FRACTURE BEHAVIOUR OF POLYPROPYLENE COPOLYMERS - INFLUENCE OF INTERPARTICLE DISTANCE AND TEMPERATURE

W.Grellmann[1], G.H.Michler[1], S.Seidler[2], K.Jung[1], I.Kotter[1], M.Gahleitner[3], J.Fiebig[3]

The toughness behaviour of heterophasic reactor grade propylene-ethylene copolymers (RAHECO®) under dynamic loading was studied. For this different fracture mechanics methods were applied, to determine values as resistance against unstable and stable crack growth. According to the results of instrumented impact tests at injection moulded SENB specimens, brittle-to-tough transitions were found in a temperature range of –20 °C up to room temperature. In situ HVEM investigations show the differences in the micromechanical behaviour of brittle and tough materials.

INTRODUCTION

In the last few years polypropylene (PP) has been able to continuos increase its market position by expansion of its application areas. This semi-crystalline thermoplastic material is characterised by a poor low temperature impact behaviour because of its relatively high glass transition temperature T_G. The incorporation of elastomer particles (for example spherical ethylene-propylene rubber (EPR) particles) offers a classical solution of this problem because the elastomer material has a glass transition temperature below the temperature of application. A very effective method to get PP materials with high toughness is the copolymerisation of the monomers directly in the reactor (1). On this way materials with a defined dispersed morphology can be achieved. The matrix material can be a PP-homopolymer or a copolymer of propylene with ethylene which is more tough than the homopolymer. Beside the amorphous EPR phase the modifier particles can also contain crystalline polyethylene. The PE lamellas are generally enveloped in the EPR phase which is useful as compatibilizing agent between the semicrystalline matrix and PE. The toughness properties of these heterophasic polymers are determined by morphological values

[1] Martin-Luther-University Halle-Wittenberg, Institute of Materials Science, Germany
[2] Vienna University of Technology, Institute of Materials Science and Testing, Austria
[3] PCD Polymere GmbH, Linz, Austria

like interparticle distance, particle diameter, the statistical distribution and the ratio of these values, the structure of the particles and also by the properties of the matrix material. There is a critical interparticle distance, which is dependent on the matrix material. The notched impact strength increases strongly, if the interparticle distance becomes smaller than this critical size (2). This effect dependends in addition on the temperature (3,4) and the particle diameter (5). If the interparticle distance is decreased, decreases also the brittle-to-tough transition temperature. So the toughness can be improved at low temperatures. Regarding the low temperature toughness, the aim of the present study is to analyse the impact behaviour of PP/EPR copolymers over a wide range of temperatures and compositions.

MATERIALS

The influence of matrix material and interparticle distance on the toughness behaviour was investigated in dependence on the temperature for two different random heterophasic copolymers (RAHECO®) based on PP. RAHECO® is a trade mark from PCD Polymere GmbH Linz. It is a combination of a propylene-ethylene-random-copolymer matrix and an EPR which contains PE lamellas. The effect which is achieved by the ethylene in the matrix material is an increase of the toughness and a decrease of the stiffness of the matrix material and also an improvement of the phase compatibility between matrix material and EPR phase by decreasing the interfacial tension. The molecular design of matrix and EPR becomes similar. So it is possible, to get materials with a finer morphology (1).
Two different RAHECO® materials were investigated. The matrix material of the first (RAHECO® 1) is a random-copolymer with 4 mol-% ethylene in the propylene chain. The disperse phase are core-shell particles with a PE core and a EPR shell. The matrix material of the second (RAHECO® 2) is a random-copolymer too but with 8 mol-% ethylene in the propylene chain. The EPR particles include up to five crystalline inclusions. The particles are smaller and finer dispersed than in the RAHECO® 1 material and the entire ethylene content is more than twice so much.
Both materials were melt compounded with the matrix material to lower particle concentrations in a single-screw extruder. The specimens were produced by injection moulding.

EXPERIMENTAL

The morphology of the different copolymers was analysed by transmission electron mi croscopy (TEM) on cryo-microtomed sections. The sections were stained with ruthenium tetroxid (RuO_4) vapour. The average particle diameter and average interparticle distance were determined by image analysis systems from the TEM micrographs (Fig. 1).
The instrumented Charpy impact test was used as a testing method to determine geometry independent fracture mechanics values as resistance against unstable and stable crack growth. The pendulum hammer speed was v_H = 1.5 m/s and the support span s = 40 mm. The dimensions of the specimens were: length, L = 80 mm; width, W = 10 mm and thickness, B = 4 mm. They were notched with a razor blade. The initial crack length for the determination of the fracture mechanical values as resistance against unstable crack growth was a_0 = 2 mm and for the determination of the fracture mechanical values as resistance against stable crack growth a_0 was 4.5 mm.

For the determination of the toughness behaviour the J-integral method was used because all materials exhibit elasto-plastic behaviour. The J_{Id} values as a resistance against unstable crack growth were determined according to the approximation method of Sumpter and Turner (ST) (6). For the quantification of the stable crack growth processes the multi-specimen crack resistance (R) curve method was used. The different amounts of stable crack growth were produced by varying the amount of deflection (stop block method). Stable crack growth, Δa, was quantified on fracture surface by light microscopy. The interpretation of the J_R curves follows the ESIS TC4 testing protocol (7).
For the determination of the instability values of the materials with dominating stable crack growth the tearing instability method was used and a J_{Qd}^{app} value was determined.

$$J_{Qd}^{app} = \beta_J \times T_{Jd} \tag{1}$$

For it the crack resistance curve (J-Δa-curve) is transformed into a J-T_J stability diagram. The tearing modulus T_J is calculated from Equation 2 (8).

$$T_J = \frac{dJ}{d(\Delta a)} \frac{E_d}{\sigma_{yd}^2} \tag{2}$$

The J_{Qd}^{app} value is the point of intersection between the J-T_J-curve and an origin straight line. The slope of this straight line depends on material behaviour as well as from the environmental and load conditions.
The micromechanical deformation structures at room temperature were observed by the high voltage electron microscope by in situ tensile tests of semi-thin sections with a thickness of 0.75 µm.

RESULTS AND DISCUSSION

In both materials the deformation behaviour changes from brittle to tough with decreasing interparticle distance and increasing temperature, whereas the Young's modulus E_d and the yield stress σ_{yd} , calculated from load-deflection-curves of unnotched specimens, linearly decrease with decreasing interparticle distance and increasing temperature (5).
In Fig.2, the J-Integral values as resistance against unstable crack growth are given as a function of interparticle distance A over a range of temperatures for the material with 4 mol-% ethylene in the matrix material. At low temperatures the material fails brittle generally and the influence of temperature is very low. Only at 20°C a brittle-to-tough transition occurs.
By extrapolation of the curves, critical interparticle distances A_{crit}, at which the increase of toughness begins, can be determined. In this material the critical interparticle distance is A_{crit} = 1.4 µm. Below this value tough materials failure occur, above the material fails brittle. In the temperature range explored a temperature dependent brittle-to-tough transition as a function of the interparticle distance could not be found. In contrast to this the brittle-to-tough transition in the material RAHECO® 2 occurs very rapidly at all temperatures (Fig.3). However, there is a obvious shift of transition to smaller interparticle distances with decreasing test temperature. The values of A_{crit} which are independent of specimen geometry due to the specimen shape and the experimental method applied (5), are shown in Fig.4 versus temperature. The linear approximation in Fig. 4 seems to agree

well with the results of Borggreve (3) and Margolina (4). The critical interparticle distance increases strongly with temperature and is independent of glass transition temperature of PP. The constants of the linear approximation are material specific constants. They are influenced by the molecular parameters of the used matrix and rubber material.
Stable crack growth at 20°C can be observed if the interparticle distance is lower than 1µm. A decrease of interparticle distance causes an increase of the resistance against stable crack initiation, $J_{0,2}$ and the tearing modulus T_J (Fig. 5).
Fig.6 shows HVEM micrographs of in situ deformed semi-thin sections of two fractions of the RAHECO® 2 material. The used materials were chosen on the basis of the results at room temperature, since the in situ tensile tests were performed at the same temperature. Material (a) deforms in a brittle manner at this temperature, whereas material (b) fails tough. At the beginning of micromechanical in situ tests, comparable deformation behaviour can be observed stretching appropriate sections on the HVEM stage. Cavitation of particles within the EPR layer was always the first step of deformation. In the brittle material (Fig. 6a), the ligaments between the cavitated particles deform by shear yielding processes forming cavitation bands, which are inhomogenously distributed within the section. They only arise at isolated positions, whereas the deformation structures in the tough material are distributed over the whole specimen (Fig. 6b). Here craze like structures were created on planes perpendicular to the deformation direction, with more extensive fibrillation of the ligaments. So, the transition of impact behaviour form brittle to tough can be correlated to a transition of micromechanical deformation structure from cavitation bands to croids (a combination of craze and voids) (9).

CONCLUSIONS

The knowledge of relations between structure and mechanical properties of heterophasic PP/EPR/PE reactor copolymers enable the manufacturer to produce materials with certain morphologies by altering processing conditions. Related to the present results, the structure of the reactor blends could be adjusted, so that the material deforms in toughened manner at practical operation temperatures.

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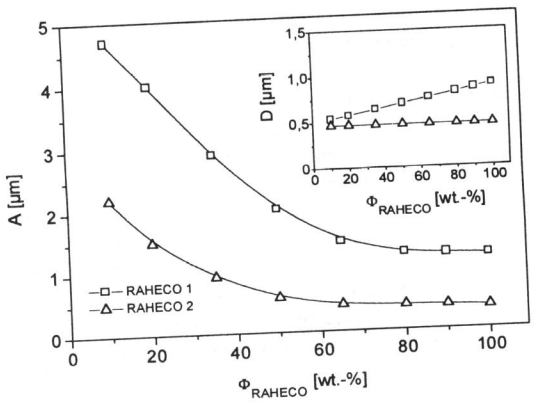

Fig. 1: Average particle diameter D and average interparticle distance A as a function of the RAHECO weight fraction for both materials

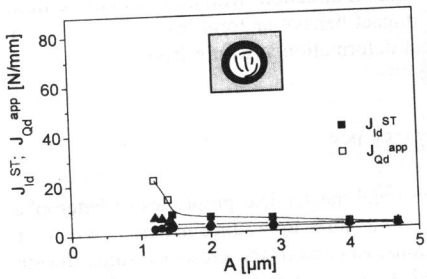

Fig. 2: J-integral values versus interparticle distance A for RAHECO® 1 in dependence on temperature

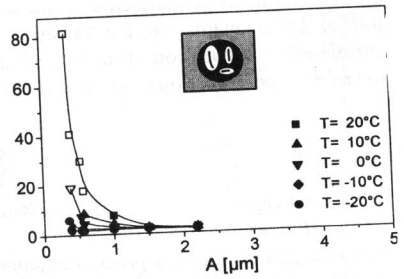

Fig. 3: J-integral values versus interparticle distance A for RAHECO® 2 in dependence on temperature

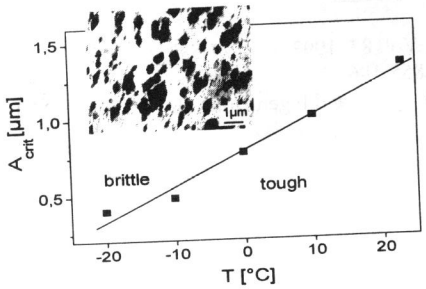

Fig. 4: Critical interparticle distance versus temperature

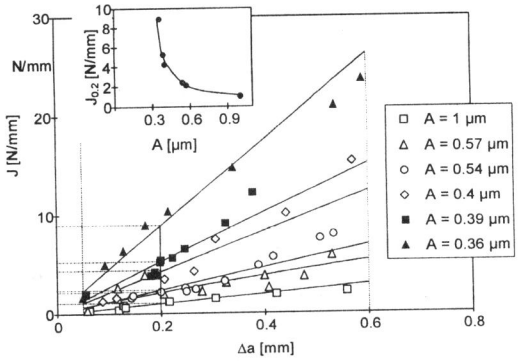

Fig. 5: J_R curves and technical crack initiation values $J_{0.2}$ as a function of interparticle distance A for RAHECO® 2 at room temperature

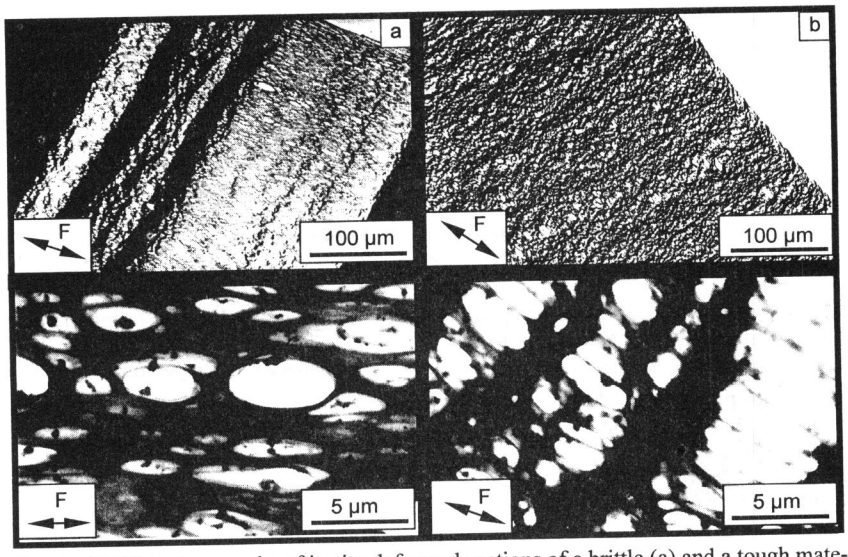

Fig. 6: HVEM micrographs of in situ deformed sections of a brittle (a) and a tough material (b)