–357.
(27) Galeski, A. In *Polypropylene: An A−Z Reference*; Karger-Kocsis, J., Ed.; Kluwer Publishers: Dordrecht, 1999; pp 545−573.

PAPER II

“The final publication is available at www.wileyonlinelibrary.com“

Effect of Annealing Temperature on Phase Composition and Tensile Properties in Isotactic Poly(1-butene)

Lenka Chvátalová,[1] Lubomír Beníček,[1,2] Kristýna Berková,[1,2,3] Roman Čermák,[1,2] Martin Obadal,[4] Vincent Verney,[1,3,5] Sophie Commereuc[3,6]

[1]*Department of Polymer Engineering, Faculty of Technology, Tomas Bata University in Zlin, Nam. T. G. Masaryka 275, 762 72 Zlin, Czech Republic*
[2]*Centre of Polymer Systems, University Institute, Tomas Bata University in Zlin, Nad Ovcirnou 3685, 760 01 Zlin, Czech Republic*
[3]*Clermont Université, Université Blaise Pascal, LPMM, BP 10448, F-63000 Clermont-Ferrand, France*
[4]*Borealis Polyolefine GmbH, St.-Peter-Strasse 25, 4021 Linz, Austria*
[5]*CNRS, UMR 6505, LPMM, F-63177 Aubière Cedex, France*
[6]*Clermont Université, ENSCCF, LPMM, BP 10448, F-63000 Clermont-Ferrand, France*

Received 18 May 2011; accepted 26 July 2011
DOI 10.1002/app.35360
Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The influence of annealing temperature on the kinetics of polymorphic changes and mechanical properties within the time in isotactic poly(1-butene) (PB-1) has been investigated by wide-angle X-ray scattering and tensile testing. Extruded tapes of PB-1 have been exposed to several annealing temperatures: −22, +5, +22, +40 and +60°C. The evolution of content of Phase I for various annealing temperatures upon time shows predominantly S-shaped trend. Annealing temperature considerably affects the overall rate of transformation in PB-1. On the other hand, the resulting mechanical properties are solely controlled by the polymorphic composition. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2011

Key words: annealing; isotactic poly(1-butene); mechanical properties; phase transformation; wide-angle X-ray scattering

INTRODUCTION

Isotactic poly(1-butene) (PB-1) is one of the members of the polyolefin family which exhibits advantages over the other polymers. From the application point of view the outstanding resistance to creep is of crucial importance. PB-1 is polymorphic material occurring in five crystallographic modifications. The modifications I, I′ and II, II′ can be prepared by the crystallization from the melt while the modification III is formed during solution crystallization.[1–6]

Phase transformation is the most important phenomenon—upon solidification from the melt PB-1 crystallizes into phase II which is kinetically favored. The structure in this state is loosely packed and the resulting density (0.907 g/cm^3) is only slightly higher than in the case of amorphous region (0.868 g/cm^3).[7] The resulting material is rather ductile and mechanically weak. However, this phase is metastable and transforms slowly into a denser (0.950 g/cm^3) and more stable phase I, which is thermodynamically favored.[5,8] As a result of this transformation PB-1 become to be a stiff material and satisfies application properties.[9–11]

The kinetics of this phase transformation is known to be influenced by pressure,[12] mechanical loading,[13] temperature,[14] and addition of comonomers in the structure.[15–17] Nakafuku and Miyaki[12] reported that crystallization of PB-1 melt under high pressure produces stable phase I′, which shows the same X-ray diffraction pattern as phase I but has much lower melting temperature (96 vs. 130°C) at atmospheric pressure. Above 200 MPa, phase I′ and phase II′ are crystallized from the melt. Phase II′ shows the same X-ray diffraction pattern as phase II, but lower melting temperature than phase II. Phase II′ is metastable at atmospheric pressure and transforms to phase I′ on standing at room temperature.[14] Fujiwara[18] investigated the transformation of oriented phase II specimens and found that the "untwinned" phase I′ appears by applying shear stress; the orientation of phase I changed according to the relative direction of the stress.

Correspondence to: L. Beníček (benicek@ft.utb.cz).

Contract grant sponsor: Operational Programme Research and Development for Innovations; European Regional Development Fund (ERDF); Czech Republic; Framework of the Centre of Polymer Systems project (reg. number: CZ.1.05/2.1.00/03.0111).

Contract grant sponsor: Ministry of Education, Youth and Sport of the Czech Republic; contract grant number: MSM7088352101.

Journal of Applied Polymer Science, Vol. 000, 000–000 (2011)
© 2011 Wiley Periodicals, Inc.

Nevertheless, significant delay in commercialization of PB-1 is caused by two principal reasons:

(i) The kinetics of phase transformation is slow and temperature sensitive. At room temperature, the total transformation from phase II to I is finished within a week. However, shifting of annealing temperature in both directions leads to even slower transformation rate.[5]

(ii) The answer to the question how the transformation in supermolecular structure is reflected by the changes in macroscopic properties is industrially crucial but still missing.

Present article brings evidence and explains the effect of annealing temperature on kinetics of both phase transformation and evolution of mechanical properties in PB-1 parts. In our best knowledge, the interrelations between the changes of supermolecular structure and macroscopic tensile properties of PB-1 are jointly discussed for the first time here. Extruded tapes of PB-1 have been exposed to several annealing temperatures. The evaluation of changes in supermolecular structure and mechanical properties within the time has been performed by wide-angle X-ray scattering (WAXS) and tensile testing.

EXPERIMENTAL PART

Material

Isotactic PB-1 PB 0300M produced by LyondellBasell, Louvain la Neuve, Belgium was used. According to producer information, PB 0300M is a semicrystalline homopolymer with balanced resistance to creep and environmental stress crack and performance at elevated temperature. The basic properties are following: density 0.915 g/cm^3—ISO 1183, melt flow index 4 g/10 min—ISO 1133 (190°C/2.16 kg).

Extrusion

The material was extruded using a Brabender Plasti-Corder PLE 651 single-screw extruder, the processing conditions were following: compression ratio of the screw 1 : 4; screw speed 20 rpm; barrel temperatures 135, 140, 145, 150°C; extrusion slit die with profile 2 × 20 mm^2 with temperature 150°C. The processed tapes were cut off to the pieces with length 140 mm.

Annealing

The prepared specimens were immediately after processing annealed at free stress state at various temperatures: −22, +5, +22, +40, and +60°C at atmospheric pressure. The temperatures were chosen with respect to utilization of PB-1, which can be used for tanks, hose, tubing, molded parts, films, etc. at various temperatures. Heating and cooling chambers with precisely controlled temperature were employed for annealing. Upon given annealing time within interval 0–64 days the specimens were immediately subjected to analysis of structure and properties.

Wide-angle X-ray scattering

A URD6 diffractometer Cu$K\alpha$ radiation monochromatized with a Ni filter (λ = 0.154 nm) was employed for evaluation of phase transformation. Measurements were performed in transmission mode, diffraction angle interval 2θ = 7°–25°, step of 0.05° and holding time of 5 s were used.

Tetragonal phase II of PB-1 gives the reflections at 11.9°, 16.9°, and 18.4° 2θ, corresponding to the (200), (220), and (301) planes. On the other hand, hexagonal phase I is characterized by four diffraction peaks at 9.9°, 17.3°, 20.2°, and 20.5° 2θ, originated by the (110), (300), (220), and (211) planes.[19] Phase transformation is unambiguously demonstrated by the changes of reflection intensities at 9.9° 2θ (110, phase I) and 11.9° 2θ (200, phase II). Therefore, the extent of phase transformation can be calculated.[20–23]

$$T_I = I_I/(I_I + I_{II}) \tag{1}$$

where T_I is content of phase I and I_I and I_{II} are intensities of the reflections at 9.9° and 11.9° 2θ. The intensities of the reflection peaks have been obtained by the integration of peak areas after the subtraction of amorphous halo.

Tensile testing

A Zwick 145665 multipurpose tester was used for the tensile testing of extruded tapes with a gauge length of 80 mm. The specimens were strained at room temperature up to break at a test speed of 100 mm/min. From the stress–strain traces, strength at break and elongation at break were derived. Besides, the elastic modulus was evaluated using a Zwick external extensometer (gauge length of 20 mm) at a test speed of 1 mm/min. Five specimens were tested and average values are reported.

RESULTS AND DISCUSSION

The evolution of polymorphic structure in PB-1 specimens exposed to −22, +5, +22, +40, and +60°C has been characterized by WAXS as can be seen in Figure 1. The crystallinity in all the samples was 85% and does not significantly vary upon annealing which is in agreement with study of Azzurri et al.[24]

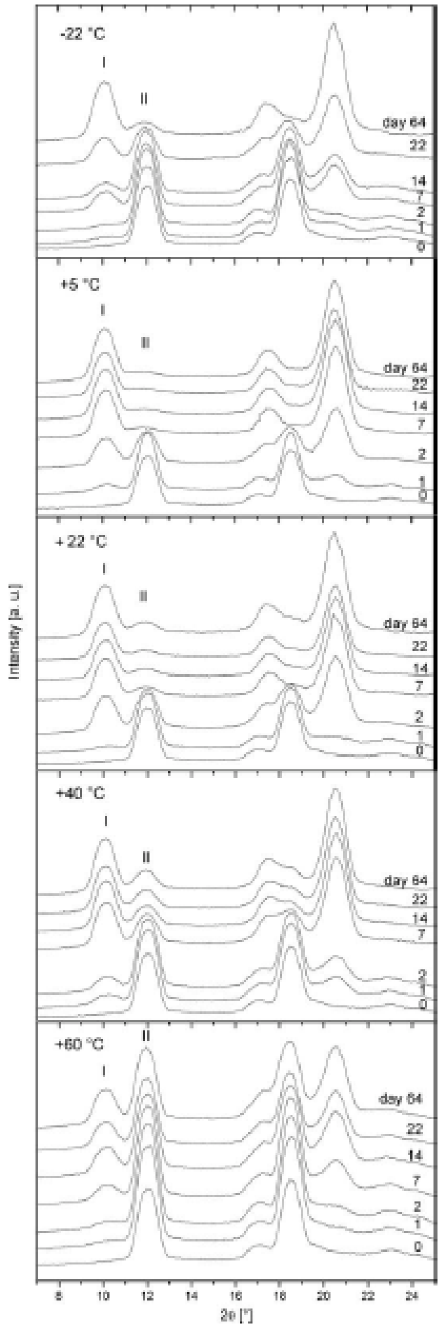

Figure 1 WAXS patterns for various annealing temperatures upon time.

Similarly, no broad changes of orientation were observed and the samples kept the shape during annealing.

Phase transformation is followed by the changes in intensities of individual reflection peaks. The content of phase I has been evaluated in accordance with eq. (1) and the data are represented in Figure 2 (up) as a function of time. As can be seen, annealing temperature has significant effect on the transformation rate. On the basis of previous studies, the crystal–crystal transformation in PB-1 is a process consisting of two common steps, nucleation and growth.[10,25,26] Many studies[10,18,25–28] agreed that the nucleation controls the overall transformation rate, in particular. As a consequence, the dependence of content of phase I on annealing (i.e., transformation) time shows typical S-shaped curve. In Figure 2, the evolution of content of phase I follows S-shaped trend in the cases of annealing temperatures of −22, +5, +22, and +40°C. The transformation rate decreases in following order of annealing temperatures: +5, +22, +40, and −22°C. This sensitivity of transformation kinetics to temperature is in agreement with previous studies.[5,25] However, at temperature of +60°C the content of phase I is virtually linear-dependent within observed annealing time. At the same time, it should be noted that the observed transformation reached only low values, therefore one can expect following S-shaped evolution upon prolonged time.

Although, the transformation of phase II to I has been extensively studied and explained, its impact on final properties of PB-1 has not been fully described. Present study gives in direct relation the

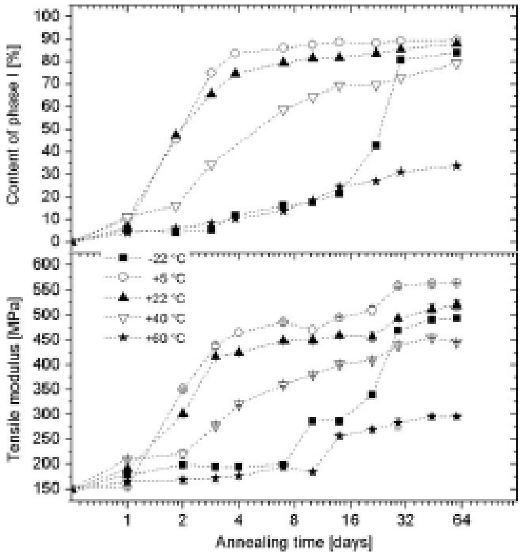

Figure 2 Evolution of the phase I content (up) and tensile modulus (down) for various annealing temperatures upon time.

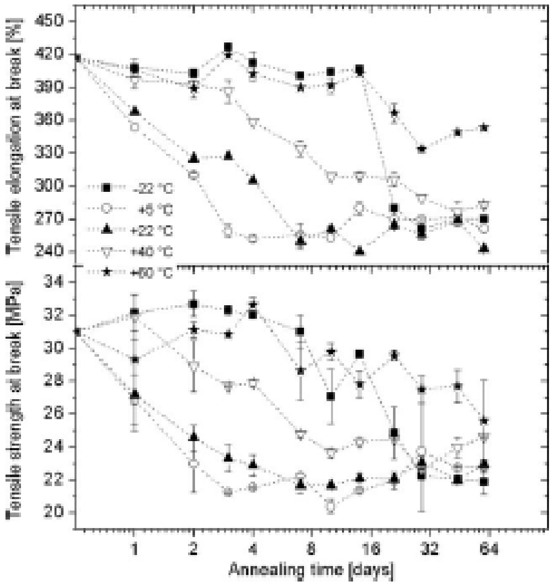

Figure 3 Evolution of tensile elongation at break (up) and strength at break (down) for various annealing temperatures upon time.

content of phase I and tensile properties. The evolution of tensile modulus at given annealing temperatures is illustrated in Figure 2 (down). Similarly to the content of phase I, tensile modulus is a growing function of annealing time. This significant improvement of stiffness reflects the changes in thermodynamic stability of the material arising from phase transformation. Figure 3 shows elongation and strength at break in tensile mode as a function of annealing time. On the contrary to the tensile modulus, the values of elongation and strength at break decrease upon annealing. Indeed, the increasing thermodynamic stability of the material upon phase transformation leads to limitation of plastic rearrangement as a response to mechanical loading. Consequently, the material with prevailing phase I cannot be dramatically oriented by cold drawing and the values of both elongation and strength at break are lower compared to ductile material full of phase II.

From comparison of Figures 2 and 3, one can suggest that the mechanical properties of PB-1 are directly controlled by the polymorphic composition. Even by naked eye, a similar trend in evolution of content of phase I and tensile modulus can be seen. However, this simple comparison cannot be applied for the strength and elongation at break. Therefore, the normalization of values of observed characteristics was performed. For normalization of increasing functions (content of phase I and tensile modulus) following equation was given:

$$X_{\mathrm{norm}} = \frac{X - X_{\mathrm{min}}}{X_{\mathrm{max}} - X_{\mathrm{min}}} \tag{2}$$

and for decreasing functions (tensile elongation and strength at break):

$$X_{\mathrm{norm}} = \frac{X_{\mathrm{max}} - X}{X_{\mathrm{max}} - X_{\mathrm{min}}} \tag{3}$$

where X_{norm} is a normalized property, X is a value at given time, X_{min} is a minimal value, and X_{max} is a maximal value of property. In Table I, X_{min} and X_{max} for given characteristics are summarized. Figure 4 shows the evolution of normalized phase I content and mechanical properties of specimens annealed at various temperatures upon time. It can be clearly seen that the normalized curves of the phase I content fairly fit with those of tensile modulus, elongation and strength at break. This comparison proves that the direct interrelation between the phase composition and mechanical properties exists.

As a consequence of the demonstrated direct sensitivity of mechanical properties to phase composition of PB-1, the measured data were statistically analyzed to describe the transformation phenomenon numerically. Figure 5 displays tensile modulus, elongation and strength at break as a function of content of phase I. It is evident that the mechanical properties are linear-dependent on phase composition, as was proved by linear regression; in all the cases, the

TABLE I
Parameters of PB-1 Samples

T (°C)	WI_{max} (%)	WI_{min} (%)	E_{max} (MPa)	E_{min} (MPa)	$\varepsilon_{\mathrm{max}}$ (%)	$\varepsilon_{\mathrm{min}}$ (%)	σ_{max} (MPa)	σ_{min} (MPa)
−22	84.0	0	493	150	427	261	32.7	21.9
+5	89.5	0	564	150	417	252	31.0	20.4
+22	88.0	0	520	150	417	241	31.0	21.7
+40	79.2	0	445	150	417	283	31.9	22.6
+60	34.0	0	295	150	420	334	32.7	25.6

T, annealing temperature; WI_{max}, maximal content of phase I; WI_{min}; minimal content of phase I; E_{max}, maximal tensile modulus; E_{min}, minimal tensile modulus; $\varepsilon_{\mathrm{max}}$, maximal elongation at break; $\varepsilon_{\mathrm{min}}$, minimal elongation at break; σ_{max}, maximal strength at break; σ_{min}, minimal strength at break.

correlation coefficient is higher than 0.80, moreover for tensile modulus it is even higher than 0.97. Generally, lower coefficient of tensile strength and elongation at break can be expected because the values refer to the structure arising from a broad inhomogeneous rearrangement of original morphology during the tensile testing.

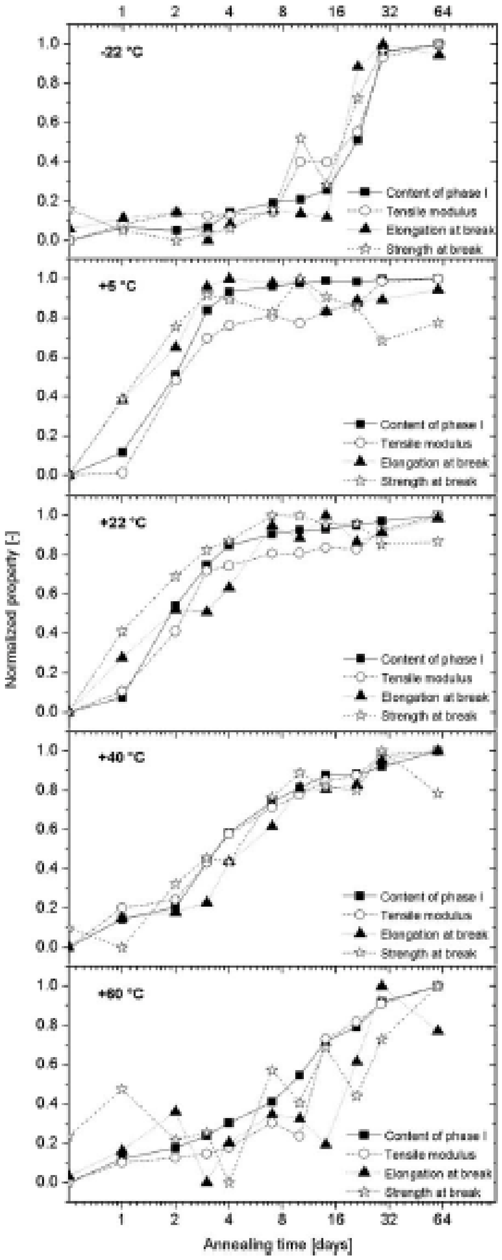

Figure 4 Evolution of normalized properties for various annealing temperatures upon time.

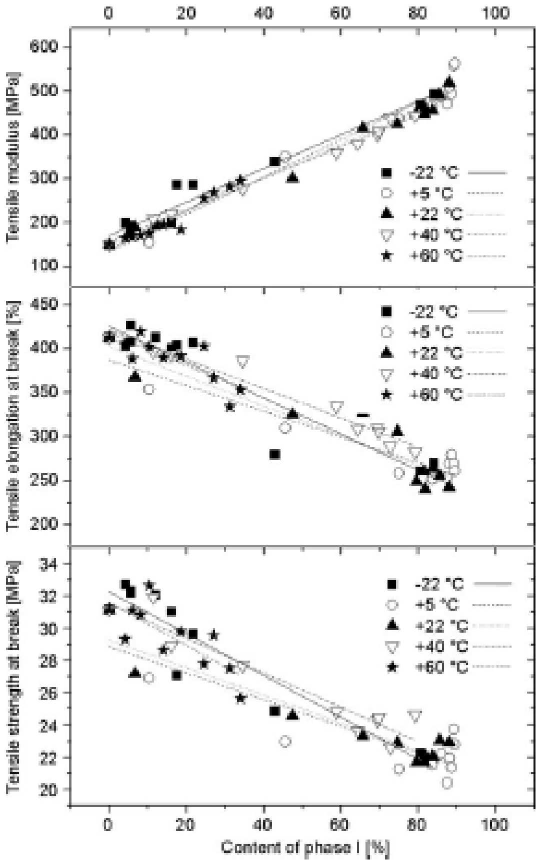

Figure 5 Dependence of tensile properties on content of phase I.

It is interesting to compare linear fits of mechanical properties as a function of phase I content for various annealing temperatures. In this context, the differences between the slopes of individual linear fits of the data at given temperatures were analyzed by the *T*-test. It was found that no significant variability between the slopes can be observed at a significance level of 0.05. This result leads to particularly important conclusions: (i) The kinetics of phase transformation performed at various annealing temperatures was proved to be insignificant for the tensile properties, therefore, (ii) the unique parameter which controls the mechanical properties is the phase composition of PB-1.

CONCLUSION

The experimental study has shown that the annealing temperature has significant effect on the kinetics of phase transformation in PB-1. Generally, the evolution of content of phase I upon annealing at a given temperature follows S-shaped trend reflecting complex process of both the nucleation and growth. It was clearly demonstrated that the mechanical properties are directly controlled by the polymorphic composition; normalized curves of tensile modulus, elongation and strength at break as a function of annealing time fairly fit with that of content of phase I. From practical point of view it is important to highlight that the annealing temperature affects the overall rate of polymorphic changes in processed PB-1 but the resulting properties are controlled solely by the extent of this transformation.

References

1. Natta, G.; Corradini, P.; Bassi, I. W. Nuovo Cimento Supp 1962, 1, 52.
2. Boor, J., Jr.; Youngman, E. A. J Polym Sci 1964, B2, 903.
3. Holland, V. F.; Miller, R. L. J Appl Phys 1964, 35, 3241.
4. Brydson, J. A. Plastics materials, 7th ed.; Butterworth-Heinemann Linacre House: Oxford, 1999.
5. Kaszonyiová, M.; Rybnikář, F.; Geil, P. H. J Macromol Sci Phys 2004, 43, 1095.
6. Luciani, L.; Sepala, J.; Lofgren, B. Prog Polym Sci 1988, 13, 37.
7. Aronne, A.; Napolitano, A. R.; Pirozzi, B. Eur Polym J 1986, 9, 703.
8. Rubin, I. D. J Polym Sci 1964, B2, 747.
9. Marigo, A.; Marega, C.; Cecchin, G.; Collina, G.; Ferrara, G. Eur Polym J 2000, 36, 131.
10. Kopp, S.; Wittmann, J. C.; Lotz, B. Polymer 1994, 35, 908.
11. Oda, T.; Maeda, M.; Hibi, S.; Watanabe, S. Koubunshi Ronbunshu 1974, 31, 129.
12. Nakafuku, C.; Miyaki, T. Polymer 1983, 24, 141.
13. Goldbach, G. A. Macromol Chem 1974, 39, 175.
14. Kalay, G.; Kalay, C. R. J Polym Sci Part B: Polym Phys 2002, 40, 1828.
15. Hong, K.; Spruiell, J. E. J Appl Polym Sci 1985, 30, 3163.
16. Alfonso, G. C.; Azzurri, F.; Castellano, M. J Therm Anal Calorim 2001, 66, 197.
17. Causin, V.; Marega, M.; Marigo, A.; Ferrara, G.; Idiyatullina, G.; Mantinel, F. Polymer 2006, 47, 4773.
18. Fujiwara, Y. Polym Bull 1985, 13, 253.
19. Lauritzen, J. I., Jr.; Hoffman, J. D. J Appl Phys 1973, 44, 4340.
20. Azzurri, F.; Alfonso, G. C.; Gómez, M. A.; Marti, M. C.; Ellis, G.; Marco, C. Macromolecules 2004, 37, 3755.
21. Samon, J. M.; Schultz, J. M.; Hsiao, B. S.; Wu, J.; Khot, S. J Polym Sci Part B: Polym Phys 2000, 38, 1872.
22. Natta, G.; Corradini, P.; Bassi, I. Nuovo Cimento Suppl 1960, 15, 52.
23. Avrami, M. J Chem Phys 1940, 8, 212.
24. Azzuri, F.; Flores, A.; Alfonso, G. C.; Calleja, F. J. B. Macromolecules 2002, 35, 9069.
25. Maruyama, M.; Sakamoto, Y.; Mozaki, K.; Yamamoto, T.; Kajioka, H.; Toda, A.; Yamada, K. Polymer 2010, 51, 5532.
26. Kopp, S.; Wittmann, J. C.; Lotz, B. J Mater Sci 1994, 29, 6159.
27. Gohil, R. M.; Miles, M. J.; Petermann, J. J Macromol Sci Phys 1982, B21, 189.
28. Chau, K. W.; Yang, Y. C.; Geil, P. H. J Mater Sci 1986, 21, 3002.

PAPER III

Status: Submitted

The Effect of Plasma Treatment on Structure and Properties of Poly(1-butene) Surface

Lenka CHVÁTALOVÁ[a], Roman ČERMÁK[a,b], Aleš MRÁČEK[b,c,*], Ondřej GRULICH[c], Alenka VESEL[d], Petr PONÍŽIL[b,c], Antonín MINAŘÍK[b,c], Uroš CVELBAR[d], Lubomír BENÍČEK[a,b]

[a]*Tomas Bata University in Zlín, Faculty of Technology, Department of Polymer Engineering, nám. T.G.Masaryka 5555, 760 01 Zlín, Czech Republic*

[b]*Centre of Polymer Systems, Polymer Centre, Tomas Bata University in Zlín, nám. T.G.Masaryka 5555, 760 01 Zlín, Czech Republic*

[c]*Tomas Bata University in Zlín, Faculty of Technology, Department of Physics and Material Engineering, nám. T.G.Masaryka 5555, 760 01 Zlín, Czech Republic*

[d]*Jozef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia*

ACKNOWLEDGMENT

The paper was supported by the Operational Programme Research and Development for Innovations co-funded by the European Regional Development Fund (ERDF) and national budget of Czech Republic within the framework of the Centre of Polymer Systems project (reg. number: CZ.1.05/2.1.00/03.0111). The authors kindly acknowledge the support provided by the Czech Science Foundation, GAČR (project 104/09/H080) and the Ministry of Education, Youth and Sport of the Czech Republic (project MSM7088352101). Ondřej Grulich research was also supported by grant of TBU No. IGA/13/FT/11/D funded from the resources of specific university research. Thanks also belong to Mr. Miroslav Janíček for his help with graphics.

ABSTRACT

This paper is focused on the chemical and morphology changes in the surface of poly(1-butene) (PB-1) generated by plasma treatment. The radio frequency capacitively coupled plasma (air, argon, argon then allylamine, argon containing ammonia and argon with octafluorocyclobutane) was used. Modified surface of PB-1 was characterized by contact angle measurements, X-ray photoelectron spectroscopy, and atomic force microscopy. The surface hydrophilisation by air and argon with ammonia plasmas was evaluated as most sufficient. Oppositely, a high level of hydrophobicity of PB-1 surface was reached by combination of argon with octafluorocyclobutane plasma. Upon plasma modification, hydrophilicity/hydrophobicity of treated surfaces remained stable within three days under air atmosphere and then values of contact angle slowly recovered to those of unmodified PB-1. However, morphology and surface chemical composition of plasma-modified samples remained generally unchanged during observed time. Changes in surface hydrophilicity/hydrophobicity of plasma-treated PB-1 were attributed to variance of conformation of the surface molecules.

KEYWORDS

isotactic poly(1-butene), plasma treatment, surface modification

INTRODUCTION

Isotactic poly(1-butene) (PB-1) is one of the semi-crystalline polymers which exhibits pronounced polymorphism and morphologies depending on thermal treatment and mechanical handling. Five different crystalline modifications designed as I, II, III, I′ and II′, have been reported.[1–4] PB-1 upon solidification from the melt crystallizes into tetragonal phase II however this phase is metastable and transforms slowly into more stable trigonal phase I.[1] Resulting polymer is stiff with satisfying properties.

Poly(1-butene) has numerous applications in many fields of industry because of its outstanding resistance to creep, good mechanical properties, chemical resistivity, easy processing, low manufacturing costs and easy recycling.[5–9] On the other hand, this polymer is known as non-polar, hydrophobic material with a low surface energy, poor adhesion and wettability, resulting in significant problems when surface coating, printing or sticking is applied. Therefore many applications of these polyolefins require improvement of their surface and adhesive properties. In this context a lot of methods have been devised and commercially used to modify the surface. Among them plasma treatment is a very effective way to enhance the hydrophilicity of polymer surface without affecting its intrinsic bulk properties including mechanical properties since only outermost atomic layers are modified.[10] Plasma can interact with the polymers through the formation of cross-linkages between adjacent polymer chains or by chain scission.[11] The improvement of surface hydrophilicity is induced by formation of new oxygen containing groups on the surface, such as carbonyl, carboxyl or hydroxyl.[12–14] On the contrary, some applications of these polymers, e.g., diffusion barrier or corrosion protection, required hydrophobic character of polymer surface. For these purposes fluorocarbon plasmas is an efficient tool to increase contact angle and improve hydrophobicity. [15–17]

Plasma processing of polymers is a common procedure. Many studies have been focused on the plasma treatment of poly(propylene),[18] poly(ethylene), poly(methyl methacrylate),[19] poly(ethylene terephthalate),[20] poly(carbonate), poly(styrene),[21] viscose textile,[22] poly(tetrafluoroethylene),[23] poly(p-phenylene sulphide),[24] poly(ether sulfone)[25] and poly(dimethylsiloxane)[26]. Nevertheless, the published studies dealing with plasma-modified poly(1-butene) are very scarce, Shen et al. used radio frequency plasma polymerization to treat glass fibres to improve the interfacial adhesion between poly(1-butene) and glass fibre.[27]

Present paper reports experimental results concerning poly(1-butene) surface properties modified by plasma treatment. Main attention has been directed to the factors that critically influence surface wettability of polymers: (i) chemical composition analyzed by X-ray photoelectron spectroscopy (XPS); (ii) morphology and roughness observed by atomic force microscopy (AFM), and (iii) molecular structure at the polymer surface, with emphasis on conformation and orientation of functional groups, and chemical bonding.[28–32] Knowledge of the local conformation of the functional groups at the surface is extremely important for understanding the surface properties of polymers. The surface hydrophilicity/hydrophobicity was characterized by contact angle (CA) – “sessile drop” method. The interrelations between these factors and surface wettability have been investigated. To improve the surface properties to the best advantage and simultaneously minimize ageing effects it is necessary adjust the gas composition and the plasma conditions to the polymer type. For this purpose plasma containing five various gasses has been chosen.

EXPERIMENTAL SECTION

Materials

In this study, two commercially-available grades of isotactic poly(1-butene) produced by LyondellBasell Louvain la Neuve, Belgium, were used, a homopolymer PB 0300M (homoPB), characterized by melt flow index of 4 g/10 min (190 °C/2.16 kg) and density of 0.915 $g.cm^{-3}$, and a random copolymer of butene-1 with low ethylene content, PB 8640M (coPB) with melt flow index 1 g/10 min and density 0.906 $g.cm^{-3}$.

PB-1 sheets, approx. 1 mm thick, were prepared by compression molding. Prior to any treatment, rectangular samples with dimension of 80 × 10 mm were cut out, washed in acetone, ethanol, distilled water and then dried at temperature of 40 °C for 20 min. The blank and treated samples were stored in desiccator (with gelatinous silicic acid for standard humidity) under pressure 20 Pa.

Methods

Plasma treatment was performed by reactor FEMTO, Diener, Germany, with capacitively coupled plasma. The reactor chamber was a cylinder of 320 mm length and 150 mm diameter. The processing conditions were selected: radio frequency 13.56 MHz, the generator power 50 W, gas flow 5 $cm^3.min^{-1}$, processing pressure 30Pa, and time of plasma treatment 60 s. The following processing gasses were used: air, argon (Ar), argon and thereafter 3 hours in allylamine vapor ($Ar/C_3H_5NH_2$), argon bubbled through ammonia (Ar/NH_4) and mixture of 50 % argon and 50 % octafluorocyclobutane (Ar/C_4F_8).

The contact angle measurement was performed on Surface Energy Evaluation System, Advex Instruments, Czech Republic, at room temperature to evaluate the hydrophilicity/hydrophobicity of the samples. A "sessile drop" technique was used in this study. Water after reverse osmosis was utilized in all experiments. The drop volume was 4 µl. Ten separated readings of contact angle were averaged to obtain one representative value for each substrate and standard deviations were evaluated. Contact angle of pure PB-1 and plasma-treated PB-1 at various time (from 10 min to 14 days) after plasma treatment were measured.

Surface composition was analyzed with an XPS instrument TFA XPS Physical Electronics, USA. The base pressure in the chamber was about 6×10^{-8} Pa. The samples were excited with X-rays over a 400 µm spot area with a monochromatic Al $K_{\alpha 1,2}$ radiation at 1486.6 eV. The photoelectrons were detected with a hemispherical analyzer positioned at an angle of 45° with respect to the normal to the sample surface. Survey-scan spectra were made at a pass energy of 187.85 eV and an energy step of 0.4 eV, while for O1s, N1s, F1s individual high-resolution spectra were taken at a pass energy of 23.5 eV and an energy step of 0.1 eV and for C1s at 11.75 eV and 0.05 eV energy step, respectively. An electron gun was used for surface neutralization. All spectra (not containing F) were referenced to the main C1s peak of the carbon atoms which was assigned a value of 284.8 eV. The spectra containing F were shifted to 291.8 eV (CF_2 binding of carbon atom). The concentration of elements and concentration of the different chemical states of carbon atoms in the C1s peak were determined by using MultiPak v7.3.1 software from Physical Electronics. Carbon C1s peaks were fitted with symmetrical Gauss-Lorentz functions. A Shirley-type background subtraction was used. To evaluate durability of surface composition the XPS analysis were carried out immediately and 14 days after plasma treatment.

The surface topography of untreated and plasma-modified PB-1 samples was studied on a nanometer scale using atomic force microscopy. The AFM images were recorded by NTEGRA-Prima, NT-MDT, Russia. A single crystal silicon probe with force constant of 11,8 N/m and scanning rate of 0.3 Hz was used. Identical area of 50 × 50 μm was scanned at the sample before and after plasma treatment.

RESULTS AND DISCUSSION

The extent of hydrophilic/hydrophobic modification of the plasma-treated PB-1 sheets was investigated by CA measurement. Figure 1 shows the variation in the CA of pure and plasma-modified homoPB (up) and coPB (down) specimens. The values of contact angle of untreated homoPB and coPB sheet reach 99° and 104°, respectively. PB-1 and other polyolefins are strongly hydrophobic due to the lack of polar function groups on their polymer chains.[33] However, plasma treatment causes change of surface properties. In most cases, except of Ar/C_4F_8 plasma, decrease of CA can be seen. The most obvious decrease of CA was observed in the case of the sample homoPB after air plasma treatment (65°) and homoPB after Ar/NH_4 plasma (67°). On the other hand, the minimum decrease of CA was achieved in the samples treated by Ar/$C_3H_5NH_2$ plasma (homoPB ~ 86° and coPB ~ 84°). This decrease of CA can be ascribed to the formation of hydrophilic groups on the plasma-treated polymer film surfaces. The plasma creates radical species on the polymer surface, mainly through polymer chain scission or hydrogen abstraction by bombardment of plasma particles. These species can combine with oxygen from air, and thus also contribute to increase of the amount of polar groups such as –OH, C=O, COOH and COO– on the plasma-treated polymer surfaces. Hence these polar groups cause that the plasma-treated polymer surfaces become more hydrophilic compared to the untreated polymer surface.[34,35] As can be seen, the drop of contact angles in homoPB are rather comparable to that of coPB. However, situation is absolutely different in the case of Ar/C_4F_8 plasma where increase of CA was observed (homoPB ~ 111° and coPB ~ 113°) reflecting pronounced surface hydrophobicity.

Upon plasma modification, hydrophilicity/hydrophobicity of treated surfaces remained stable within three days under air atmosphere. Nevertheless, with prolonged time slow increase of CA can be observed. This process of hydrophobic recovery of the plasma-treated PB-1 samples results from the tendency to reduce surface energy and increase its contact angle to be more resemble to the intrinsic bulk of polymer. From thermodynamic point of view, the polar functional groups tend to rearrange toward bulk reaching homogeneous distribution within outer layer of polymer surface.[24,28-32] Moreover, variations of both chemical composition and morphology in surface may contribute to the partial recovery of contact angle.

Surface chemical composition of neat and plasma-treated PB-1 samples was characterized by XPS measurements. Figure 2 (up) shows the concentration of atoms in surface of untreated materials and plasma modified samples directly upon treatment. Neat homoPB and coPB samples (measured immediately – Fig 2 up and 14 days after plasma treatment – Fig 2 down) contain predominantly carbon (approximately 99.0 %, resp. 99.1 %) and insignificant amount (under 0.95%) of oxygen and nitrogen was similar for all untreated materials. As can be seen, plasma-treated samples (except of those modified by Ar/C_4F_8 plasma) have generally similar surface composition: nitrogen concentration up to 8 at.% and oxygen concentration up to 15 at.%. Since nitrogen and oxygen are found already on untreated samples, it can be concluded that insignificant amount of nitrogen is incorporated into the surface during treatment in Ar/$C_3H_5NH_2$ or Ar/NH_4. Chemical composition is considerable different in the case of the Ar/C_4F_8 treated samples where 57–61 at.% of F was detected at the surface. Furthermore, higher content of nitrogen on the surface up to 6 at.% and neglectable concentration of oxygen – less than 1 at.% can be found. XPS measurements were repeated again 14 days after plasma treatment (Figure 2, down) to assess the effect of ageing process (post-reactions) on the surface atom composition of homoPB and coPB samples. From comparison of Figure 2 up and down it can be clearly seen that the differences of chemical composition of plasma treated surfaces measured immediately and 14 days after plasma treatment are insignificant. Therefore, hydrophobic recovery of contact angle in plasma-modified samples cannot be ascribed to the time-dependent changes of surface integral chemical composition.

A more detailed analysis of the XPS spectra of the carbon C1s region of the untreated homoPB and coPB samples revealed the formation of different functional groups (Figure 3). Prevailing component of the C1s peak located approx. at 284.8 eV indicates the existence of hydrocarbon components (C–C and/or C–H bonds)[35]. A weak shoulder is consistent with the levels of oxygen and carbon detected in the survey scans and was fitted with two peaks corresponding to carbon singly bonded to oxygen and to nitrogen (C–O/C–N)[36,37] at approx. 285.9 eV, and to carbon doubly bonded to oxygen (C=O)[38] at approx. 288.0 eV. In some components, like C–O and C–N, the binding energies of the C1s peak are very close, making it almost impossible to identify unambiguously the component.

As expected, according to the surface composition shown in Figure 2, carbon peaks of homoPB and coPB samples treated by air, Ar, Ar/$C_3H_5NH_2$ and Ar/NH_4 plasma looks quite similar indicating that there are only small differences between the samples. Figure 4 shows XPS spectra of the carbon C1s region of the homoPB sample 14 days after Ar/NH_4 plasma treatment. The majority of carbon atoms can be found in C–C bonds (binding energy 284.6 eV) and minority in C–O/C–N bonds (286.5/286.3 eV), C=O bonds (287.9 eV) and O=C–O bonds (289.2 eV)[37]. Similar spectra have been also observed for the other treated samples. The C1s peaks of all surface-treated samples show significantly stronger contributions at the higher binding energy side of the C–C peak, arising from the creation of oxygen-containing functional groups at the surface.

Curve fitting of carbon C1s peaks of homoPB and coPB samples 14 days after Ar/C_4F_8 plasma treatment are shown in Figure 5. Very broad spectrum indicates formation of various different carbon–fluorine bonds at the higher binding energies. The majority of carbon atoms can be attributed to CF_3 and CF_2 bonds located at approx. 293.8 and 291.8 eV[39] and minority to C–C/H bonds (285.1 eV). In the case of coPB results apparent increase of CF and CF_2 bonds at the expense of C–C/H bonds can be observed.

To evaluate the extent of morphological changes on the surface, AFM images of untreated and plasma-modified homoPB samples have been reproduced. It has been reported that influences of surface roughening on contact angles disappear if the surface roughness is smaller than 0.1 μm.[40–44] According Busscher,[40] surface roughening tends to increase observed contact angles, if the contact angle on the smooth surface is above 86°, whereas contact angles decrease if the contact angle on the smooth surface is below 60°. For contact angles on the smooth surface between 60° and 86°, surface roughening was found not to influence measured contact angles. Figure 6 depicts the representative images of samples before and after air and fluorocarbon plasma treatment. Figure 7 shows histograms of the brightness distribution of roughness height of homoPB samples before and after air plasma treatment (up) and before and after fluorocarbon plasma treatment (down). It can be seen that the differences in morphology and roughness of surfaces before and after plasma treatment are neglectable independently on plasma modification.

As mentioned above, surface hydrophilicity/hydrophobicity can be affected by chemical composition, surface roughness and variance in conformation of functional groups. Our observations suggest that the time-dependent changes in surface wettability of plasma-treated PB-1 samples cannot be attributed to the variation of surface morphology and surface chemical composition. Therefore changes in conformation of the surface molecules should play a main role. Mechanism of conformation changes is depicted in Figure 8. Untreated PB-1 consists predominantly of carbon and hydrogen which results in non-polar structure. This polymer is hydrophobic with a high values of CA (Figure 8, up). However, plasma treatment induces formation of polar functional groups which are preferentially ordered on the tips of the surface. During contact with water droplet, presence of these polar groups causes increase of hydrophilicity and thereby decreases contact angle (Figure 8, middle). However, the introduced polar functional groups tend to equilibrium positions via conformation and orientation gradual changes. Thus the concentration of functional groups on the interfacial area is reduced which is followed by the increase of CA (Figure 8, down).

CONCLUSIONS

The experimental study has been focused on modification of the poly(1-butene) surface using radio frequency plasma. The influence of various processing gasses was investigated. Plasma treatment greatly changed the surface chemistry. The polar functional groups generated upon almost all used types of plasma treatment caused decrease in contact angle and increase of surface hydrophilicity. Contradictory effect can be observed in the case of fluorocarbon plasma which causes increase of contact angle and increase of hydrophobicity. In all the samples, the recovery of contact angle, i.e. wettability, to the initial values was observed upon a given time. Surface morphology and chemical composition of plasma-treated samples samples remain nearly unchanged within observed period. Therefore, the gradual changes in surface hydrophilicity/hydrophobicity of plasma-treated PB-1 samples can be attributed to the variation of the conformation of plasma-introduced functional groups.

REFERENCES

(1) Natta, G.; Corradini, P.; Bassi, I. W.; Nuovo Cimento Suppl. 1960, 1, 52–67.

(2) Nakafuku, C.; Miyaki, T. Polymer 1983, 24, 141–148.

(3) Holland, V. F.; Miller, R. L. J. Appl. Phys. 1964, 35, 3241–3248.

(4) Hong, W.; Spruiell, J. E. J. Appl. Polym. Sci. 1985, 30, 3163–3188.

(5) Tosaka, M.; Kamijo, T.; Tsuji, M.; Kohjiya, S.; Ogawa, T.; Isoda, S.; Kobayashi, T. Macromolecules 2000, 33, 9666–9672.

(6) Marigo, A.; Marega, A.; Cecchin, G.; Collina, G.; Ferrara, G. Eur. Polym. J. 2000, 36, 131–136.

(7) Azzurri, F.; Flores, A.; Alfonso, G. C.; Balta´Calleja, F. J. Macromolecules 2002, 35, 9069–9073.

(8) Azzurri, F.; Alfonso, G. C. Macromolecules 2004, 37, 3755–3762.

(9) Kopp, S.; Wittmann, J. C.; Lotz, B. Polymer 1994, 35, 908–915.

(10) Tusjek, L.; Nitschke, M.; Werner, C.; Stana-Kleinschek, K.; Ribitsch, V. Colloids Surf. A: Physicochem. Eng. Aspects 2001, 195, 81–95.

(11) Kauling, A. R.; Soares, G. V.; Figueroa, C. A.; de Oliveira, R. V. B.; Baumvol, I. J. R.; Giacomelli, C.; Miotti, L. Mater. Sci. Engin. 2009, 29, 363–366.

(12) Cui, N. Y.; Brown, N. M. D. Appl. Surf. Sci. 2002, 189, 31–38.

(13) Johnston, E. E.; Ratner, B. D. Elec. Spec. J. 1996, 81, 303–317.

(14) Keil, M.; Rastomjee, C. S.; Rajagopal, A.; Sotobayashi, H. Appl. Surf. Sci. 1998, 105, 273–286.

(15) Ningel, P.; Theirich, D.; Engemann, J. Surf. Coat. Tech. 1998, 98, 1142–1147.

(16) Vasekova, E.; Drage, E. A.; Smith, K. M.; Mason, N. J. J. Quantit. Spectr. Rad. Transfer 2006, 102, 418–424.

(17) Motomura, H.; Imai, S.; Tachibana, K. Thin Solid Films 2001, 390, 134–138.

(18) Schonherr, H.; Hruska, Z.; Vancso, G. J. Macromolecules 1998, 31, 3679–368.

(19) Hegemann, D.; Brunner, H.; Oehr, Ch. Nucl. Instrum. Meth. Phys. Resear. B. 2003, 208, 281–286.

(20) Navaneetha Pandiyaraj, J.; Selvarajan, V.; Deshmukh, R. R.; Gao, Ch. Vacuum 2009, 83, 332–339.

(21) Grace, I. M.; Gerenser, L. J. J. Disp. Sci. Techn. 2003, 24, 305–341.

(22) Vesel, A.; Mozetič, M.; Strnad, S.; Stana-Kleinschek, K.; Hauptman, N.; Peršin, Z. Vacuum 2010, 84(1), 79–82.

(23) Vesel, A.; Mozetič, M.; Zalar, A. Surf. Interface Anal. 2008, 40(3/4), 661–663.

(24) Cvelbar, U.; Mozetič, M.; Junkar, I.; Vesel, A.; Kovač, J.; Drenik, A.; Vrlinič, T.; Hauptman, N.; Klanjšek Gunde, G.; Markoli, B.; Krstulović, N.; Milošević, S.; Gaboriau, F.; Belmonte, T. Appl. Surf. Sci. 2007, 253(19), 8669–8673.

(25) Vesel, A.; Mozetič, M. Vacuum 2001, 61(2/4), 373–377.

(26) Morra**,** M.; Occhiello**,** E.; Marola, R.; Garbassi**,** F**.;** Humphrey**,** P.; Johnson**,** D**.** J. Coll. Interf. Sci. 137, 1990, 11–24.

(27) Shen, Ch.; Shih, K.; Chen, S. Polym. Polym. Compos. 2001, 9, 185–200.

(28) Dorai, R.; Kushner, M. J. J. Phys. D. Appl. Phys. 2003, 36, 666–685.

(29) Strobel, H. M.; Strobel, M.; Lyons, C. S.; Dunatov, C.; Perron, S. J. J. Adhes. Sci. Technol. 1991, 5, 119–130.

(30) Hyun, H. Polymer 2001, 42, 6473–6477.

(31) Kim, B. K.; Kim, K. S.; Park, C. E.; Ryu, C. M. J. Adhes. Sci. Technol. 2002, 16, 509–521.

(32) Wei, Z.; Zhennan, Z.; Xinping, W. J. Col. Interf. Sci. 2009, 333, 346–353.

(33) Kaminska, A.; Kaczmarek, H.; Kowalonek, J. Eur. Polym. J. 2002, 38, 1915–1919.

(34) Wheale, S. H.; Barker, C. P.; Badyal, J. P. S. Langmuir 1998, 14, 6699–6704.

(35) Garbassi, F; Morra, M.; Occhiello, E. Polymer Surfaces from Physics to Technology, John Wiley & Sons, Chichester, UK, 1998, p. 291.

(36) Pringle, S. D.; Joss, V. S.; Jones, C. Surf. Interf. Anal. 1996, 24, 821–829.

(37) Wilson, D. J.; Eccles, A. J.; Steele, T. A.; Williams, R. L.; Pond R. C. Surf. Interf. Anal. 2000, 30, 36–39.

(38) Girardeaux, C.; Idrissi, Y.; Pireaux, J. J.; Caudano, R. Appl. Surf. Sci. 1996, 96-98, 586-590.

(39) Liang, R. Q.; Su, X. B.; Wu, Q. C.; Fang, F. Surf. Coat. Technol. 2000, 131, 294–299.

(40) Busscher, H. J.; van Pelt, A. W. J.; de Boer, P.; de Jong, H. P.; Arends, J. Coll. Surf. 1984, 9, 319–331.

(41) Extrand, C. W.; Kumagai, Y. J. Coll. Interf. Sci. 1997, 191, 378–383.

(42) Chau, T. T.; Bruckard, W. J.; Koh, P. T. L.; Nguyen, A.V. Adv. Coll. Interf. Sci. 2009, 150, 106–115.

(43) Sheng, E.; Sutherland, I.; Brewis D. M.; Heath, R. J. J. Adhes. Sci. Technol. 1995, 9, 47–60.

(44) Eske L. D.; Galipeau, D. W. Coll. Surf. A Physicochem. Eng. Asp. 1999, 154, 33–51

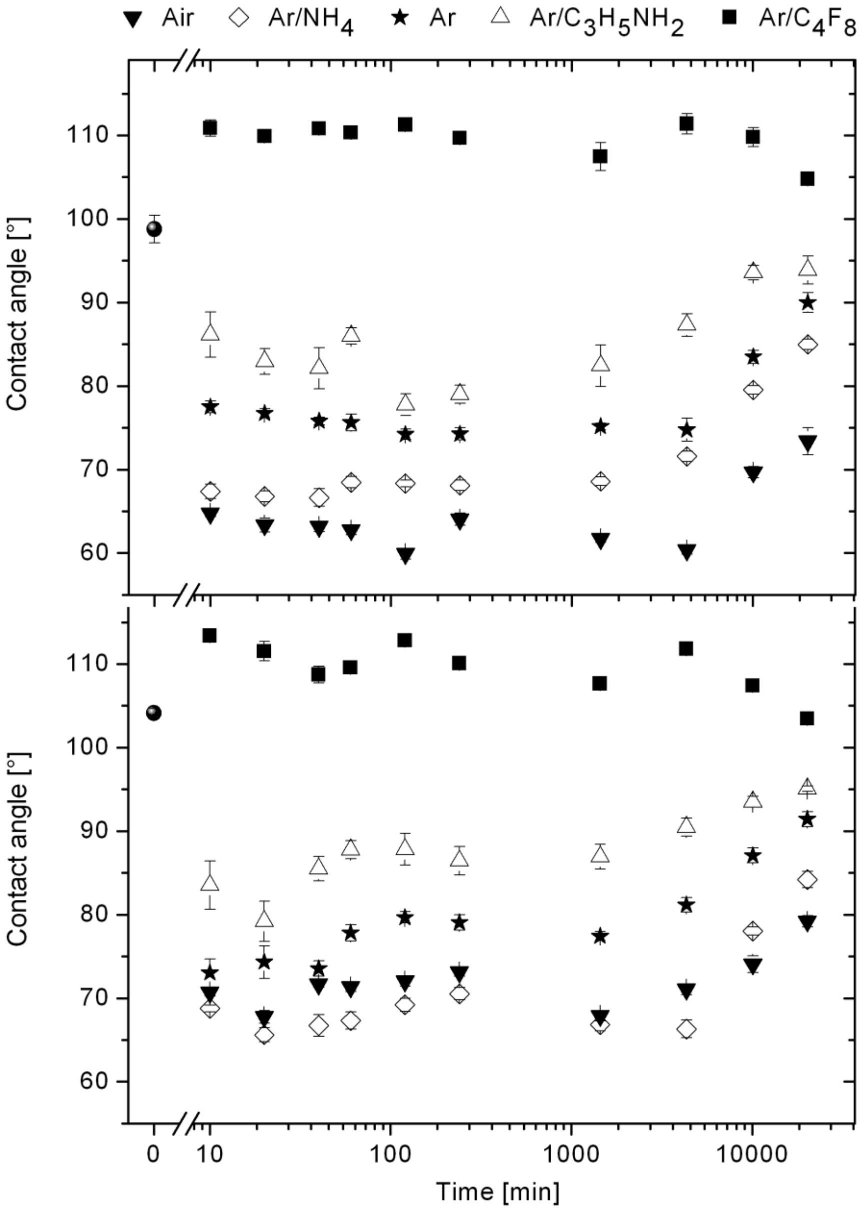

Figure 1 Contact angle variation of plasma-treated homoPB (up) and coPB (down) specimens as a function of time.

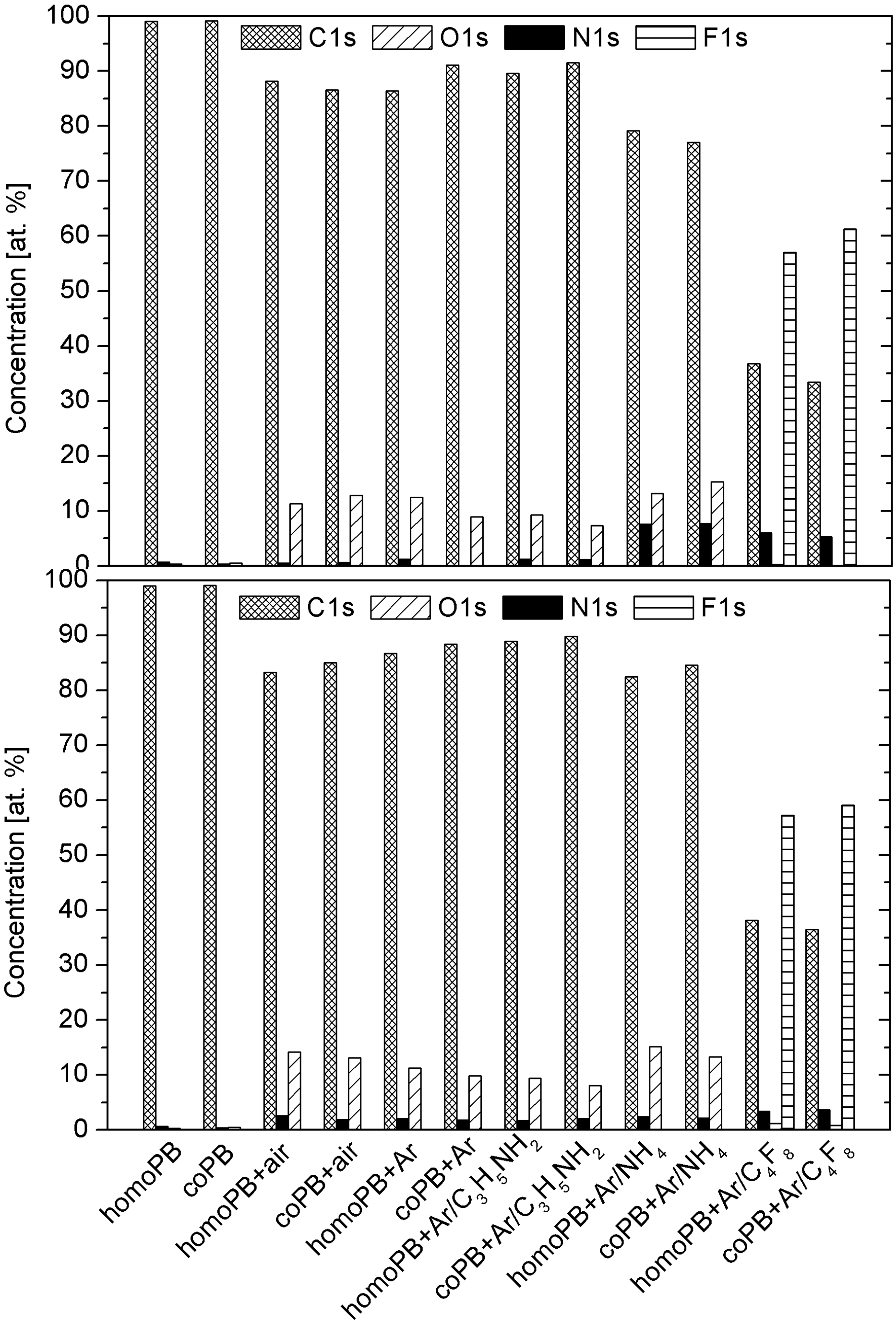

Figure 2 Surface composition of homoPB and coPB samples measured immediately (up) and 14 days (down) after plasma treatment.

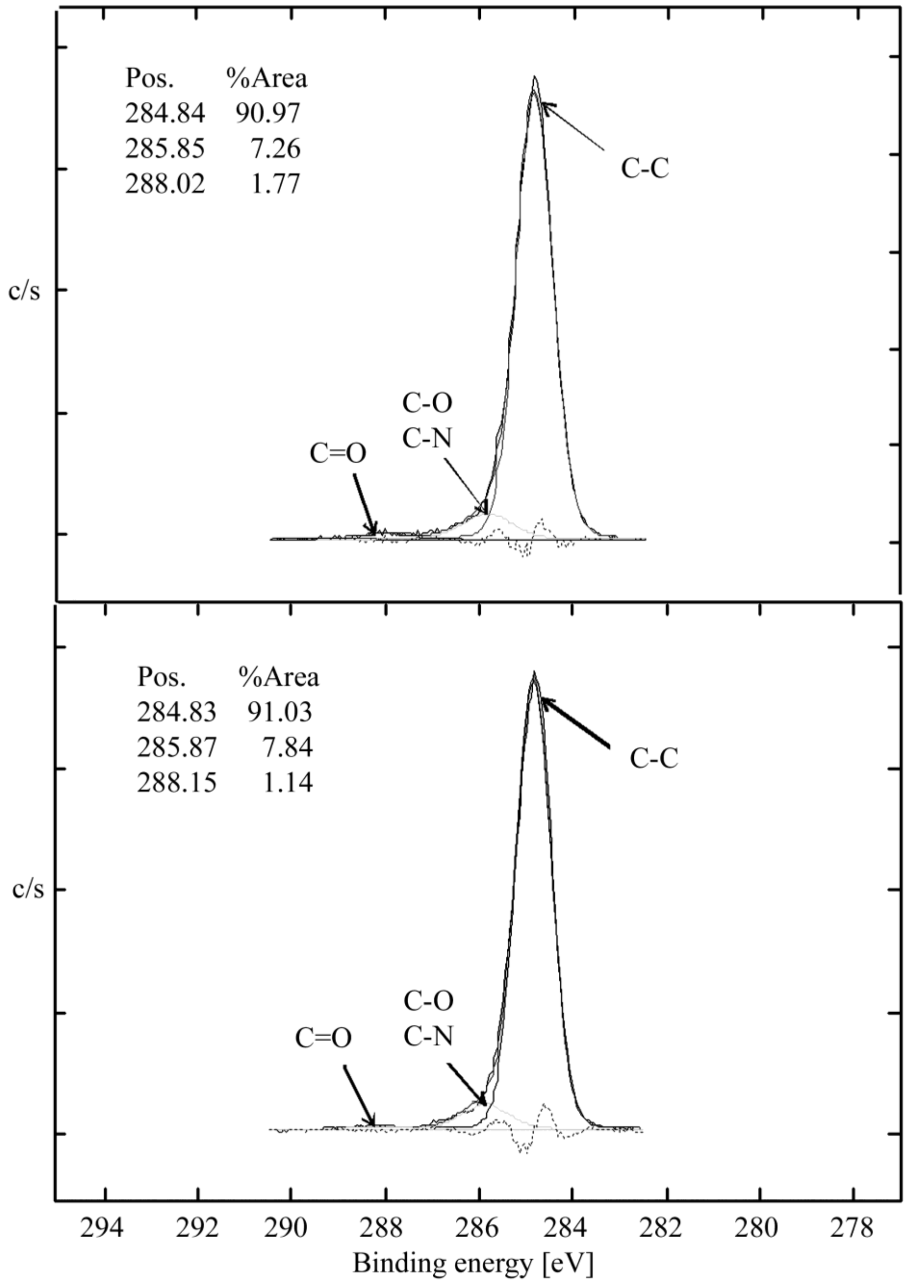

Figure 3 Carbon C1s peak of untreated homoPB (up) and coPB (down) samples.

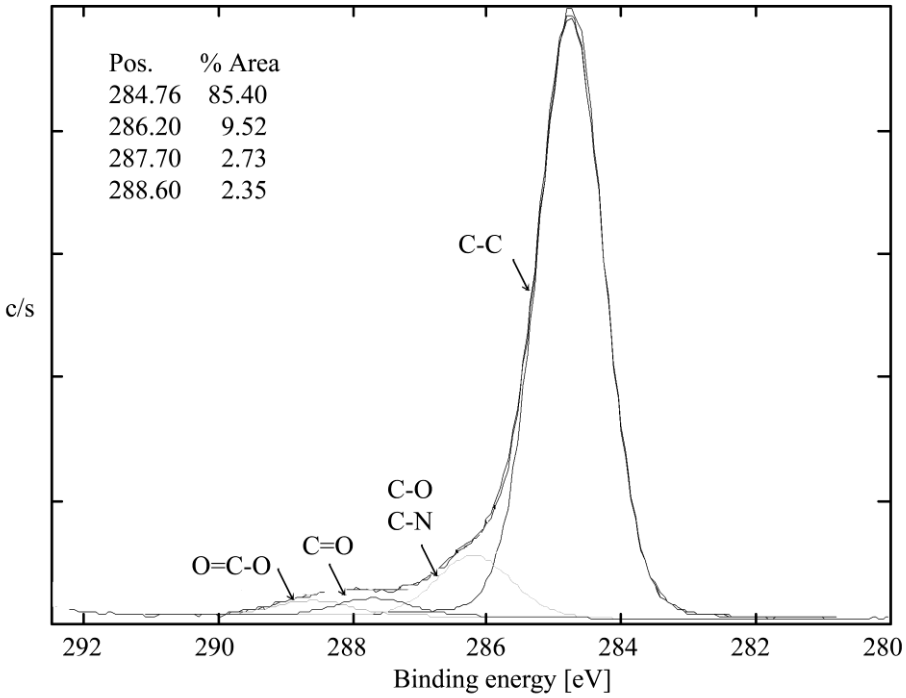

Figure 4 Curve fitting of carbon peak of sample homoPB+Ar/NH_4 14 days after plasma treatment.

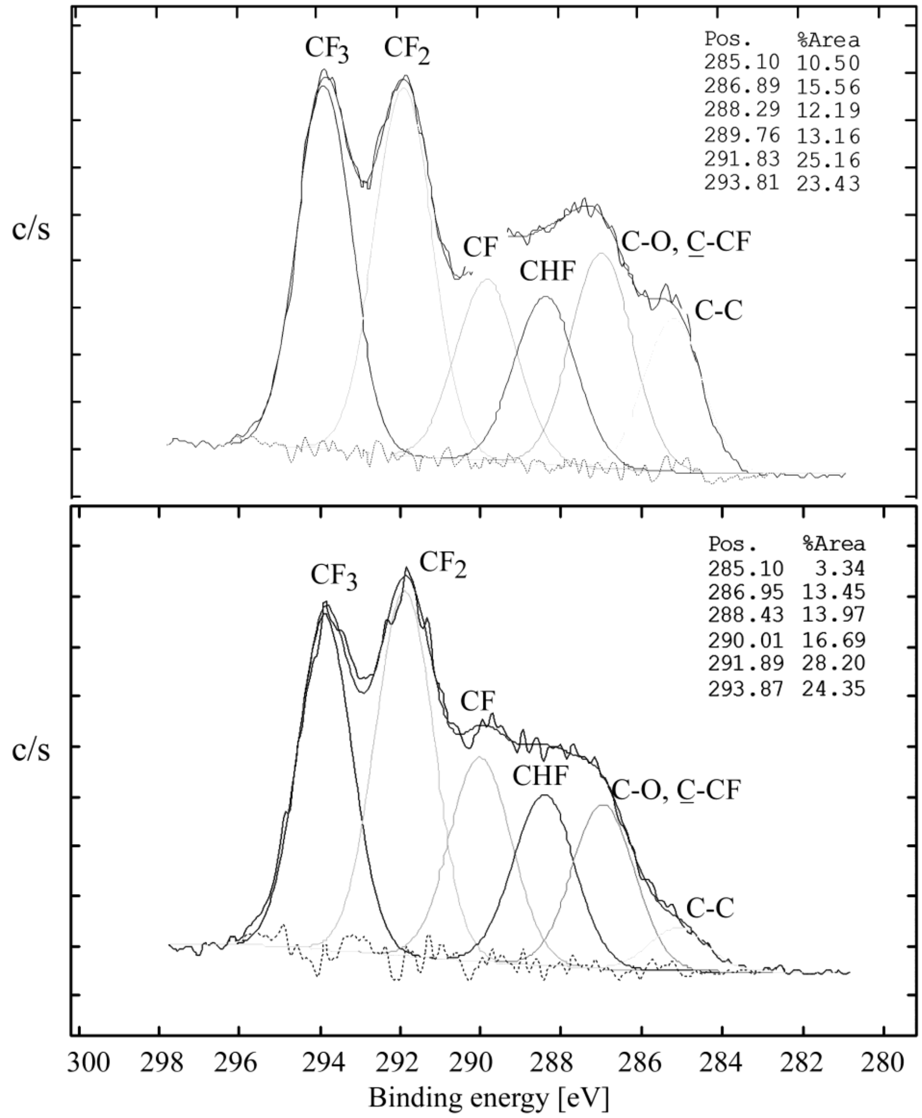

Figure 5 Curve fittings of carbon peak of homoPB (up) and coPB (down) samples treated by Ar/C_4F_8 plasma, 14 days after treatment.

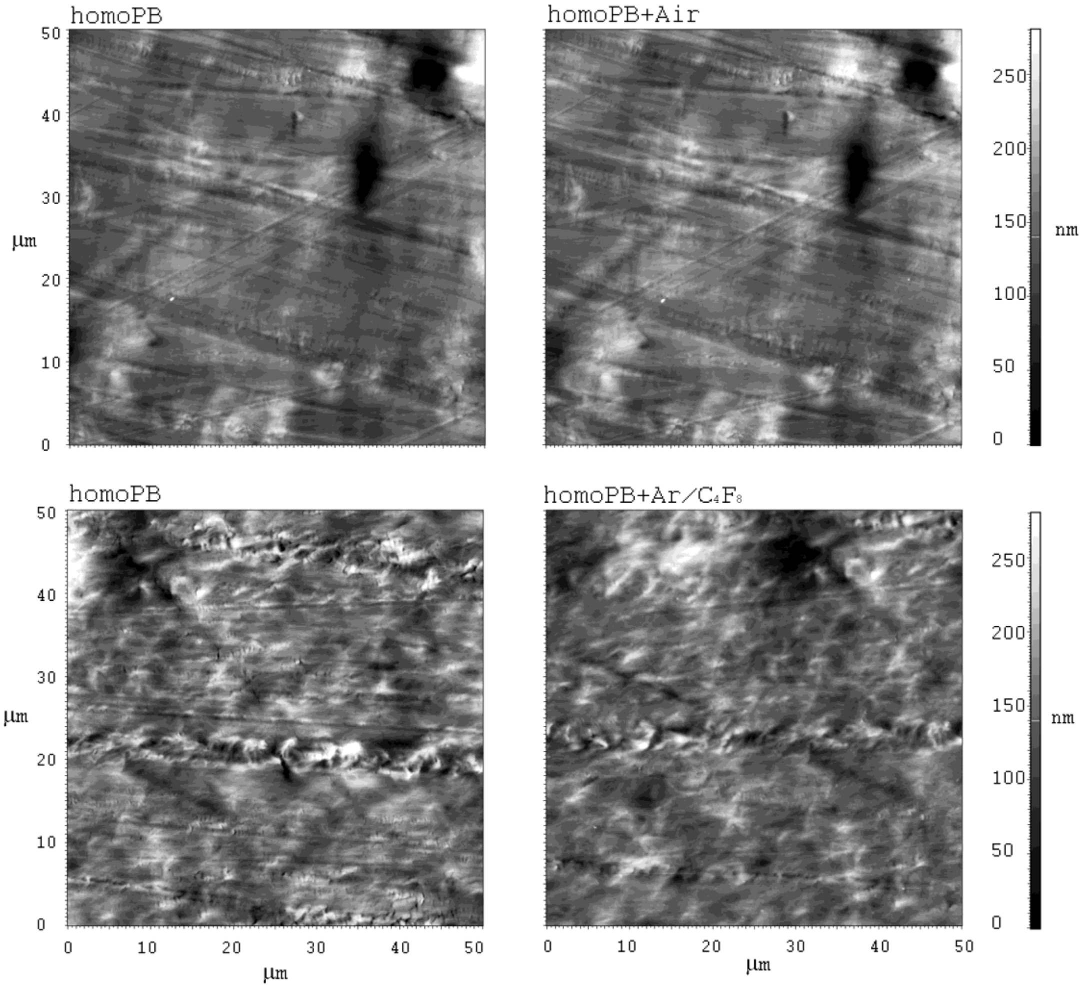

Figure 6 AFM images of homoPB samples topography before and after air plasma treatment (up) and before and after fluorocarbon plasma treatment (down).

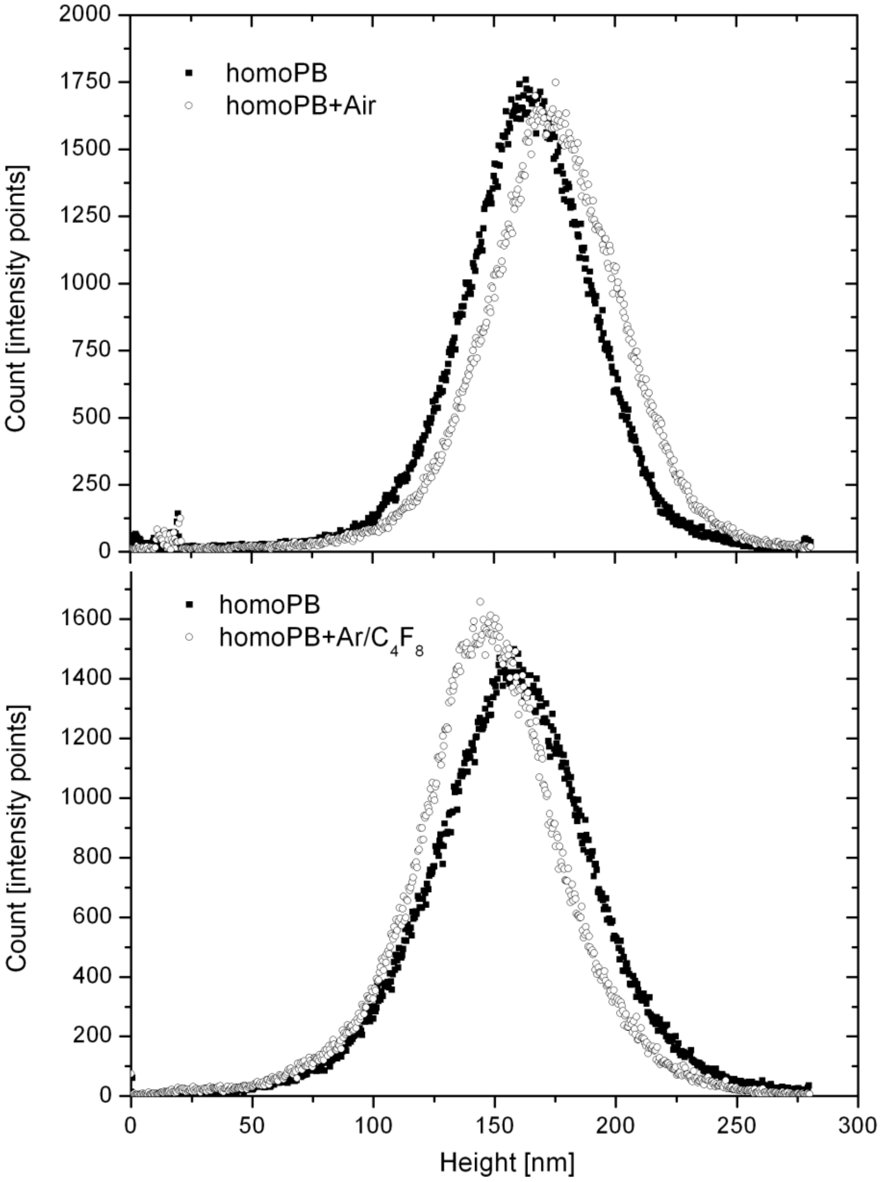

Figure 7 Histograms of the brightness distribution of roughness height of homoPB samples before and after air plasma treatment (up) and before and after fluorocarbon plasma treatment (down).

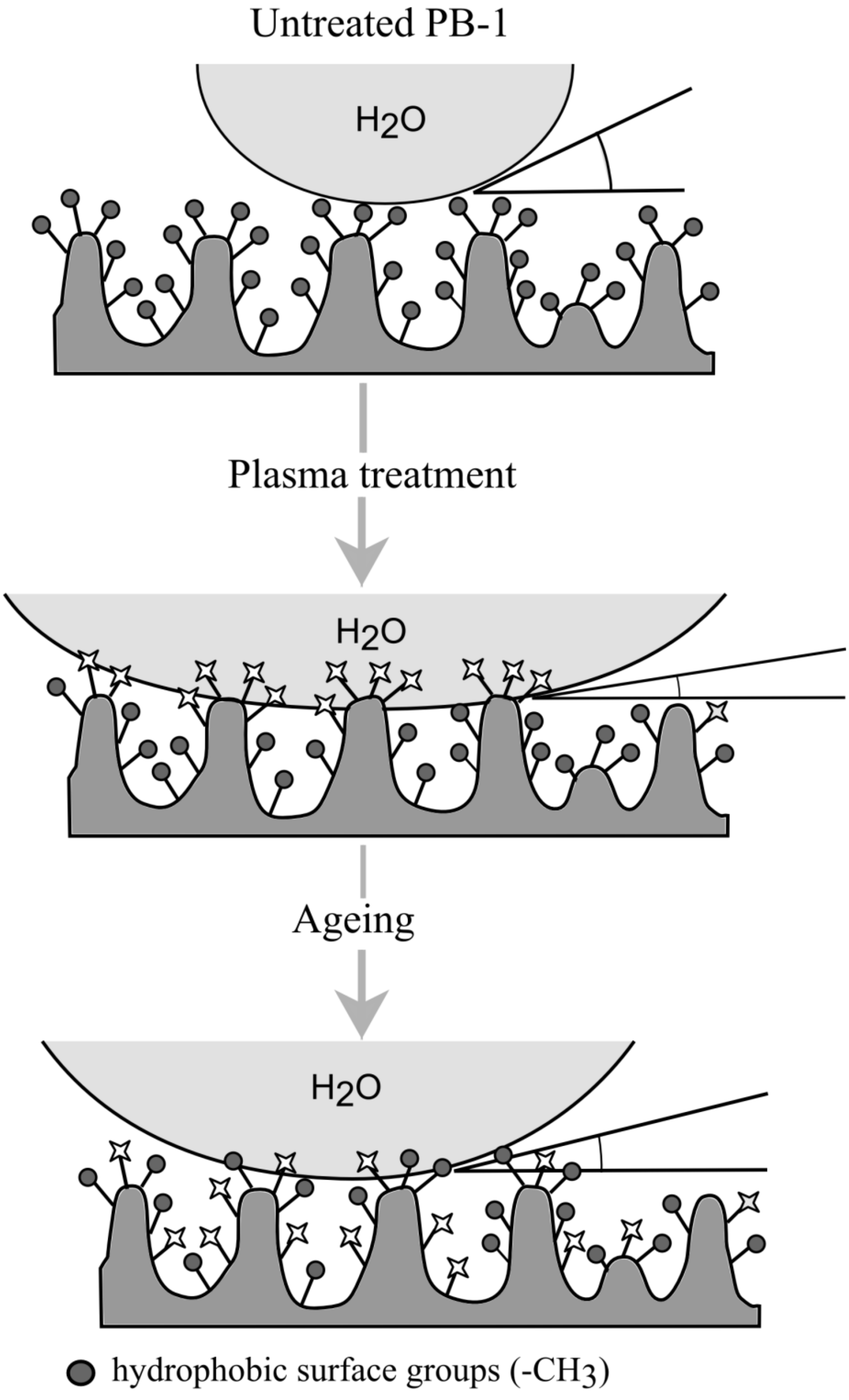

Figure 8 Scheme of mechanism of surface conformation changes.

PAPER IV

“The final publication is available at www.elsevier.com/locate/polydegstab“

Polymer Degradation and Stability 96 (2011) 1740–1744

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Photodegradation of isotactic poly(1-butene): Multiscale characterization

Lubomír Beníček [a,b,*], Lenka Chvátalová [a], Martin Obadal [c], Roman Čermák [a,b],
Vincent Verney [d,e], Sophie Commereuc [d,f]

[a] Tomas Bata University in Zlin, Faculty of Technology, Department of Polymer Engineering, nam. T.G.Masaryka 275, 762 72 Zlin, Czech Republic
[b] Tomas Bata University in Zlin, University Institute, Centre of Polymer Systems, Nad Ovcirnou 3685, 760 01 Zlin, Czech Republic
[c] Borealis Polyolefine GmbH, St.-Peter-Strasse 25, 4021 Linz, Austria
[d] Clermont Universite, Université Blaise Pascal, LPMM, BP 10448, F-63000 Clermont-Ferrand, France
[e] CNRS, UMR 6505, LPMM, F-63177 Aubiere Cedex, France
[f] Clermont Universite, ENSCCF, LPMM, BP 10448, F-63000 Clermont-Ferrand, France

ARTICLE INFO

Article history:
Received 30 May 2011
Received in revised form
29 July 2011
Accepted 2 August 2011
Available online 7 August 2011

Keywords:
Isotactic poly(1-butene)
Rheology
Infrared spectroscopy
Thermal behaviour
Photodegradation

ABSTRACT

The effect of photodegradation in isotactic poly(1-butene) (PB-1) have been investigated using rheology, differential scanning calorimetry and infrared spectroscopy. Two commercially available grades of PB-1 with different average molecular weight were chosen. Specimens prepared by compression moulding were UV irradiated in the interval from 0 to 70 h. UV-induced changes in molecular structure have been followed by evolution of rheological properties, thermal properties and degradation by-products. Thermal analysis showed significant changes in crystallization behaviour influencing morphology and resulting thermal properties. Moreover it has been confirmed that the degradation significantly retards the phase transformation. Rheological measurement has been found as an effective method for determination of early stages of photodegradation of PB-1.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Isotactic poly(1-butene) (PB-1) possesses a number of attractive properties that distinguish it from the most common polyolefins like isotactic polypropylene or polyethylene. However, even after more than 50 years from its discovery, and despite its potential, PB-1 is still a relatively unexplored material being produced in limited quantities and has not yet found a large commercial success as compared to the other polyolefins. This is particularly due to the peculiar polymorphic crystallization behaviour and polymorphism, which are not currently fully understood.

Five different crystalline modifications have been reported, which are referred to as hexagonal forms I, I′, tetragonal forms II, II′ and orthorhombic form III [1]. The most important phenomenon is specific transformation – upon solidification from the melt PB-1 crystallizes into phase II which is kinetically favoured. During several days the material transforms into phase I, which is thermodynamically favoured [2,3].

Similarly, the degradation behaviour of PB-1 is not still clearly understood; it is supposed to be similar to isotactic polypropylene due to presence of tertiary carbon on the backbone. Neat PB-1 contains only C–C and C–H bonds and therefore, absorption of light at wavelengths longer than 200 nm can be expected. The fact that photodegradation of polymers occurs even at wavelength longer than 300 nm indicates that some kind of chromophoric groups must be present in these polymers. The chromophores in commercial PB-1 are developed during polymerization and thermal processing [4].

During polymer photodegradation two types of processes occur: (i) primary photochemical reactions due to the absorbed radiation, resulting in the formation of free radicals or non-radicals rearrangement; (ii) secondary reactions in which radicals formed initiate a number of reactions which are independent of the light [4,5].

As generally accepted, degradation reactions of semicrystalline polymers proceed predominantly in amorphous regions. Nevertheless, physical factors, such as the size, arrangement and distribution of crystalline regions, affect the degradation as well. Photodegradation kinetics in polymeric systems depends on oxygen

---

[*] Corresponding author. Tomas Bata University in Zlin, Faculty of Technology, Department of Polymer Engineering, nam. T.G.Masaryka 275, 762 72 Zlin, Czech Republic. Tel.: +420 576 031 326; fax: +420 576 032 733.

E-mail addresses: benicek@ft.utb.cz (L. Beníček), chvatalova@ft.utb.cz (L. Chvátalová), martin.obadal@borealisgroup.com (M. Obadal), cermak@ft.utb.cz (R. Čermák), vincent.verney@univ-bpclermont.fr (V. Verney), sophie.commereuc@univ-bpclermont.fr (S. Commereuc).

0141-3910/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2011.08.001

permeability throughout the material [6] and the rate of oxidation drops with decreasing oxygen diffusion [7,8].

On the other hand, the crystallinity and the molecular orientation determine the mobility of the radicals and therefore reduce the rate of termination, allowing an increase in the propagation of chemical reactions leading to molecule scission, and this effect is opposite to that caused by reduced oxygen mobility. Which of these two effects will predominate depends on the oxidation conditions, including the type of degradation, temperature and oxygen concentration [9].

Specified by-products of the free radical oxidation of most polymers are hydroperoxides [10]. The mechanism of radical oxidation in poly(1-butene) is still unknown, nevertheless, the similar mechanism as in the case of polypropylene is suggested, where resulting hydroperoxides are predominantly tertiary (≈90%), the remainder being essentially secondary [11]. In contrast in polyethylene only secondary hydroperoxides are present [12]. The general mechanism is as follows [13]:

$$\mathrm{P}\xrightarrow{h\nu}\mathrm{P}\cdot\xrightarrow{\mathrm{O_2}}\mathrm{POO}\cdot\xrightarrow{\mathrm{R}}\underset{[\mathrm{R}=\mathrm{H,P}]}{\mathrm{POOR}}\xrightarrow{h\nu}\mathrm{PC{=}O} \qquad (1)$$

Formation of peroxide species in the polymer backbone is encountered as the primary step of the oxidative degradation. The hydroperoxide groups not only play an important role in inducing both thermal and photooxidation of polymers but are also important intermediates in the overall oxidation reactions. Thus, hydroperoxides are the key products in the clear understanding of a mechanism, as well as to gain better insight into correlation between chemical evolution of carboxyl groups and evolution of the molecular structure (scission/recombination/crosslinking) [14–16].

It has been also confirmed that the evolution of the rheological material properties directly reflects changes in molecular parameters, such as molecular weight (MW), and molecular weight distribution (MWD). The linear viscoelastic properties in dynamic experiments are sensitive both to the chain scission and to the three-dimensional network formation. Thus, melt rheology provides a convenient tool to view the particular behaviour due to the competition of chain scissions and recombination reactions occurring through ageing [17].

In conclusion, photodegradation leads to induction of both chemical and physical heterogeneities. Consequently an exact prediction of the material durability needs to be analyzed and quantified. For these reasons the objective of this study is to analyze PB-1 upon photodegradation using various conventional methods: oscillatory shear rheology for analysis of molecular chain motions; infrared spectroscopy (IR) characterizes evolution of chemical species in PB-1 and differential scanning calorimetry observes changes in melting and crystallization behaviour and moreover shows the impact of photodegradation on kinetics of phase transformation II–I.

2. Material and methods

In this study, two different commercially available grades of PB-1 homopolymers produced by Basell Polyolefins, Louvain la Neuve, Belgium were used: DP 0401M, density of 0.915 g cm^{-3}, melt flow rate of 15 g/10 min (190 °C/2.16 kg, ISO 1133); and PB 0300M, density of 0.915 g cm^{-3}, melt flow rate of 4 g/10 min (190 °C/2.16 kg, ISO 1133), both with the same package of stabilizers.

PB-1 sheets, approx. 0.3 mm thick, were prepared by compression moulding at temperature of 190 °C, compression time of 5 min and subsequent cooling to 20 °C for 5 min.

For accelerated UV irradiation, a SEPAP 12/24 MPC type of commercial device (ATLAS company) was employed at temperature of 60 °C, wavelength longer than 300 nm and the sampling was performed in various ageing times.

Molecular changes were characterized by melt viscoelasticity experiments in oscillatory shear mode using a TA ARES mechanical spectrometer, equipped with parallel plate geometry with diameter of 8 mm and the gap between the plates was fixed at 1 mm. The experiments were carried out under air atmosphere at reference temperature 140 °C. Thermal stability of both materials was tested by time test and no degradation changes were observed within 2 h at temperature of 140 °C.

The rheological behaviour of the UV irradiated samples was also used as a tool for evaluation of degradation extent [18–20]. The relative changes in complex viscosity $\Delta\eta^*$ of the samples was measured at frequency 0.2 rad s^{-1} and expressed by following equation:

$$\Delta\eta^* = \frac{\eta_0^* - \eta_t^*}{\eta_0^*}100(\%) \qquad (2)$$

where t represents time of UV irradiation, η_0^* and η_t^* is the complex viscosity for degradation times of zero and t, respectively.

A Nicolet 800 spectrometer with nominal resolution of 4 cm^{-1} was employed in transmission mode with a 32-scan summation. Molecular degradation was characterized by carbonyl index (CI).

$$CI = A_C/A_R, \qquad (3)$$

where A_C is the area of the carbonyl absorption bands (in the range from 1650 to 1820 cm^{-1}) and A_R is the area of a reference band not affected by photooxidation and varying crystallinity (in the range from 2700 to 2750 cm^{-1}) [7].

Melting, re-melting and crystallization behaviours of UV irradiated specimens were observed using a DSC-Pyris1 power compensated differential scanning calorimeter. Nitrogen as a purge gas was used and constantly passed (20 cm^3 s^{-1}) through the heat sink and over the cells. Temperature calibration was performed using indium as a standard. Approx. 5 mg of irradiated material was loaded into standard aluminium pans. Observation was performed at a rate of ±10 °C/min in interval from 40 to 170 °C. To observe melting temperature of the form II, second subsequent melting and crystallization were performed. The specimens were kept at room temperature and the phase transformation followed.

It is generally known that differences in melting temperatures of the forms I and II are approx. 10–15 °C. Thus melting curves obtained from DSC exhibit partial superposition. Only one melting peak of the form I or II on the melting curve is detected immediately after crystallization or when polymorphic transformation terminates respectively.

In this respect, the melting curves must be deconvoluted to reliably evaluate the transformation. Therefore, we particularly followed the approach of Alfonso et al. [21].

It is supposed that overall degree of crystallinity does not change during transformation [5,21,22]. Unfortunately, there are no exact values of melting enthalpy of forms I and II.

Thus, the individual peaks of forms I and II were deconvoluted using a Gaussian function and then areas under both peaks were by integration obtained. The content of the increasing form I in time was calculated as the ratio of area of the peak form I and sum of heights of both peaks forms I and II.

3. Results and discussion

3.1. Rheological behaviour

Fig. 1 shows complex viscosities of both materials DP 0401M (up) and PB 0300M (down) during initial stage of photodegradation up to

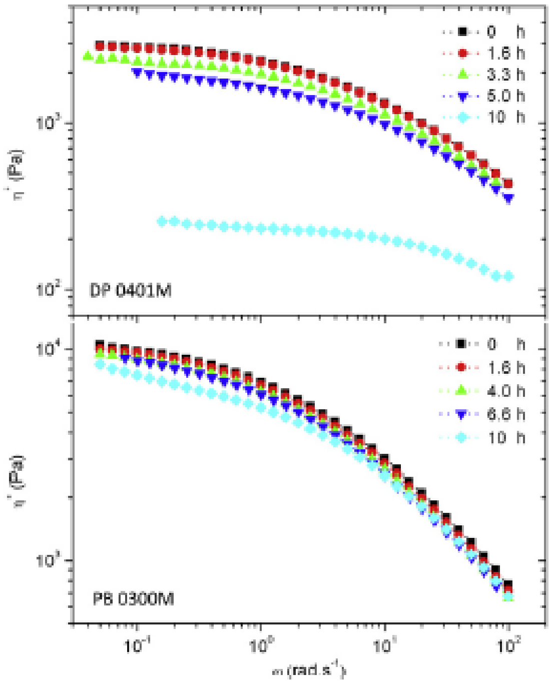

Fig. 1. Effect of accelerated UV irradiation on complex viscosity in materials DP 0401M (up) and PB 0300M (down).

10 h of accelerated UV irradiation. It can be clearly seen that material PB 0300M is less sensitive to photodegradation than DP 0401M. It is evident that the method is convenient to determine molecular changes in the short UV irradiation times for PB-1 with respect to MW. In case of DP 0401M at the beginning of UV irradiation complex viscosity η^* gradually decreases up to 5 h and after 10 h the material is entirely degraded by chain scission reactions. On the other hand, material PB 0300M shows gradual decrease of viscosity and even after 10 h of UV irradiation no significant changes are observed. This difference is contributed to approx. 3 times higher viscosity of PB 0300M than DP 0401M. It is obvious that chain scission reactions are dominant during initial stage of UV irradiation even if recombination reactions occurs simultaneously [17].

Dependence of η^* at frequency of 0.2 rad s^{-1} on UV irradiation time is illustrated in Fig. 2 (up). What can be seen is a similar profile of decreasing η^* for both materials, which differs only in initial values of η^*. While the initial values of η^* are notably different, their evolution upon UV irradiation is similar.

Using Equation (2), relative change in complex viscosity ($\Delta\eta^*$) of both sets of samples was evaluated and illustrated in Fig. 2 (down). It is evident that during initial 1.6 h of UV irradiation, degradation possesses virtually the same trend. With increasing time of UV irradiation the difference between both materials becomes significant and material with higher melt flow rate (DP 0401 M) is more sensitive to photodegradation. After 10 h of UV irradiation the $\Delta\eta^*$ reaches 26% in PB 0300M and 90% in DP 0401M. This significant increase of degradation is caused by fully enhanced chain scission reactions.

3.2. *Infrared spectroscopy*

Fourier transform – infrared spectroscopy (IR) is traditional and convenient method for analysis of chemical changes during various types of degradation. UV irradiation leads to significant changes in the IR absorption spectra in PB-1. The evolution of chemical species in degraded PB-1 can be seen in following Fig. 3. The major by-products resulting from presence of atmosphere oxygen are carbonyl products. As the oxidation proceeds, broad absorption bands growth at 1640, 1712, 1735 and 1780 cm^{-1} are observed. A gradual formation of carboxylic acid (1712 cm^{-1}) can be seen in all cases. With further exposition the formation of esters becomes dominant at 1735 cm^{-1} in case of DP 0401M; the formation at absorption of 1780 cm^{-1} is assigned to peresters or γ-lactones; a weak peak at absorption 1640 cm^{-1} is assigned to vinyl groups [23]. The UV irradiation in DP 0401M and PB 0300M (Fig. 3 up and down) shows similar mechanism of degradation, however in DP 0401M the evolution of chemical species is faster in the initial stage compared to PB 0300M, and the esters (1735 cm^{-1}) become dominant from 60 h.

When carbonyl indexes of both materials are plotted versus exposure time, the chemical evolution of PB 0300M is weaker than in DP 0401M as can be seen in Fig. 4. Both materials show similar induction period during initial 10 h (which is defined as the time lag during which no by-products are detected by IR) and then the slope of the curves increase. For material with higher melt flow rate – DP 0401M, the slope is higher than for PB 0300M. It should also be noted that IR is not able to detect peroxide species, which are during radical chemical reactions transformed to detectable chemical groups.

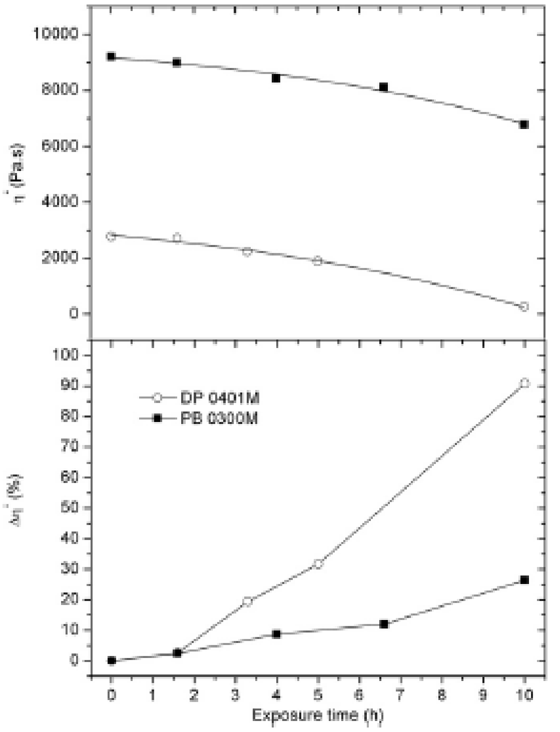

Fig. 2. Evolution of complex viscosity at frequency 0.2 rad s^{-1} (up) and relative change in complex viscosity (down) upon accelerated UV irradiation.

3.3. *Thermal behaviour*

Thermal analysis is the last step to identify changes in PB-1 during initial 40 h of UV irradiation. Since the rheological behaviour showed a significant changes during initial 10 h of UV irradiation in material

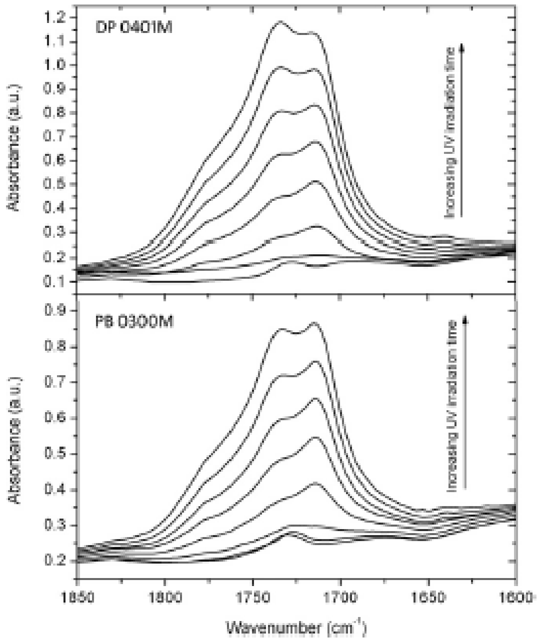

Fig. 3. Absorption bands in the carbonyl area of DP 0401M (up) and PB 0300M (down).

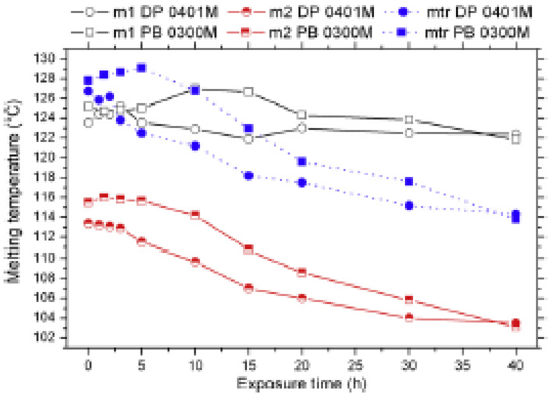

Fig. 5. Melting behaviour during first melting (*m1*), second melting (*m2*) and melting after transformation is completed (*mtr*).

DP 0401M, it can be suggested that thermal analysis provides further information concerning PB-1 photodegradation.

The melting behaviour of degraded specimens of both materials is illustrated in Fig. 5. It can be seen that the melting temperature of the form I (*m1*), observed by first melting, vary interval of 122–127 °C in both materials. No distinct trend is observed compared to the second melting (*m2*). It was performed immediately after the first melting and subsequent controlled which corresponds to the melting of the form II. In both materials a decrease of melting temperature with increasing irradiation time is observed with total drop of 10–12 °C between time 0 and 40 h. Since the PB-1 is a polymorphic material with peculiar phase transformation of the kinetically favoured form II into the thermodynamically stable form I, melting after transformation II–I is completed (*mtr*) was performed. Upon the polymorphic transformation from the form II into the form I, a virtually identical thermal behaviour with shifted melting temperatures can be seen as the slopes of *m2* and *mtr* curves are similar.

What can be expected in the initial stage of degradation is a prevailing effect of chain scission, which can positively influence the crystallization kinetics. As a consequence, final structure is thermodynamically more stable, and its melting temperature in short-term irradiated specimens can even exceed that of non-irradiated. This is particularly evident in PB 0300M from the melting of phase I upon transformation. However, chain scission is followed by the introduction of impurities into the molecular structure. This effect leads to the decrease of crystallisability and the crystallization to less stable structure [24]. In thermograms (Fig. 5), it is presented by gradual decrease of melting temperatures of both forms I and II with prolonged irradiation time.

The effect of photo-induced changes on crystallization is even more evident from the crystallization temperature (T_c), as shown in Fig. 4. In the case of PB 0300M, the non-monotonic evolution of T_c can be seen. At the beginning, a significant increase of T_c from 78 to 91 °C is observed and after 10 h of UV irradiation the initial T_c is reached. This observation confirms that the chain scission positively influences the crystallization rate (as the chain entanglements are partly released, the molecular mobility increases) and this effect prevails in the initial stage of UV irradiation. However, an increasing number of introduced heterogeneities in polymer chains then cause a linear drop of T_c about 30 °C between 5 and 20 UV irradiation hours. Further in time, a gradual decrease of T_c to 55 °C occurs. The evolution in T_c of DP 0401M upon UV irradiation is slightly different. Crystallization temperature decreases with exposure time. During first 5 h degradation leads into a significant drop of T_c and then from 15 up to 40 h only a small decrease can be seen up to 55 °C, i.e. the same values as that of PB 0300M. Clearly, the first stage with increasing crystallization rate upon chain scission is missing. It can be supposed that the competition between (i) the increase in crystallization kinetics upon chain scission and (ii) the retardation of crystallization caused by introduction of molecular irregularities is influenced by initial molecular weight. Indeed, the feasible maximum of crystallization rate is faster reached in lower-molecular systems, thus in DP 0401M, in this case its crystallization temperature decreases even upon the initial stage of UV irradiation.

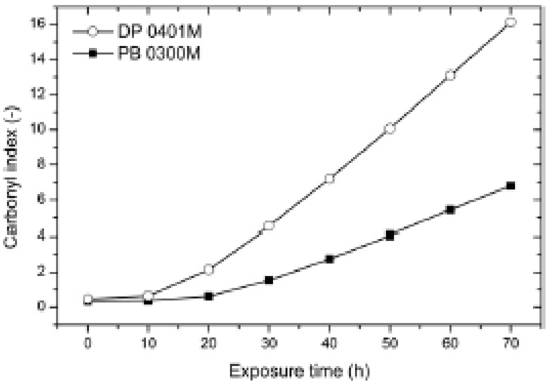

Fig. 4. Effect of accelerated UV irradiation on the carbonyl index.

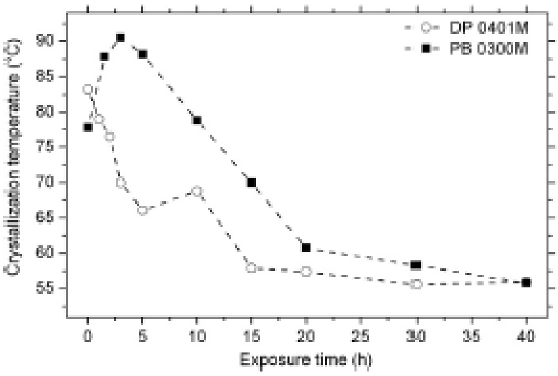

Fig. 6. Crystallization behaviour upon accelerated UV irradiation.

The evolution of subsequent phase transformation in re-melted UV irradiated specimens is illustrated in Fig. 7. The Fig. 7 (up) shows evolution of form I content during phase transformation of degraded DP 0401M. It is evident that after 2 h of UV irradiation no significant change in transformation rate is observed. However, the change of transformation rate is evident between 3 and 10 irradiation hours when decreasing trend occurs. It correlates to decrease of crystallization temperature (Fig. 6). Further minor change in transformation rate between 15 and 40 irradiation hours confirms its dependence on crystallization temperature.

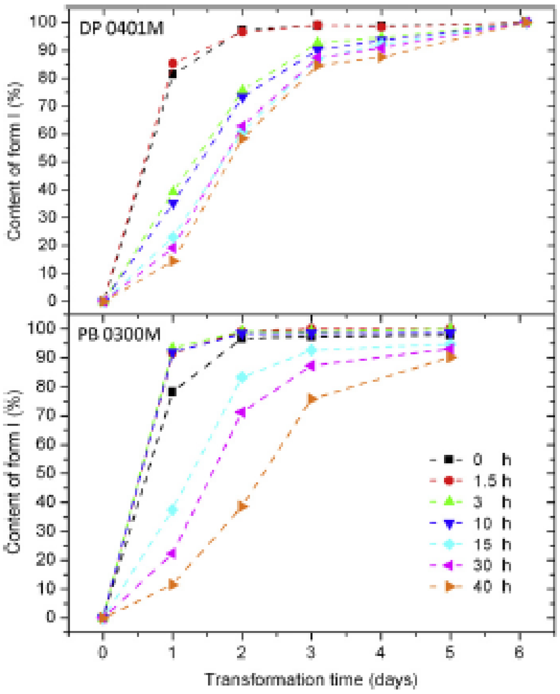

Fig. 7. Effect of accelerated UV irradiation on phase transformation II–I of DP 0401M (up) and PB 0300M (down).

This fact is supported by Fig. 7 (down) focused on material PB 0300M. The transformation rate of non-irradiated specimen which has a lower T_c compared to UV irradiation time of 1.5 and 3 h possesses also slower transformation rate. Further irradiation (10–40 h) is followed by decreasing trend the same as in Fig. 7 (up). Again, the competition between the molecular mobility and regularity is a key factor influencing the transformation. Thus the transformation rate follows the changes in crystallization temperature; the process is overall slower but with similar mechanism.

4. Conclusions

The multiscale characterization of UV-induced changes in isotactic poly(1-butene) showed that the kinetics of degradation are strongly influenced by initial molecular weight. Both the rheology and IR measurements demonstrated faster degradation in material with lower-molecular weight. In this context, rheology was rated as a powerful tool for characterization of initial stages of photodegradation. Thermal analysis showed significant changes in crystallization behaviour influencing morphology and resulting thermal properties. In addition, the effect of degradation on the phase transformation has been proven; the degradation significantly retards the phase transformation.

Acknowledgements

The paper was supported by the Operational Programme Research and Development for Innovations co-funded by the European Regional Development Fund (ERDF) and national budget of Czech Republic within the framework of the Centre of Polymer Systems project (reg. number: CZ.1.05/2.1.00/03.0111). The authors also kindly acknowledge the support provided by the Ministry of Education, Youth and Sport of the Czech Republic (project MSM7088352101).

References

[1] Luciani L, Seppälä J, Löfgren B. Prog Polym Sci 1988;13:37–62.

[2] Marigo A, Marega C, Cecchin G, Collina G, Ferrara G. Europ Pol J 2000;36:131–6.

[3] Kopp S, Wittmann JC, Lotz B. Polymer 1994;35:908–15.

[4] Rabek JF. Polymer photodegradation: mechanism and experimental methods. Kluwer Academic Publisher; 1995.

[5] Azzurri F, Flores A, Alfonso GC, Baltá Calleja FJ. Macromolecules 2002;35:9069–73.

[6] Audouin L, Langlois V, Verdu J, de Bruijn JCM. J Mater Sci 1994;29:569–83.

[7] Rabello MS, White JR. Polym Degrad Stab 1997;56:55–73.

[8] Rabello MS, White JR. Polymer 1997;38:6389–99.

[9] Verney V, Michel M. Rheological Acta 1989;28:54–60.

[10] Commereuc S, Vaillant D, Philippart JL, Lacoste J, Lemaire J, Carlsson DJ. Polym Degrad Stab 1997;57:175–82.

[11] Lacoste J, Vaillant D, Carlsson DJ. J Polym Sci A Polym Chem 1993;31:715–22.

[12] Lacoste J, Carlsson DJ, Falicki S, Wiles DM, Lacoste J. Polym Degrad Stab 1991;34:309–23.

[13] Grassetete T, Gonon L, Verney V. Polym Degrad Stab 2002;78:203–10.

[14] Commereuc S, Verney V. Polym Degrad Stab 2002;78:561–9.

[15] Kumar A, Commereuc S, Gonon L, Verney V. Polym Degrad Stab 2002;75:509–16.

[16] Lemaire J, Gardete JL, Lacoste J, Delprat P, Vaillant D. Adv Chem Ser 1996;249:574–5.

[17] Kumar A, Commereuc S, Verney V. Polym Degrad Stab 2004;85:751–7.

[18] Saha N, Zatloukal M, Saha P. Polym Adv. Technol 2003;14:854–60.

[19] Zatloukal M, Vlcek J, Slanik A, Lengalova A, Simonik J. Appl Rheol 2002;13:126–32.

[20] Sedlarik V, Saha N, Saha P. Polym Degrad Stab 2006;91:2039–45.

[21] Alfonso GC, Azzurri F, Castellano M. J Therm Anal Calorim 2001;66:197–207.

[22] Rubin ID. J Polym Sci 1964;82:747–9.

[23] Delprat P, Duteurtre X, Gardette JL. Polym Degrad Stab 1995;50:1–12.

[24] Obadal M, Čermák R, Raab M, Verney V, Commereuc S, Fraïsse F. Polym Degrad Stab 2005;88:532–9.