BRITTLE-TO-TOUGH TRANSITION IN TOUGHENED POLYPROPYLENE COPOLYMERS

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ABSTRACT

The toughness behaviour of polypropylene copolymers was investigated in dependence on the morphological parameters of multi phase materials, i.e. particle diameter and interparticle distance and the ratio of both, to get morphology-toughness correlations. For it two heterophasic reactor grade propylene-ethylene copolymers (RAHECO®) were diluted with propylene-ethylene random copolymers to get materials with constant EPR/PE-particle diameter but various interparticle distances. According to the results of instrumented impact tests, 'brittle-to-tough' transitions were found at different temperatures. The critical interparticle distances shift linearly over the observed range of temperature. Critical interparticle distances could be determined not only in the region of predominantly unstable crack growth but also in the region of predominantly stable crack growth.

INTRODUCTION

Polypropylene is characterized by a poor low temperature impact behaviour because of its relatively high glass transition temperature. Modifying by elastomer particles improved the fracture toughness. PP/EPR-blends can be more effectively produced by polymerisation of the monomers directly in the reactor. On this way, it is possible to get materials with distinctive, well dispersed morphologies.

The size, shape and spatial packing of elastomer particles varied by manufacturing and processing conditions are important parameters in controlling the micromechanical and mechanical behaviour of PP/EPR-blends and copolymers.

Wu [1] explained that a critical interparticle distance or critical matrix ligament thickness exists below which the notched Izod impact strength of nylon blends increases rapidly. He defined this increase of notched Izod impact strength as 'brittle-to-tough' transition and the critical value of interparticle distance, A_c, as a specific parameter of the material. Borggreve [2] and Margolina [3] showed that the critical interparticle distance in nylon blends is strongly affected by rate, method of loading and test temperature. They proved an approximately linear dependence of the critical interparticle distance on temperature.

The aforementioned theories about the nature of transition from brittle to tough are based on conventional notched impact strengths. That means the part of stable crack growth is included in the 'notched impact strength', and it is not possible to separate the stable and the unstable part of the crack growth process. There is a possibility that the controversial discussion about the nature of transition from brittle to ductile mode of fracture is due to the fact that the crack growth behaviour is unknown.

Fracture mechanics tests for unstable crack growth as well as stable crack growth are applied to determine 'brittle-to-tough' transitions influenced by morphological parameters in the region of both, predominant stable and predominant unstable crack growth.

EXPERIMENTAL

Fracture mechanics characterization

A Charpy impact tester with 4 J work capacity was used and load (F)-deflection (f) curves were recorded [4-6]. Semiconductor strain gauges were used to measure the impact load. The deflection was recorded with the help of a photo-optical system. The dimensions of the injection moulded single edge notched bend (SENB-) specimens were length L = 80 mm, width W = 10 mm and thickness B = 4 mm. The specimens were notched with a razor blade (notch tip radius = 0.2 µm). For this specimens the test conditions were optimized by simulating specimen loading by finite element method [6]. Experimental parameters were initial crack length a = 2 mm (a/W = 0.2), support span s = 40 mm (s/W = 4) and pendulum hammer speed ν_H = 1.5 ms^{-1}. With regard to the elastic-plastic material behaviour of polymers for the determining of J-integral values the evaluation method of Sumpter and Turner [7] is especially suited for assessing the toughness behaviour. A separation of the deformation energy of test specimen, A_G, in an elastic share, A_{el}, and a plastic share, A_{pl}, is necessary for the calculation of J-integral values correspond to this method. J_R-curves were determined by application a multiple specimen method, the stop-block technique [8] where the deformation process is characterized by dominant stable crack growth. Different amounts of stable crack growth are produced by varying the limitation of deflection.

Whereas the specimen geometry is the same like in the unstable region, the optimized test conditions are changing. The initial crack length amounts to 4.5 mm (a/W=0.45). The experimental results in [9,10] show also the necessity of the energy separation.

The constructed J_R-curves enable the quantification of the critical value at the onset of stable crack initiation, for instance the technical crack initiation value, $J_{0.2}$, and also the determination of material resistance against stable crack growth with the Tearing modulus, T_J.

$$T_J = \frac{dJ}{d(\Delta a)} \frac{E_d}{\sigma_d^2} \tag{1}$$

Additionally the investigated materials were characterized by:

- dynamic-mechanical analysis (DMA), to determine the glass transition temperature, T_g, of the amorphous PP-phase and EPR-phase,
- differential scanning calorimetry (DSC), to detect the crystallinity and the crystallization temperature, T_k
- further mechanical tests, to determine the flexural modulus and the notched Charpy impact strength of the materials,
- transmission electron microscopy, to analyse the morphology of the materials (interparticle distance, A, particle diameter, D). The microtomed ultrathin sections were stained with rutheniumtetroxid (RuO_4) vapour.

Materials

For the investigations two different propylene copolymers (heterophasic ethylene-propylene random copolymers (RAHECO$^{®}$) [11]) were used, which are designated as material 1 and material 2. The matrix material of material 1 is an ethylene-propylene random copolymer with 4 mol.-% ethylene in the propylene chain. The ethylene-propylene rubber (EPR-) particles are core shell particles with a PE-lamellae core and an EPR-shell. Material 2 is also a combination of an ethylene-propylene random copolymer matrix and EPR-particles, but with 8 mol.-% ethylene in the propylene chain of the matrix material. The EPR-particles contain one and more crystalline PE-inclusions here. The particles are smaller and finer dispersed than in material 1.

Both basic materials were melt compounded with the matrix material to lower particle concentrations in a single-screw extruder. The random copolymers used for the dilution were ethylene-propylene copolymers with comparable molecular structures as the matrix material. The specimens were produced by injection-moulding.

RESULTS AND DISCUSSION

Basic characterization

Mechanical and thermal behaviour as well as the characteristic material parameters are given in Table 1.
The phase separation during copolymerisation is indicated by separately detected tan δ peaks of PP- and EPR-glass transitions. The PP-glass transition temperature of 1 °C (material 1) or -5 °C (material 2) respectively is not affected by blending processes. In contrast to that, a T_g-shift of EPR for material 2 was observed. For the description of the mechanical behaviour the flexural modulus E_f, the flexural strength at periphal strain of 3.5%, $\sigma_{f3.5}$, according to ISO 178 [12] and the Charpy impact strength a_{cN} of notched specimens according to ISO 179 [13] were used. Whereas the flexural modulus and the flexural strength decrease with increasing RAHECO®-content, the Charpy impact strength of both materials increase with increasing RAHECO®-content. In the range from 35 to 65 wt.-% the toughness strength of material 2 increases rapidly and above 65 wt.-% it is nearly constant.

TABLE 1

SUMMERY OF CHARACTERISTIC MATERIAL PARAMETERS

RAHECO®-content (wt.-%)	$T_{g\ EPR}$ (°C)	$T_{k\ PP}$ (°C)	E_f (MPa)	$\sigma_{f3.5}$ (MPa)	$a_{cN\ (+23°C)}$ (kJ/m²)	A (µm)	D (µm)	A/D
Material 1								
100	-51.4	110	586	15.3	19.5	1.20	0.90	1.33
90	-52.0	111	589	15.4	16.3	1.30	0.74	1.76
80	-51.7	109	641	16.8	14.7	1.40	0.73	1.92
65	-52.8	109	686	18.2	11.4	1.45	0.80	1.81
50	-52.2	108	745	19.7	9.8	2.00	0.66	3.03
35	-53.8	108	798	21.3	8.1	2.90	0.65	4.46
20	-54.3	107	861	23.0	6.6	4.00	0.54	7.41
10	-52.2	106	899	24.2	6.3	4.70	0.54	8.70
0	-	104	1009	27.1	4.8	-	-	-
Material 2								
100	-47.1	98.8	329	8.9	69.0	0.36	0.47	0.77
90	-46.8	98.8	363	9.9	70.6	0.39	0.50	0.78
80	-47.6	98.5	401	10.8	70.3	0.40	0.48	0.83
65	-49.9	97.3	459	12.5	68.4	0.54	0.45	1.20
50	-51.3	97.7	514	14.1	54.6	0.57	0.46	1.24
35	-51.8	97.2	583	16.0	16.6	1.00	0.49	2.04
20	-54.4	96.5	652	17.8	11.4	1.50	0.46	3.26
10	-55.0	96.2	697	19.1	9.4	2.20	0.47	4.68
0	-	94.3	730	21.9	7.6	-	-	-

Adjustment of matrix and elastomer viscosity in combination with random copolymerisation of PP with ethylene, which decreases the surface tension between the two phases, realises a very fine morphology of the materials. For material 1 the average interparticle distance decreases from 4.7 µm at 10 wt.-% RAHECO® to 1.2 µm at 100 wt.-% RAHECO®. Material 2 shows also a decrease of average interparticle distance with increasing RAHECO®-content from 2.2 µm to 0.36 µm. The average particle diameter is constant for material 2. For material 1 an increase of particle diameter from 0.5 µm to 0.9 µm with increasing RAHECO®-content was observed.
The elastomer particles are well dispersed in the matrix in both materials, as illustrated in the TEM-micrographs (Figure 1). The particles appear dark owing to staining with RuO_4, Material 1 shows approximately a core shell structure. The higher magnification represents the internal structure of EPR/PE-particles. The PE-inclusion is surrounded by a dark shell of EPR, which providing to a good adhesion between matrix and modifier particle (Figure 1a).

The particles in material 2 are smaller and finer dispersed than in material 1. The internal structure of the particles consist of one and more PE-rich inclusions, which are not clearly separated from each other. Within the inclusions, single PE-lamellae exist. The PE-rich inclusions are surrounded by a dark amorphous shell of EPR too (Figure 1b).

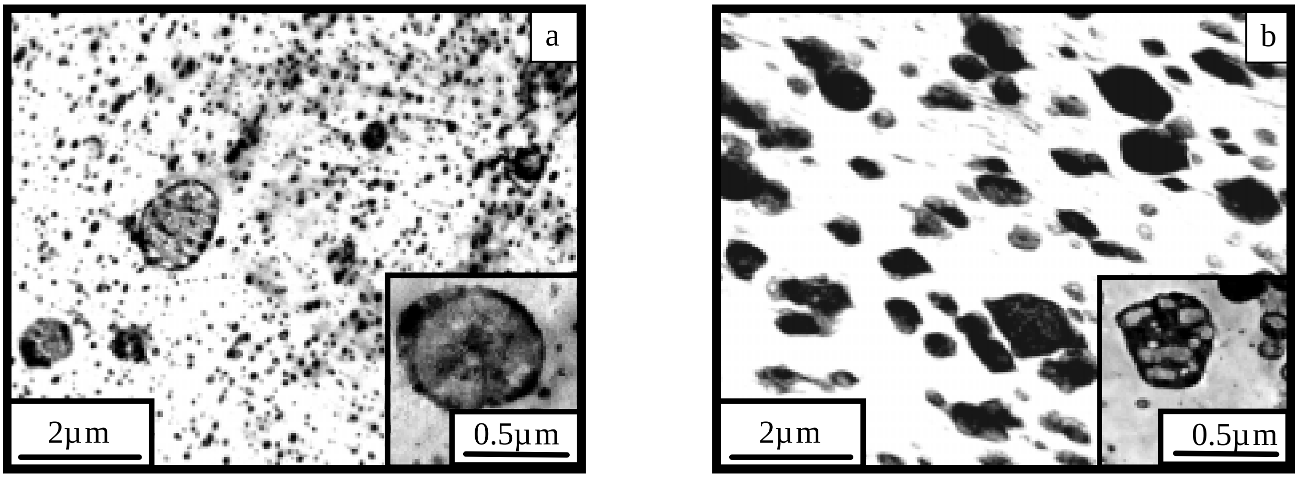

Figure 1: TEM-micrographs of particle distribution and internal structure of EPR/PE-particles of material 1 (a) and material 2 (b)

Fracture mechanics tests

The crack resistance values against unstable crack growth, J_{Id}^{ST}, in dependence on interparticle distance and test temperature (-20 °C ≤ T ≤ 20 °C) for material 2 are given in Figure 2. For temperatures above T = 0 °C a very strong rise of toughness properties can be observed. The dependencies in Figure 2a explain that the determination of quantitative dependencies of crack resistance values against unstable crack growth with conventional experimental fracture mechanics values, e.g. J_{Id}^{ST}, is impossible due to a change in the dominant crack growth mechanism from unstable to stable. In the stable region no specimen fracture occurs (for instance at T = 20 °C and interparticle distances of $A \leq 0.54$ µm) and therefore no J_{Id}^{ST}-values can be determined.

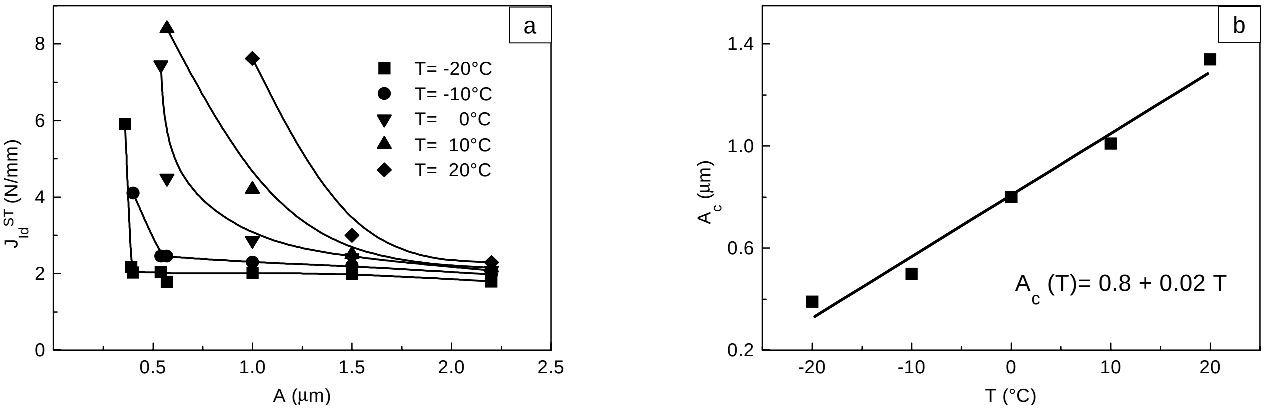

Figure 2: Influence of interparticle distance, A, on the J_{Id}^{ST}-values (a) and critical interparticle distance, $A_{c,}$ of the 'brittle-to-tough' transition versus temperature (b) for material 2

The results for material 1 show a similar material behaviour. The toughness increasing at T = 20 °C is much lower than in material 2. The 'brittle-to-tough' transition is dependent on the interparticle distance and the test temperature too, and critical interparticle distances, A_c, can be determined. A linear dependence between /A_C/ and test temperature was found for both materials [16]. Differences between the constants of the linear fits should be influenced by molecular parameters of the different matrix materials and different particle structures.

From the temperature dependence of J_{Id}^{ST} it becomes clear, that the mechanical behaviour changes in a characteristic manner. Typical load(F)-deflection(f) curves of materials with different interparticle distances are shown in Figure 3. In the materials two transitions in the load-deflection behaviour can be observed. A sharp notched PP-specimen exhibits brittle failure under impact conditions at room temperature. The material behaviour can be characterized as liner-elastic. The first transition occurs from pure elastic (a,b) to elastic-plastic material behaviour (c) with decreasing interparticle distance. In both cases the materials break in a brittle manner. The crack growth is predominant unstable. The second transition to predominantly stable crack growth without specimen fracture is characterized by a large increase in toughness and the 'brittle-to-tough' transition can be determined. At the end of this process only stable crack growth without specimen fracture occurs (Fig. 3d). All materials with such load-deflection behaviour are not considered by the determination of critical interparticle distances (Figure 2).

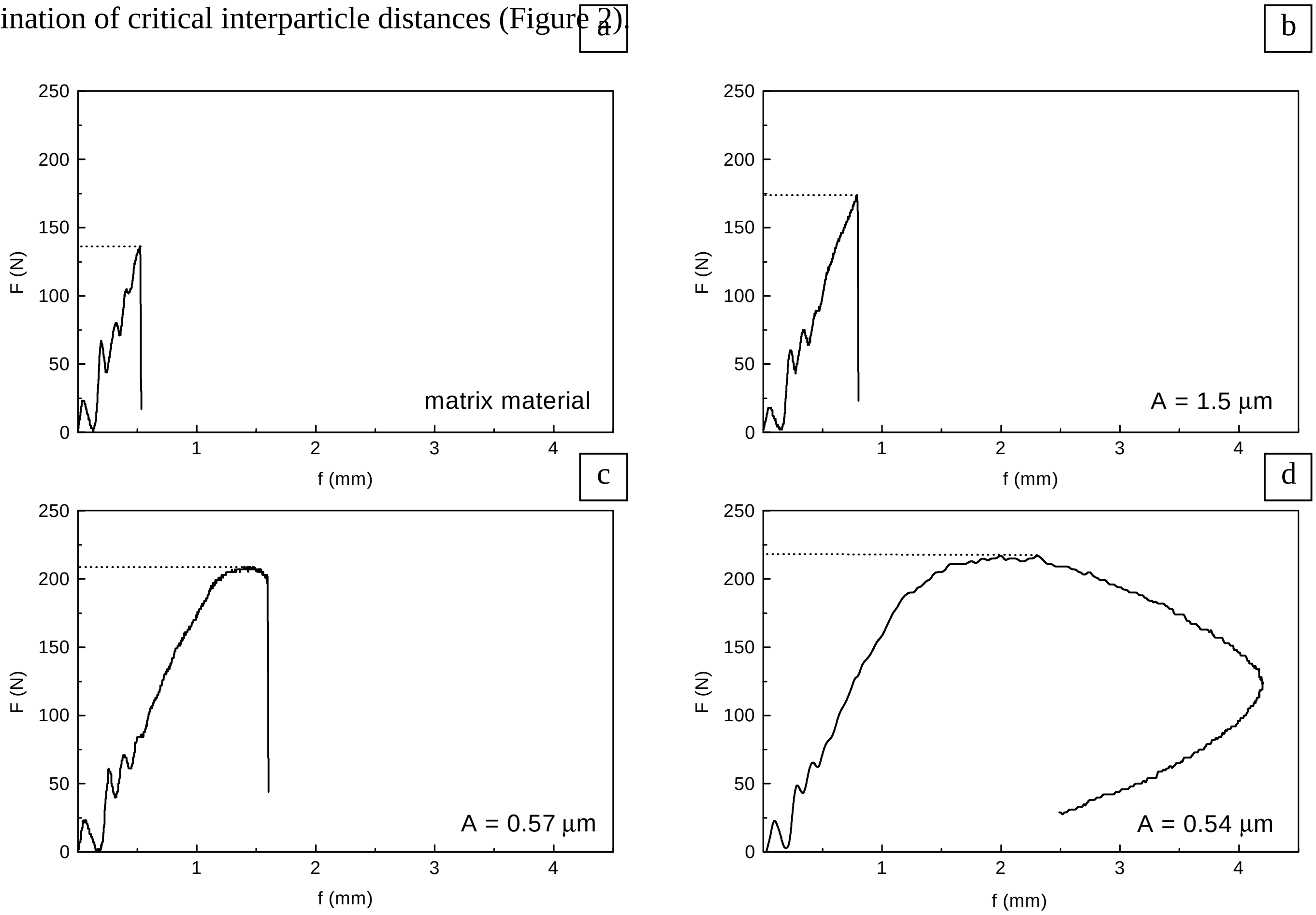

Figure 3: Load (F) - deflection (f) curves of selected materials recorded in the instrumented Charpy impact test (material 1)

The determination of fracture mechanics values as resistance against stable crack growth requires the determination of crack resistance curves.

The J_R-curves of material 1 at T = 30 °C for different interparticle distances are given in Figure 4. With decreasing interparticle distance an obviously increasing of the technical crack initiation values. $J_{0.2}$ as well as the Tearing modulus, T_J, can be proved. In the right part of Figure 4 the $J_{0.2}$-values as a function of the interparticle distance at T = 30 °C are shown. The crack initiation values show a strong decrease in dependence on interparticle distance between 1.2 and 1.5 µm and the determination of a critical interparticle distance at A_c = 1.4 µm is possible.

On principle the dependencies $J_{0.2}$ = f (A) and J_{Id}^{ST}= f (A) show a similar behaviour. That means two transitions occur, one in the region of predominant unstable crack growth and a second in the region of predominant stable crack growth.

This second value is clearly smaller than the value in the region of unstable crack growth. Below both 'critical interparticle distance' a characteristic increasing of toughness values occurs.

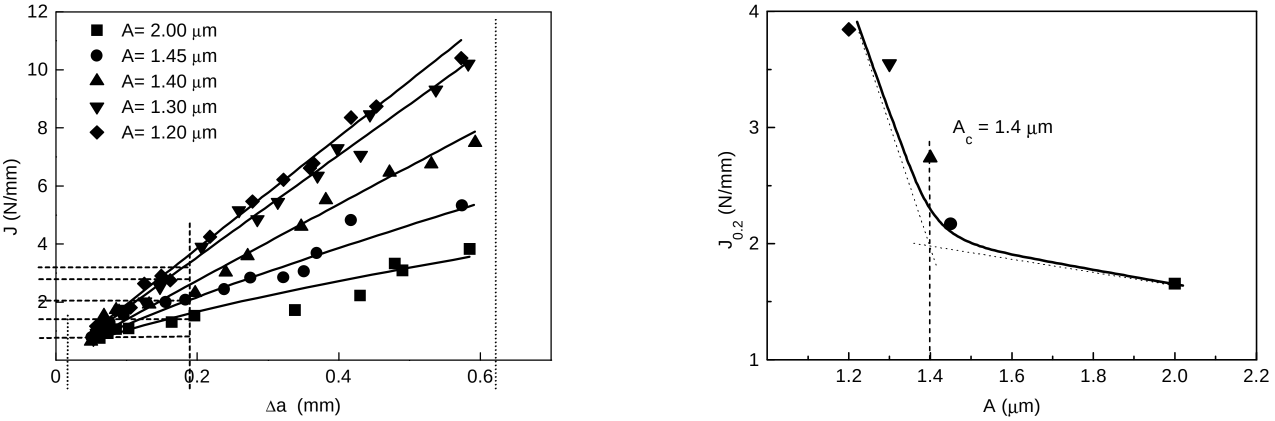

Figure 4: J_R-curves of material 1 (T = 30 °C) and technical crack initiations values, $J_{0.2}$, versus average interparticle distance, A

SEM-observations (Figure 5) show that cavitation is the main deformation mechanism in these materials below the second 'critical interparticle distance'. The materials differ only in the number of cavities that means in the intensity of cavitation process (Figure 5 a, predominant unstable crack growth below first 'critical interparticle distance'; Figure 5 b, predominant stable crack growth in the region of second 'critical interparticle distance'). A further decreasing of interparticle distance results in an overlapping of cavitation and fibrillation processes (Figure 5c, above second 'critical interparticle distance'). The quantity as well as the quality of deformation process changes. The cavitation process itself can be reduced to deformation processes in the EPR-shell or on the interface EPR/PE respectively.

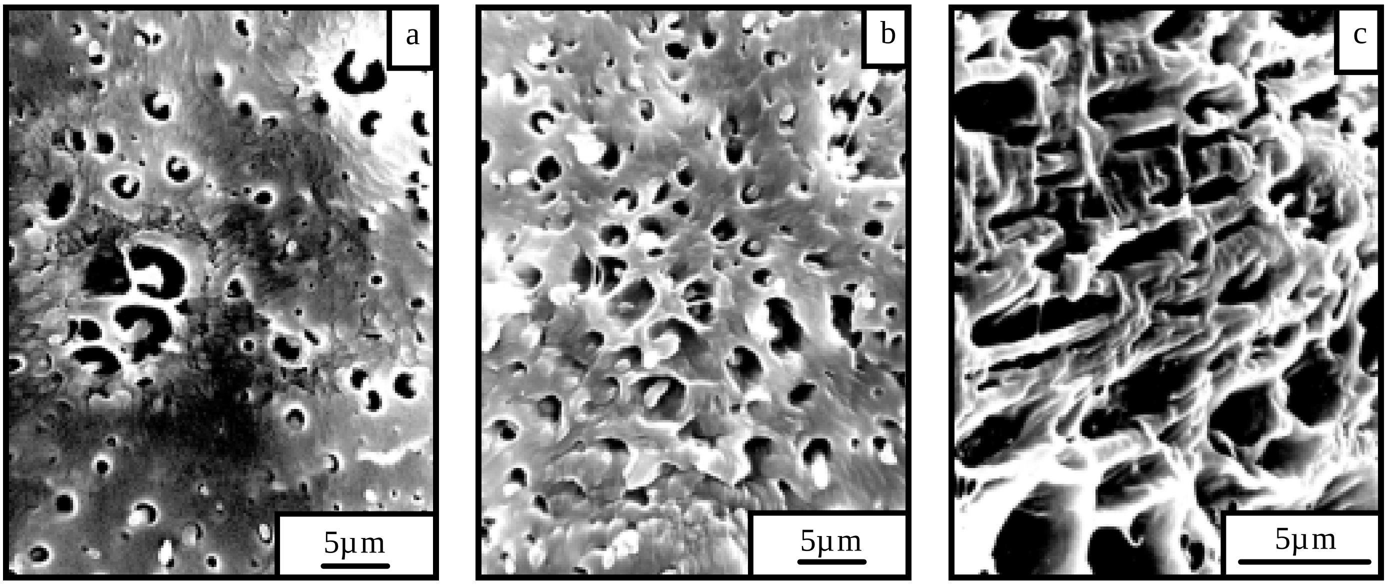

Figure 5: SEM-micrographs of material 1: a) cavitation in the damage zone, unstable crack growth (A=2.9 µm), b) cavitation in the region of stable crack growth (A=1.4 µm), c) cavitation and fibrillation in the region of stable crack growth (A=1.3 µm)

Material 2 shows comparably results. With decreasing interparticle distances technical initiation values and Tearing modulus increase and a second 'critical interparticle distance' can be determined too. The calculated value ($A_c \approx 0.4$ µm) is clearly smaller than the value in the region of unstable crack growth.

The effect of a second 'critical interparticle distance' presented as 'tough-to-high-impact' transition was found in other PP-blends at different test temperatures [4,16].

On the basis of the different crack growth mechanisms and therefore on the basis of different fracture mechanics values a 'brittle-to-tough' and a 'tough-to-high-impact' transition can be proved. For a direct comparison of both materials it is necessary to use the $(A/D)_c$-ratio (ratio of critical interparticle distance and particle diameter) . Figure 6 shows the $(A/D)_c$-ratio in dependence on temperature for both materials. The two characteristic dependencies in the region of predominant unstable crack growth and in the region of predominant stable crack growth are represented. In both materials a stronger dependence on temperature for the unstable than for the stable crack initiation values can be proved. On the basis of the results given in Figure 6 two additional effects are evident:

- In material 2 toughness increasing starts above the glass transition temperature of the EPR and in material 1 above the glass transition temperature of the PP. Altogether the toughness increasing in material 2 is much higher than in material 1.
- To change the predominant crack growth mechanism from unstable to stable in the more brittle material (material 1) a stronger reduction of interparticle distance is necessary than in the more tough material (material 2). That means the differences between these values becomes larger.

The toughness optimization in the region between the glass transition temperatures of the EPR and the PP, i.e. low temperature toughness, requires an adjustment of particle diameter and interparticle distance to matrix material.

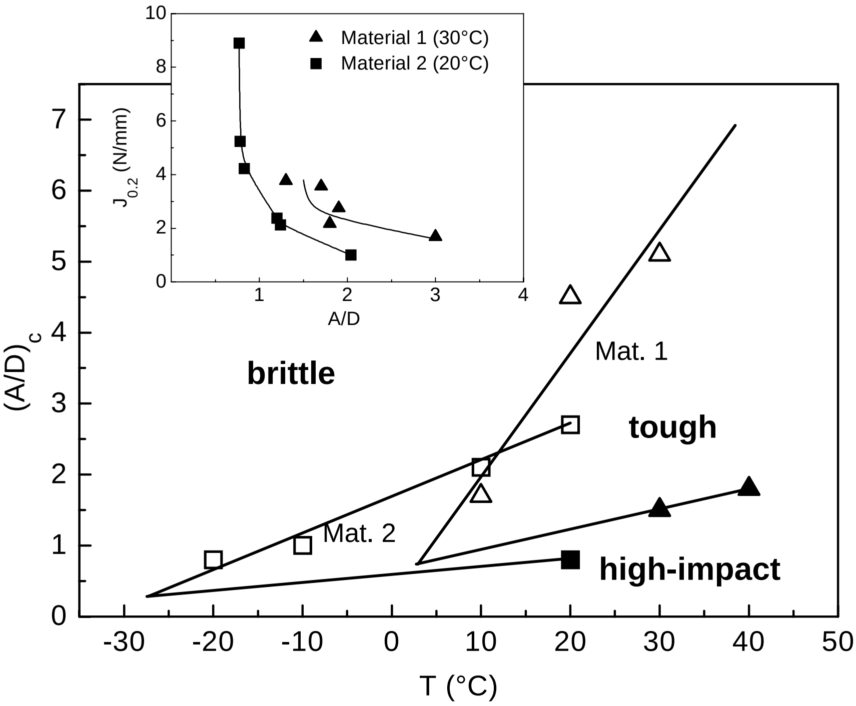

Figure 6: Dependence of critical ratio, $(A/D)_c$, on temperature in the region of stable and unstable crack growth

The results of the fracture mechanics tests indicate a validity of Wu`s percolation theory [1] if predominant unstable fracture occurs. In the region of predominant stable crack growth the theory by Margolina et al [3] is valid. This theory is based on the consideration that changes from plane strain to plane stress conditions in thinner matrix ligaments (i.e. with decreasing interparticle distance) reducing the critical stress for matrix yielding.

In both theories [1,3] the matrix deformation processes are primarily considered. As can be proved for example in [15] the particles play a decisive role in the deformation process. Therefore it is necessary to include the deformation processes of the particles in the discussion. These considerations must be specified and their validity must be checked on other materials.

CONCLUSIONS

- Based on optimized test conditions it is possible to determine geometry independent fracture mechanics values as resistance against stable and unstable crack growth. These intrinsic values enable a micromechanical interpretation of toughness mechanisms.
- The crack resistance behaviour is strongly affected by the critical interparticle distances and the temperature. Critical interparticle distances can be determined in the region of predominant unstable crack growth as well as in the region of predominant stable crack growth.
- With increasing temperature the 'brittle-to-tough' transition in the region of unstable crack growth shifts to higher interparticle distance linearly .
- The structural parameters of morphology, like interparticle distance or $(A/D)_c$-ratio have a stronger influence on crack growth behaviour than on the crack initiation behaviour.

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