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Fracture mechanics properties of polymorphic polypropylene

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Abstract

Polypropylene (PP) is a widely used thermoplastic and polymorphic polymer. Three different types of PP were prepared, namely non-nucleated, \(\alpha\)- and \(\beta\)-nucleated PP. These materials were pressed using different cooling rates to influence the degree of crystallinity \(\chi\) within the materials, which was determined by differential scanning calorimetry (DSC). The materials resistance against stable crack propagation was described by R-curves. The \(J\textsubscript{d}\textendash\Delta\alpha\) curves were determined using the instrumented Charpy impact test (ICIT) to apply single edge notch bending specimens (SENB) with a high loading velocity. The results show not only the influence of the cooling rate on the degree of crystallinity but also a correlation between the degree of crystallinity and the materials resistance against stable crack propagation. The lower the cooling rate of the material is the higher is the degree of crystallinity and the higher seems to be the materials resistance against stable crack propagation.

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1. Introduction

The structure and morphology of polymeric materials influence the material properties and especially their toughness very strongly. Polypropylene (PP) is a widely used polymorphic polymer, which can crystallize in several crystalline modifications, namely the α, β, and γ forms (Phillips and Wolkowitz (1996), Chiu et al. (2004)). All polymorphic forms can coexist and can be changed from one into another (Maier and Calafut (1998)). The α form is characterized by a helical structure in a monoclinic unit cell and is the thermodynamically most stable and therefore most common modification of PP (Maier and Calafut (1998), Foresta et al. (2001), Chiu et al. (2004)). The β form is more disordered than the α form and is hexagonal, having non-parallel, crossed lamellae (Maier and Calafut (1998), Marigo et al. (2004a), Marigo et al. (2004b)). The orthorhombic γ modification can be formed under high pressure (Maier and Calafut (1998)) or by using a nucleating agent (Marigo et al. (2004a), Marigo et al. (2004b)).

The crystal form influences the mechanical properties, due to the different physical and mechanical characteristics of the modifications of the crystallites (Marigo et al. (2004a), Marigo et al. (2004b)). PP with predominantly β crystals shows lower elastic modulus and yield strength at a given strain rate, but higher impact strength, strain of break values (Maier and Calafut (1998)), and higher crack toughness (Raab et al. (2001)) than materials with the α form of PP. It is known for a long time, that PP containing crystals in β forms show a higher toughness and ductility than PP containing only crystals in α form (Karger-Kocsis (1996)). Raab (Raab et al. (2001)) already showed, that the structure, crystalline modification and the amount of β phase influences the toughness of PP dramatically. With increasing content of β phase, the fracture toughness increases (Raab et al. (2001)).

The crystalline structure can be changed either by nucleating agents or by the cooling rate. Both methods are applied here by using α or β nucleation agent. Additionally, the pressed PP plates are cooled with different rates. This setting reflects the change of structure due to the cooling gradient within a thicker bulk material along the transverse section.

2. Materials

In this contribution the crystalline structure of isotactic PP (named PP, Mosten EH 801 by Unipetrol) was modified by nucleating agents to attain PP with crystallites in α-form (αPP, ADK) and β-form (βPP, NU100 Star). These materials were pressed to plates with length \( l = 170 \) mm, width \( w = 100 \) mm and thickness \( t = 4 \) mm. The plates were cooled with a rate of \( v_c = 1 \) K/min, \( v_c = 15 \) K/min and quenched, indicated by abbreviation -1, -15 and -Q, respectively. For quenching, the hot plates were transferred from the hot press into a cold press (ca. 15 °C) which was immediately closed and pressure applied. Specimens were prepared via cutting and milling to achieve a smooth surface.

3. Experimental

3.1. Differential scanning calorimetry DSC

The degree of crystallinity \( \chi \) of the materials was determined by differential scanning calorimetry (DSC) type Q100 from TA Instruments. The sample was heated up to 170 °C with a heating rate of 10 K/min, kept at this temperature for 10 min to eliminate previous structures and then cooled with different cooling rates \( v_c \). The cooling rates were 0.06 K/min, 0.1 K/min, 0.5 K/min, 1 K/min, 2 K/min, 5 K/min, 10 K/min and 20 K/min. The melting enthalpy of the PP was determined using the thermogram of the second heating and \( \chi \) was calculated by dividing the melting enthalpy by the melting enthalpy of completely crystalline PP \( \Delta H_m = 207 \) J/g (Ton-That et al., 2006). The calculation of the total amount of \( \chi \) of the different PP materials was done here without distinguishing between α- and β-form.

3.2. Instrumented Charpy impact test ICIT

The materials resistance against stable crack propagation was characterized by fracture mechanics means of R-curve. To create the R-curve, the \( J \) value \( J_{\Delta a} \) was determined and plotted as a function of stable crack length \( \Delta a \).
To determine $J_D$, the instrumented Charpy impact test (ICIT) with an impact velocity of 1 m/s combined with the stop-block method was used (Grellmann et al. (2012a), Grellman et al. (2012b), Grellman and Seidler (2013)). By ICIT, the load ($F$)–displacement ($f$) curves of unnotched and notched specimens (SENB with the initial notch length $a = 4.5$ mm) were recorded and the characteristic loads maximum load $F_{\text{max}}$, the load at the transition from elastic to elastic–plastic material behavior $F_{\text{gy}}$ and the corresponding displacements $f_{\text{max}}$ and $f_{\text{gy}}$ were determined. Based on the $F$–$f$ curves of the unnotched specimens, the elastic modulus $E_d$ and the yield stress under dynamic load $\sigma_d$ can be determined (equations (1) and (2)) with support span $s = 40$ mm, thickness $B = 4$ mm and width $W = 10$ mm.

$$E_d = \frac{F_{\text{gy}}s^3}{4BW^3f_{\text{gy}}}$$  \hspace{1cm} (1)

$$\sigma_d = \frac{3F_{\text{gy}}s}{2BW^2}$$  \hspace{1cm} (2)

By means of the recorded load ($F$)-displacement ($f$) curves of the notched specimens the total energy can be splitted into the amount of elastic energy $A_{\text{el}}$ and plastic energy $A_{\text{pl}}$ and $J_D$ calculated according to equation (3), with $\eta_{\text{el}}$ and $\eta_{\text{pl}}$ being the elastic and plastic part of the geometry function.

$$J_D = \eta_{\text{el}} \frac{A_{\text{el}}}{B(W-a)} + \eta_{\text{pl}} \frac{A_{\text{pl}}}{B(W-a)} \left[1 - \frac{(0.75\eta_{\text{el}} - 1)\Delta a}{W - a}\right]$$  \hspace{1cm} (3)

During the experiment the crack propagation was interrupted by the stop-block at different displacements of the specimens. Thereafter, the specimens were cooled in liquid nitrogen and cracked at a high velocity. The stable crack length $\Delta a$ was measured by light microscopy. $J_D$-$\Delta a$ curves were constructed following the rules of validity (Hale and Ramsteiner (2001), Grellman et al. (2012a)) and fitting them according to equation (4). From their slope the tearing modulus $T_J$, which describes the resistance to stable crack propagation, was derived (see equation (5)).

$$J_D = C_1\Delta a^{C_2}$$  \hspace{1cm} (4)

$$T_J = \frac{dJ}{d\Delta a} \frac{E}{\sigma_d^2}$$  \hspace{1cm} (5)

Additionally, the fracture surfaces were investigated by scanning electron microscopy (SEM) to characterize the deformation mechanics.

4. Results

4.1. Degree of crystallinity $\chi$

The degree of crystallinity $\chi$ determined by DSC of the different PP-materials depends on the cooling rate of samples as shown in Fig. 1. The crystallinity is high at very low cooling rates like 0.06 K/min and decreases with rising cooling rates, as expected. With increasing $v_c$, the time to form crystallites and their growth decreases, leading to a decrease of the amount of the crystalline phase. The total degree of crystallinity within the materials PP, $\alpha$PP and $\beta$PP differs only slightly, showing a little bit higher $\chi$ for the nucleated $\alpha$PP and $\beta$PP by trend. At cooling rates higher than 2 K/min the $\chi$–$v_c$ curve is almost constant within the tested range. Therefore, the difference of the total degree of crystallinity $\chi$ between the materials cooled with 1 K/min and 15 K/min is quite small.
4.2. Influence of the cooling rate on the resistance against stable crack propagation

The resistance against stable crack propagation is influenced by the cooling rate of the materials. The $J_d$-$\Delta a$ curves of PP prepared with different cooling rates are shown in Fig. 2a. At higher cooling rates, the $J_d$-$\Delta a$ curves of PP-15 and PP-Q are more flat than that of PP-1. At comparable stable crack propagation $\Delta a$, the $J_d$ of PP-1 is higher than $J_d$ of PP-15 and PP-Q. The $J_d$-$\Delta a$ curves of PP-15 and PP-Q are very similar. So the resistance of PP-1 against stable crack growth is higher than that of PP-15 and PP-Q, although deformation mechanisms seem to be very similar (see Fig. 2b).

In Fig. 3 the $J_d$-$\Delta a$ curves of the nucleated PP at different cooling rates are shown. The $J_d$-$\Delta a$ curves of $\alpha$PP (see Fig. 3a) show a strong influence of the cooling rate on the materials resistance against stable crack propagation. At a slow $v_c$ of 1 K/min (PP-1), $J_d$ is higher than $J_d$ of $\alpha$PP-15 and $\alpha$PP-Q at comparable $\Delta a$. But on the other hand, the curves of $\alpha$PP-15 and $\alpha$PP-Q show only marginal differences. The influence of the cooling rate on the resistance of $\beta$PP against stable crack propagation is almost negligible. The $J$ values $J_d$ of $\beta$PP-Q are at comparable stable crack propagation a little bit smaller by trend.

![Fig. 1. Degree of crystallinity $\chi$ as a function of the cooling rate $v_c$ measured by DSC](image)

![Fig. 2. (a) $J_d$-$\Delta a$ curves of PP prepared at different cooling temperatures; (b) Selected SEM pictures of PP-1 and PP-15](image)
The tearing modulus $T_{J}^{0.5}$ derived at $\Delta a = 0.5$ mm of the different materials depends on the cooling rate and the form of the crystals (see Fig. 4). The biggest differences of $T_{J}^{0.5}$ exist for the materials prepared with a cooling rate of 1 K/min. With increasing cooling rate and decreasing degree of crystallinity $\chi$, $T_{J}^{0.5}$ of nucleated $\alpha$PP decreases. This effect is most pronounced for $\alpha$PP. With regard to PP and $\beta$PP, the correlation between cooling rate and degree of crystallinity is diminished. Therefore, additional research about the crystalline structure and morphology is inevitable.

5. Conclusions

Three different types of PP were prepared. Virgin PP, PP with an $\alpha$-nucleation agent ($\alpha$PP) and PP with a $\beta$-nucleation agent ($\beta$PP) were pressed to plates using three different cooling rates, namely 1 K/min, 15 K/min and quenched. The degree of crystallinity $\chi$ was determined by DSC-measurements at a variety of cooling rates. To describe the materials resistance against stable crack propagation R-curves were made using the ICIT combined with the stop-block method and also the tearing modulus $T_{J}^{0.5}$ determined. It was shown, that the materials resistance against stable crack propagation correlates with the degree of crystallinity $\chi$ for PP and $\alpha$PP. The higher $\chi$ is the higher is the materials resistance against stable crack propagation. But this correlation cannot be proofed for $\beta$PP. The R-curves of $\beta$PP are here not influenced by $\chi$, but seem to depend on additional structural parameters.

Fig. 3. (a) $J_{F}$-$\Delta a$ curve of $\alpha$PP and (b) $J_{F}$-$\Delta a$ curve of $\beta$PP prepared at different cooling rates

Fig. 4. Tearing Modulus $T_{J}^{0.5}$ determined at $\Delta a = 0.5$ mm of the different PP-materials
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