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Morphology – Property Correlations of PP Materials by Means of Microhardness

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Summary: The present work deals with the influence of crystallization temperature, cooling rate and annealing conditions on microhardness, indentation modulus and creep behaviour of ethylene/propylene (E/P) random copolymers with 4, 6 and 8 mol% ethylene as well as α- and β-spherulites in a homopolymer and an E/P random copolymer. The materials are unnucleated, the formation of β-spherulites occurs sporadically. Additionally the indentation creep behaviour of α- and β-nucleated PP is investigated.

A nearly linear correlation between hardness as well as indentation modulus and crystallintity of the E/P copolymers can be proved. An increasing cooling rate leads to decreasing hardness and modulus values due to the hindered crystallization.

For the investigation of the α- and β-phases different crystallization and annealing temperatures are used. Independent of these conditions, microhardness and modulus determined by indentation testing are lower for the β-phase in both materials. Increasing crystallization temperature and annealing lead to an increasing hardness and modulus in both phases. However, an effective annealing effect takes place only at short times and elevated temperatures above 100 °C. The increasing of microhardness and modulus is correlated with an increasing in lamellae thicknesses. Additionally, indentation creep experiments were carried out on nucleated materials that show the stronger creep tendency of the β-phase PP and the stronger influence of annealing on this phase.

Keywords: annealing; creep; crystallization; microhardness; poly(propylene)

Introduction

The search for quantitative structure - property correlations for the control and prediction of the mechanical behaviour of polymers has occupied a central role in the development of polymer science and engineering. Mechanical performance factors such as creep resistance, fatigue life, toughness and the stability of properties with time, stress and temperature have become subjects

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of major activities. Within this context microhardness is a property which is sensitive to structural changes. Nowadays, the microhardness technique, being an elegant, nearly non-destructive, sensitive, and relatively simple method, enjoys wide application. In addition to some methodological contributions to the technique, the microhardness method has to be successfully used to gain a deeper understanding of the microhardness – structure correlation of polymers. A very attractive feature of this technique is that it can be used for the micromechanical characterization of some components, phases or morphological entities that are otherwise not accessible for direct determination of their hardness and modulus.[1]

These possibilities are very useful for the quantification of phase properties, for example, in semicrystalline polymorphic materials such as polypropylene. Besides the most common monoclinic α-modification of isotactic polypropylene (iPP), an amount of triclinic β-modification is often forming during polymer processing. This amount influences the mechanical properties; the material becomes tougher.[2] Pure β - phase or a high amount of it can be reached by adding a β-nucleating agent or by crystallization in a temperature gradient.[3,4] However, the β-phase is unstable upon stretching, which produces a transition to α-iPP or to the "smectic" form depending on whether the processing is above or below 60 °C.[5] With the transition, mechanical properties are changed and, therefore, knowledge of the phase properties and their interactions have an important practical meaning. This requires a measurement technique that enables the determination of phase and bulk properties on one specimen. The microhardness technique allows this by controlling the indentation load or the indentation depth. Its sensitivity to morphological changes has been shown in a number of scientific works: in the following some examples for PP materials are given. One can find possible ways of detecting the glass transition temperature and of quantifying hardness and modulus of the α- and β-spherulites.[6,7] Some other works deal with the correlation between hardness and mechanical properties. Chua and Henderson show that creep modulus and microhardness have the same time dependence after different ageing times.[8] Microhardness increases linearly with the degree of crystallinity and the elastic modulus is related to the microhardness by means of a power law.[9] Hardness and modulus of transcrystalline PP are described by Amitay-Sadovsky et al and Flores et al dealed with the influence of molecular weight and rubber content in PP/EPR blends.[10,11] Because of its practical meaning the polymorphic β-α transition is of a special interest. Results about its influence on microhardness are given in Ref. [5], mechanisms are discussed in Ref. [12,13].

The present work deals with the influence of crystallization temperature, cooling rate and annealing conditions on microhardness, indentation modulus and creep behaviour of ethylene/propylene (E/P) random copolymers as well as α- and β-spherulites in a homopolymer and an E/P random copolymer. The materials are unnucleated, the formation of β-spherulites occurs sporadically. Additionally the indentation creep behaviour of α- and β-nucleated PP has been investigated.

Experimental

The correlation between the properties determined in microhardness experiments and the copolymer content is shown on example of E/P random copolymers with 4, 6 and 8 mol% ethylene ($MFR_{230/2.16}$ = 8 g/10 min) as well as the appropriate polypropylene (PP) homopolymer ($MFR_{230/2.16}$ = 8 g/10 min) (Manufacturer: Borealis AG, Linz).

To investigate the properties of α- and β-spherulites in two-phasic materials, two unnucleated PP materials (Manufacturer: Borealis AG, Linz) are used: a high molecular weight homopolymer ($MFR_{230/2.16}$ = 0.4 g/10 min) and an E/P random copolymer with 4 mol% ethylene ($MFR_{230/2.16}$ = 8.6 g/10 min). Both materials tend towards sporadic partial β-crystallization (Figure 1).

Films of 40 - 50 µm thicknesses were prepared in a hot stage. For isothermal crystallization conditions these films were fixed between two thin glass sheets. The specimens were heated above the melting temperature and then suddenly immersed in a silicon oil bath maintained at constant temperatures in the range between 100 °C $\leq T_c \leq$ 150 °C. Annealing (after crystallization at a cooling rate of 10 K/min) was carried out in a nitrogen atmosphere for different times in the temperature range between 80 °C $\leq T_a \leq$ 150 °C for the homopolymer and between 80 °C $\leq T_a \leq$ 140 °C for the random copolymer. The films used for the indentation creep tests were made of α- and β-nucleated iPP (Mosten 58412, Chemopetrol, Litvinov) respectively and had a thickness of 100 µm. They were prepared in a hot stage at a cooling rate of 10 K/min.

The microhardness measurements were carried out on an instrumented indentation tester Nano Indenter® XP for determining hardness and indentation modulus values as well as on an Anton Paar MHT 4 conventional microhardness tester for determining the Vickers microhardness

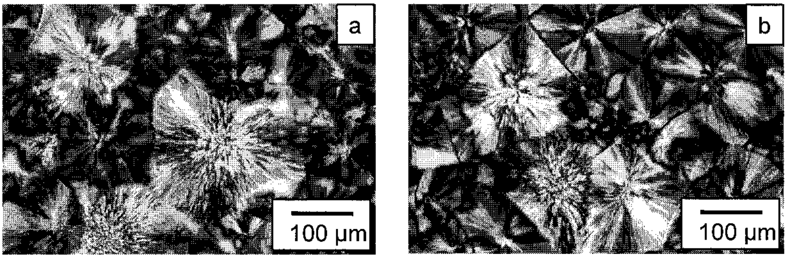

Figure 1. Spherulites of α- and β-type in the investigated PP materials: high molecular weight iPP (a) and E/P random copolymer with 4 mol% ethylene (b).

(MHV). For the MHV-measurements a maximum load of 10 mN and a holding time of 30 s were used. The maximum load was reached within 10 s. The indentation creep experiments were realized with holding times of 5, 30, 100, 10^3 and 10^4 s, maximum load was reached within 1 s. During the instrumented indentation tests, the holding time was also 30 s and the loading rate was 5% per second. The conditions for the loading and the unloading part were kept constant. From the unloading part, the elastic modulus was determined following Ref. [14].

For controlling the crystalline structure, a TA Instruments MDSC 2920 differential scanning calorimeter was used. The instrument was calibrated with high-purity metal specimens according to standard procedures. The measurements were performed with 10 K/min heating rate on samples of about 1 mg masses.

For light microscopy, a Zeiss Axiolab Pol was used.

Influence of Copolymer Content

Random copolymerization of PP is one possibility to change the properties of this material. It leads for example to an improved toughness and transparency but to a decreasing melting temperature and stiffness.[15] This change in properties can be reduced to a hindered crystallization in comparison to the homopolymer which is caused by the disordered macromolecules in the copolymer.

In the materials investigated, crystallization and melting temperature as well as crystallinity, determined by DSC ($\Delta H_m^0 = 207$ J/g), and glass transition temperature decrease linearly with increasing ethylene content (Figure 2). Simultaneously the chain mobility increases as the increasing relaxation peak shows. Additional, supermolecular spherulitic structure changes from more or less perfect large spherulites to smaller irregular ones and the WAXS diagrams indicate an increasing amorphous halo with formation of β- (4 mol% ethylene) and γ-phase PP (6 and 8 mol% ethylene).[16] All these effects indicate a lower tendency to crystallization which is connected with an increase in hardness and indentation modulus (Figure 3). The nearly linear correlation between hardness as well as indentation modulus and crystallintity is based on the linear correlation between crystallinity and copolymer content.

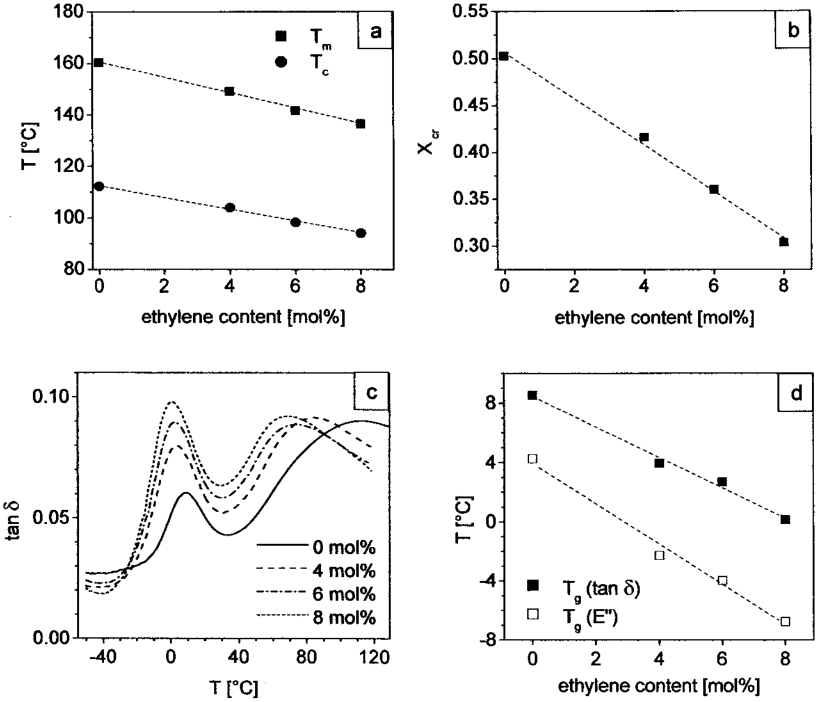

Figure 2. Dependence of melting, T_m, and crystallization temperature, T_c (a), crystallinity, X_{cr} (b), dynamic loss factor, tan δ (c) and glass transition temperature, T_g (d) on ethylene content.

For technical applications the knowledge of the influence of cooling rate on the mechanical properties is of a special practical meaning. It is well known that an increasing cooling rate leads to a decreasing crystallization temperature. Simultaneously the increasing ethylene content causes also a decrease in crystallization temperature and enthalpy (i.e. crystallinity) as it is shown in

Figure 2. The shape of the DSC-peaks changes in dependence of cooling rate and copolymer content (Figure 4). One characteristic is the formation of a wide peak at T ≈ 130 °C at low cooling rates in the copolymers with 6 and 8 mol% ethylene. This peak probably characterizes the melting of the γ-phase. Following the Ref. [17,18] γ-phase content increases with increasing comonomer content and decreasing cooling rate. Figure 5 shows that hardness as well as indentation modulus decrease with increasing cooling rate and ethylene content. For discussion of these results one has to consider the interaction between cooling rate and molecular structure on the one hand and crystalline structure on the other hand. The better the crystallization conditions, i.e. the lower cooling rate and ethylene content, the higher are the mechanical values. But, whereas cooling rates between 20 K/min and 100 K/min have no significant influence on the hardness values (Figure 5a) the indentation modulus decreases continuously following a linear dependence on the cooling rate in a single-logarithmic plot (Figure 5b).

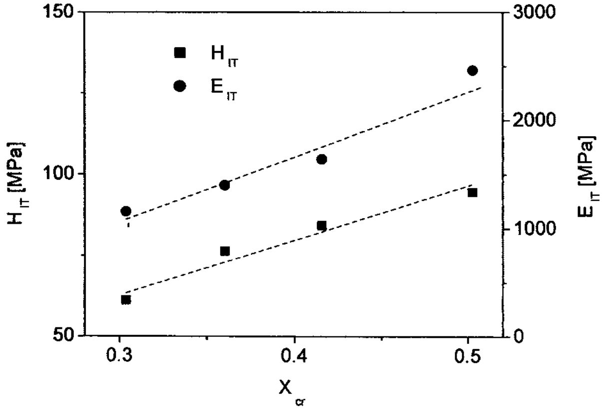

Figure 3. Influence of crystallinity, X_{cr}, on indentation hardness, H_{IT}, and indentation modulus, E_{IT}, in E/P copolymers.

The determined hardness and indentation modulus values can also be used for an evaluation of the toughness properties. For this, the hardness/modulus ratio, H/E, is used. Lawn et al and Baltá-Calleja could show that lower values of H/E characterize a higher plasticity that correlates with a higher impact strength.[19,20] Figure 6 shows the decreasing ratio H_{IT}/E_{IT} with increasing ethylene content, which describes an increasing toughness.

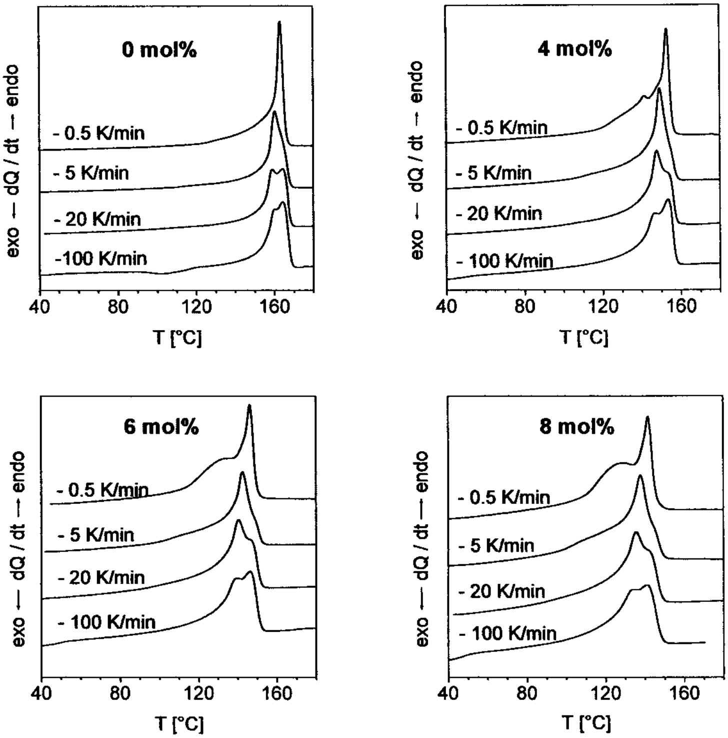

Figure 4. DSC traces of E/P copolymers after cooling with different cooling rates.

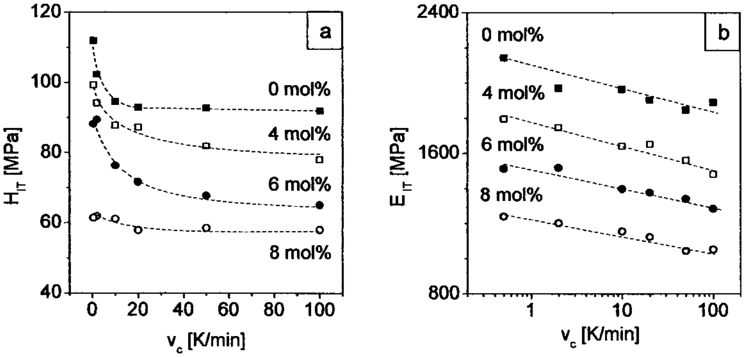

Figure 5. Dependence of hardness (a) and modulus (b) of E/P copolymers on cooling rate, v_c, and ethylene content.

Toughness values of the E/P copolymers increase under quasi-static as well impact loading conditions with increasing ethylene content. Thus a nearly linear decrease in the toughness value with increasing H_{IT}/E_{IT} ratio can be proved.[16]

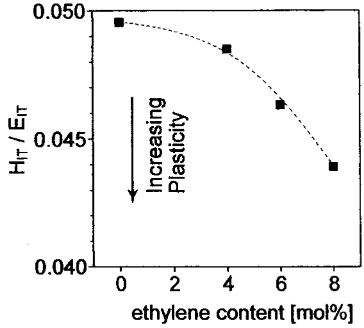

Figure 6. Correlation between hardness and toughness values.

Note that such correlations strongly depend on the failure process of the materials. Toughness behaviour of high impact polymers is strongly influenced by the so-called post-yield processes, which depend on phase interactions and molecular parameters like tie-molecule density. In polymers that tend to stable crack growth such correlation cannot be proved because stable crack growth processes in the propagation state are nearly independent on modulus and yield strength.

Comparison of the PP α- and β-phases

It is well known that β-crystalline phase polypropylenes are tougher than α-crystalline ones, with a lower elastic modulus, hardness and a stronger tendency to creep. This principal mechanical behaviour can be reduced to the different phase properties as shown in Figure 7. The load-indentation depth curves illustrate the lower hardness and the stronger creep tendency, which is caused by the higher chain mobility in the β-phase spherulites. The tan δ curve reflects this higher mobility at temperatures near and above the glass transition temperature.

Isothermal crystallization at different temperatures causes a lot of different effects. The most obvious are differences in spherulite appearance. An overview about the variety in spherulite appearance at different crystallization temperatures of the PP homopolymer and the copolymer with 4 mol% ethylene is given in Ref. [21].

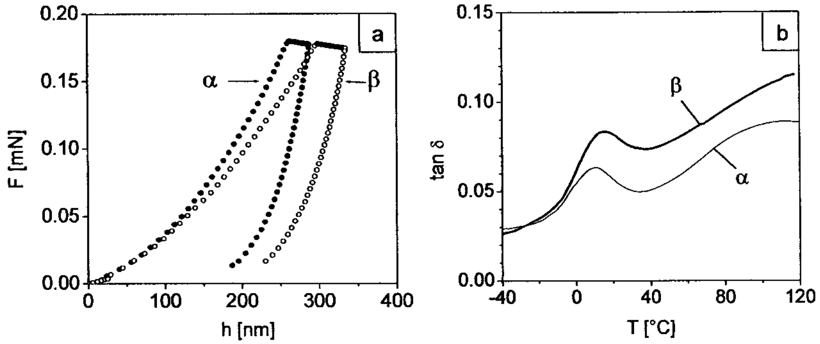

Figure 7. Typical load-indentation depth diagram of an α- and a β-spherulite (a) and dynamic loss factor of α- and β-nucleated PP (b).

In the homopolymer, as well as the random copolymer, an increasing crystallization temperature leads to an increasing microhardness in both phases (Figure 8b and d). In the homopolymer, the microhardness increase in the α- and the β-phases takes place with the same slope in the experimental region recorded. At temperatures $T_c > 120$ °C microhardness measurements using the chosen test conditions are impossible in the β-phase because of the small spherulites.[21] The DSC traces (Fig. 8a) also illustrate that isothermal crystallization influences the internal structure of the spherulites. The melting temperature increases with increasing crystallization temperature and the shape of the melting peak changes. Note that for discussion of these conventional DSC traces it has to be considered that some processes are overlapping: partial melting of the β-phase, β-α recrystallization and melting of the α-phase.[12,22] Besides this experimental effect, one has to consider that the materials are unnucleated and the β-content is very low. Thus, the DSC results can only give a qualitative idea about the changes. The changes in the shape of the melting peak indicate a shift of the lamella thickness distribution to higher values. At room temperature, microhardness increases linearly with the degree of crystallinity.[9] Thus, the microhardness values in the random copolymer are on a lower level. The β-phase shows a stronger increase in microhardness with increasing crystallization temperature (Figure 8d). This tendency can be related to the higher chain mobility during crystallization at a temperature with a smaller distance to the melting point (Figure 8c) and therefore to better possibilities for crystallization with a lower number of defects which can lead, e.g., to higher lamellae thicknesses. The leading

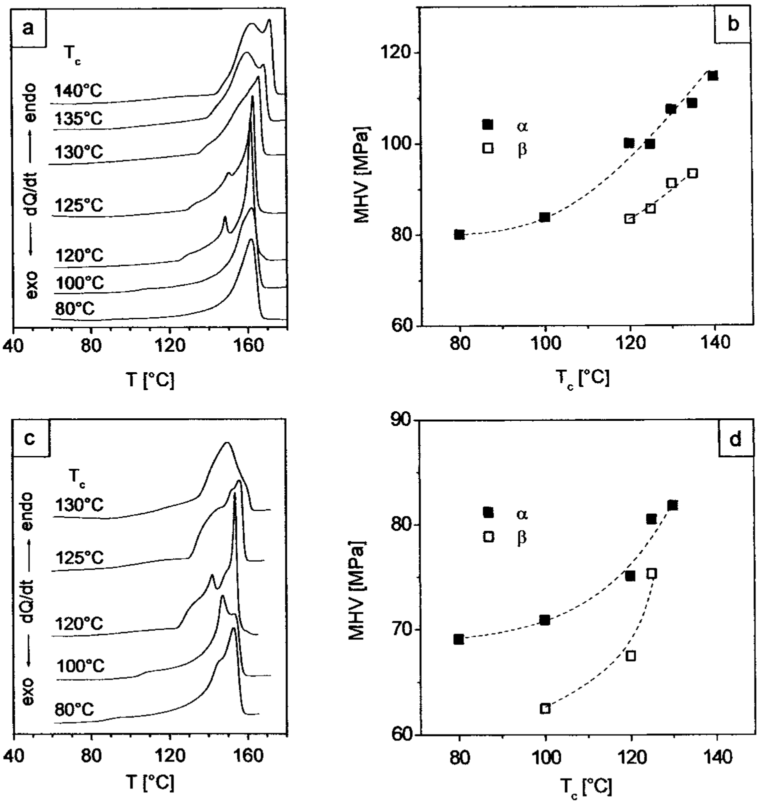

Figure 8. Influence of crystallization conditions on melting behavior (a, c) and microhardness (b, d) of the PP homopolymer (a, b) and the E/P copolymer with 4 mol% ethylene (c, d).

contributing factor toward the contrasting elastic and plastic properties of α and β seems to be mostly their different lamellar arrangements. The β-spherulites consist of parallel-stacked lamellae, tending to pack into bundles. On the other hand, the α-spherulites consist of an aggregate of lamellae that radiate from the central nucleus outward. Moreover, when the α-phase is crystallized at high undercooling, a secondary set of crystallites grows along the tangential direction of the spherulites and a so called "cross-hatched" network forms, which hinders the deformation of the amorphous component in the intercrystalline zone.[7,23-25] This model can be used for explanation of the general differences between the mechanical properties between α and β, but it is not sufficient for the strong increase in microhardness with increasing crystallization temperature in the copolymers.

Annealing leads to molecular rearrangements, dependent on the temperature, up to an increasing of crystallinity at annealing temperatures near the melting point. The time and temperature controlled molecular rearrangement processes lead to an increase in microhardness and indentation modulus. Simultaneously lamella thickness distributions change. The frequency distribution shifts to higher values and in dependence on annealing temperature it becomes more homogeneous. Under annealing conditions, the increase in microhardness and elastic modulus can be correlated with an increase in lamellae thickness.[21]

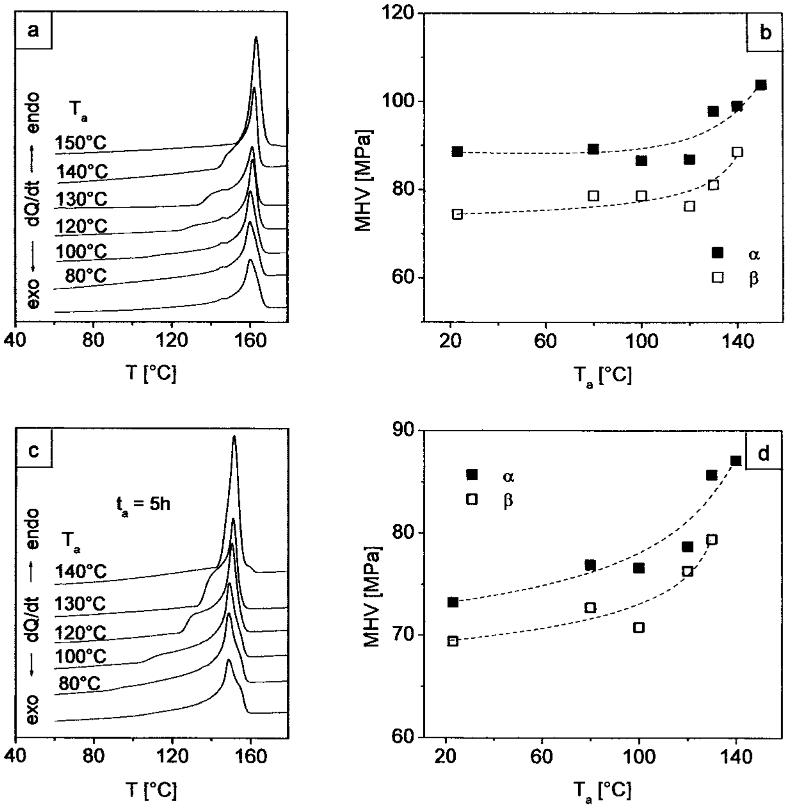

Figure 9. DSC traces and Vickers Microhardness, MHV, versus annealing temperature of the PP homopolymer (a, b) and the E/P copolymer (c, d).

The influence of annealing on the melting behaviour and the microhardness of the α- and the β-phase in the homopolymer is given in Figure 9. The melting curves of the annealed materials show shoulder-shaped characteristics that start at temperatures about the annealing temperature. High annealing temperatures lead to a steep melting peak. These shape changes are caused by the described lamellea thickness distribution change and shift to higher values. The melting peak of the β-phase can hardly be proved due to the low content in the used 50 μm thick films. The α- and the β-phases show a similar behaviour. As expected, microhardness increases at annealing temperatures above 120 °C (Figure 9b) and the values of the β-phase are lower. Because of the lower melting temperature of the random copolymer, the temperature range for annealing was adjusted. But on principle, no differences can be detected in annealing behaviour between the homopolymer and the random copolymer (Figures 9b and d). In both materials and both phases, an increase in hardness and modulus occurs only after an increase in lamella thickness. In Ref. [7] it is assumed that spherulites of each form have the same proportion of crystalline and amorphous phases. Considering this assumption, the present results indicate that in both phases the crystallinity changes in the same way. At higher annealing temperatures, an additional β-α transition cannot be excluded. This transition would also lead to an increase in hardness.

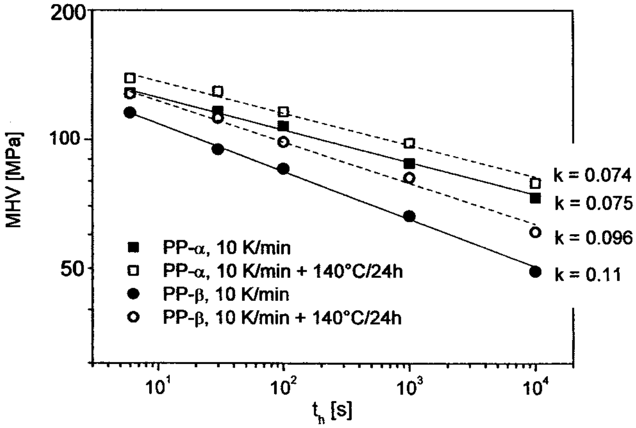

Figure 10. Indentation creep behaviour of α- and β-nucleated PP.

The example given in Figure 7 shows the higher tendency to creep of the β-phase. Therefore indentation creep experiments were realized on α- and β-nucleated PP materials (Figure 10). The nucleation leads to nearly the same crystallization temperatures and WAXS results prove a high β-content in the appropriate nucleated PP.[16] In a double logarithmic scale the dependence of hardness on holding time is nearly linear. Using the general creep law, hardness decrease can be described by Eq. 1.[1]

$$H(t) = H_0 \, t^{-k} \tag{1}$$

H_0 ... constant; t ... holding time ; k ... creep constant

The stronger decrease in hardness of the β-nucleated PP quantifies the stronger tendency to creep and the values of the creep constant are higher. Annealing for 24 h at $T_a = 140$ °C reduces the creep constant of the β-nucleated PP which indicates strong structural changes as described above including partial β-α transitions.

Conclusion

Microhardness measurements are a useful tool for characterization of supermolecular structure properties of semicrystalline polymers. On example of PP it has been shown that both hardness and modulus are sensitive indicators of morphology changes in such materials. Conventional and especially instrumented microhardness tests allow a mechanical characterization of miniaturized specimens which is an increasing demand of the basic as well as the industrial research.

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