Application of the crack resistance concept to the toughness characterization of high-impact thermoplastics

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SUMMARY: Heterophasic reactor-grade polypropylene-ethylene copolymers were diluted with a propylene-ethylene random copolymer to obtain materials with a constant EPR/PE-particle diameter but various interparticle distances. In addition to these copolymers, PP/EPR blends were investigated. According to the results of instrumented impact tests, brittle-to-tough transitions were found at different temperatures. In the materials with PP matrix, two transitions in the load-deflection behaviour were seen. The first transition occurs from the elastic to the elastic-plastic material behaviour, the second from the unstable to stable crack growth. "Critical" interparticle distances could be determined in the region of predominantly unstable crack growth as well as in the region of predominantly stable crack growth. With increasing test temperature, both transitions shift to higher interparticle distances. From this theoretically similar behaviour of fracture mechanical values quantifying different proportions of the crack growth process, one can conclude that different processes must be occurring.

INTRODUCTION

An important recent development in polymer materials concerns the extension of their applicability. Possible ways are filling, reinforcing and the development of polymer blends as well as copolymerization. The applicability of the crack resistance concept for toughness optimization has been examined on some PP (polypropylene)/EPR (ethylene-propylene rubber) blends and copolymers.

Polypropylene is characterized by poor low-temperature impact behaviour because of its relatively high glass transition temperature T_g. The incorporation of elastomer particles offers a classic solution to this problem. PP blends with increased toughness were first developed by melt-compounding PP with various polyolefins[1)] or prefabricated ethylene-propylene copolymers[1,2)] as well as ethylene-diene terpolymers[3)]. Particularly, PP/EPR blends have been more effectively produced by polymerization of the monomers directly in the reactor[4)]. In this way, it is possible to get materials with distinctive, well dispersed morphologies. Besides the

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amorphous EPR phase, the modifier particles in these so-called "reactor blends" can also contain crystalline PE (polyethylene). The PE lamellas are generally enveloped in the EPR phase, which is useful as a compatibilizer between the semicrystalline PP matrix and PE.

The size, shape and spatial packing of elastomer particles produced by manufacturing and processing conditions are important parameters in controlling the micromechanical[5)] and mechanical[6)] behaviour of PP/EPR blends. Wu[7)] explained that a critical interparticle distance or critical matrix ligament thickness, A_C, exists, below which the notched Izod impact strength of nylon blends rapidly increases. He defined this increase in notched Izod impact strength as the brittle-to-tough transition and the critical value of A_C as a specific parameter of the material. However, Borggreve et al.[8)] and later Margolina[9)] show that the critical interparticle distance in nylon blends is strongly affected by the rate and method of loading and test temperature. They found, for instance, that A_C indeed decreases approximately linearly with temperature.

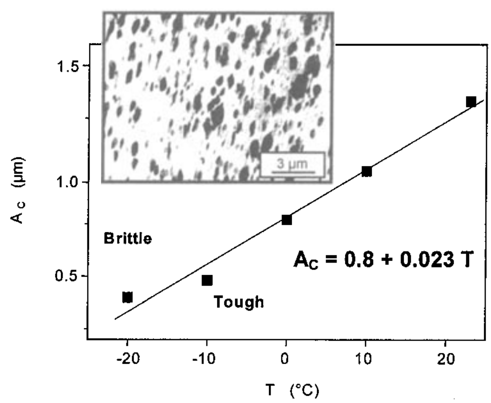

Fig. 1: Critical interparticle distance A_C for brittle-to-tough transition in RAHECO® materials versus test temperature T. The values of A_C result from extrapolation of experimental data (J versus average interparticle distance) given in[12)].

The nature of transition from the brittle to ductile mode of failure is controversially discussed. Besides Wu's percolation theory[7)], another interpretation[8,10,11)] exists, which assumes that the stress field overlap begins if the interparticle distance is smaller than A_C. Some of these aspects are discussed in[12)] on the example of the brittle-to-tough transition in a RAHECO® material. The results (see Fig. 1) seem to agree well with those of Borggreve[8)] and Margolina[9)]. The critical interparticle distance A_C increases strongly with temperature and is independent of T_g of PP. On the basis of experimental data, an empirical equation can be derived (see Fig. 1), which differs from the formula suggested by Margolina[9] due to the special nature of the materials analysed. Hence, the constants in this equation should be influenced by the molecular parameters of the matrix and the rubber material used. This dependence was determined from fracture mechanical values as resistance against unstable crack growth. From the temperature dependence of the critical interparticle distance, it could be seen that the mechanical behaviour changed in a characteristic manner. The experiments were performed using an instrumented Charpy impact test at an impact speed of 1.5 m/s.

Figure 2 shows typical load (F) - deflection curves of PP/EPR blends and copolymers with different interparticle distances. In the materials with the PP matrix, two transitions in the load-deflection behaviour were seen. A sharp-notched PP specimen exhibited brittle failure under impact conditions. The material behaviour can be characterized as elastic. With increasing EPR content, i.e., decreasing interparticle distance, a transition from elastic to elastic-plastic material behaviour initially occurs.

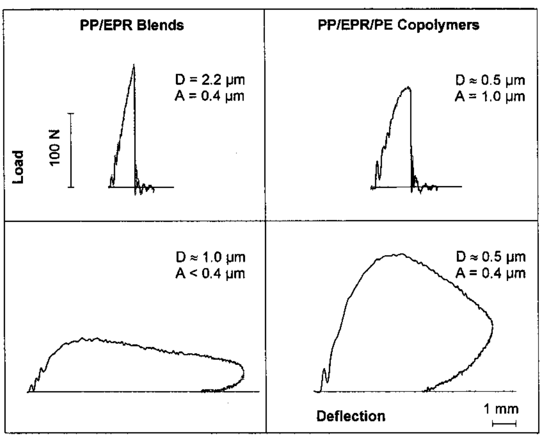

Fig. 2: Load (F) - deflection (f) curves of selected materials recorded during instrumented Charpy impact tests

In both cases, the specimens break in a brittle manner. The crack growth is predominantly unstable. Decreasing the interparticle distance further causes an enhancement in the plastic deformation processes. The second transition occurs to produce predominantly stable crack growth. This transition is characterized by a large increase in toughness[12,13] and the brittle-to-tough transition can be determined. At the end of this process, only stable crack growth without specimen fracture occurs. The deflection at the end of the experiment decreases (Fig. 2) due to reflection of the pendulum striker from the specimen. All materials with such load-deflection behaviour are not considered by the determination of critical interparticle distances (Fig. 1). A toughness characterization in this region requires the application of the crack resistance concept.

The determination of fracture mechanics values as resistance against stable crack growth requires the determination of the connection between a fracture mechanics loading parameter and the stable crack growth, Δa. The concepts of yield fracture mechanics (i.e., J-integral and COD concept) are well established for the determination of the loading parameters in the case of elastic plastic material behaviour. Between the limits of J- or δ-controlled stable crack growth, the J_R or δ_R curves, respectively, characterize the crack resistance in the ductile failure area. Thus it is possible to quantify the stages of stable crack growth: crack tip blunting, crack initiation and stable crack growth (Fig. 3).

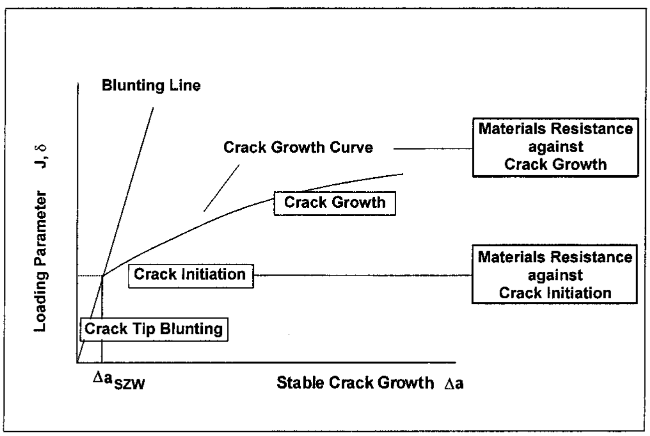

Fig. 3: Crack resistance curve of yield fracture mechanics (schematic) including the crack tip blunting, crack initiation and stable crack growth processes

EXPERIMENTAL

A Charpy impact tester PSW 0.4 with 4 J work capacity was used for the measurements, and load deflection diagrams were recorded. Figure 4 shows the test equipment with stop-block arrangement. Some details about the method and the determination of fracture mechanics values are reported in[13,14]. Single-edge notched (SENB) specimens were used for the study. The dimensions of the specimens were: length, L = 80 mm, width, W = 10 mm and thickness, B = 4 mm. The experimental parameters were set as follows: notch depth, a = 4.5 mm, support span, s = 40 mm, pendulum hammer speed, v_H = 1 m/s. A notch tip radius of ≈ 0.2 μm was realized using a razor blade. For R-curve determination the multiple-specimen-stop-block technique was used (see Fig. 4). Critical technical crack initiation values were determined on the basis of the procedure for determination of the crack resistance behaviour with the instrumented Charpy impact test[13].

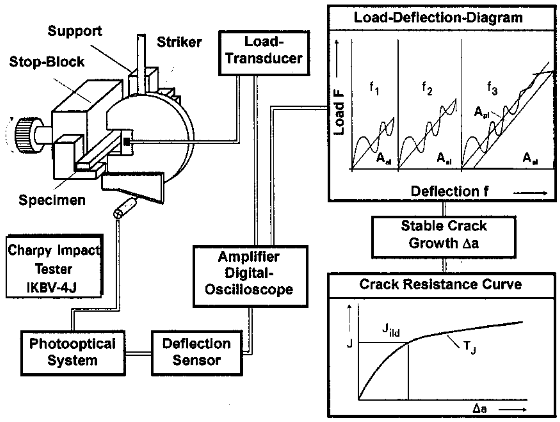

Fig. 4: Test equipment with stop block arrangement

MATERIALS

The PP/EPR blends and copolymers were kindly supplied by the PCD Polymere AG. The blends were melt-compounded with EPR, the copolymers with the matrix material in a single-screw extruder. It was therefore possible to get copolymers with a nearly constant particle diameter and different interparticle distances.

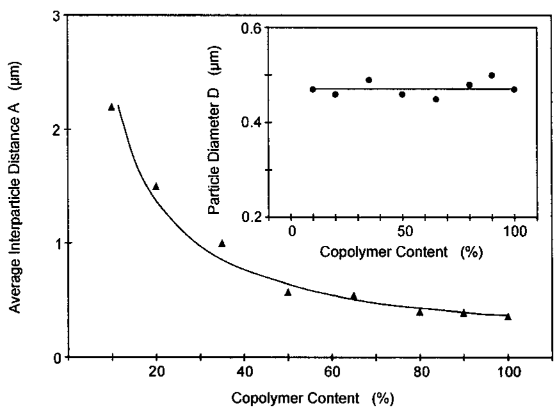

Fig. 5: Results of the quantitative morphology analysis (copolymer RAHECO®)

Figure 5 shows the results of the quantitative morphology analysis on example of the random heterophasic copolymer RAHECO®. In the PP/EPR blends, the particle diameter is also nearly constant, at 2 μm, the interparticle distance decreases with increasing EPR content from 2.3 μm (5 % EPR) to 0.4 μm (30 % EPR). The blends with 50 % of EPR show the beginning of the phase transition; at this EPR content, a quantitative morphology analysis was not possible.

Figure 6 shows DMA curves for two blends and two copolymers. Separately detected tan δ peaks of the PP and EPR glass transition indicate that in both materials, phase separation takes place.

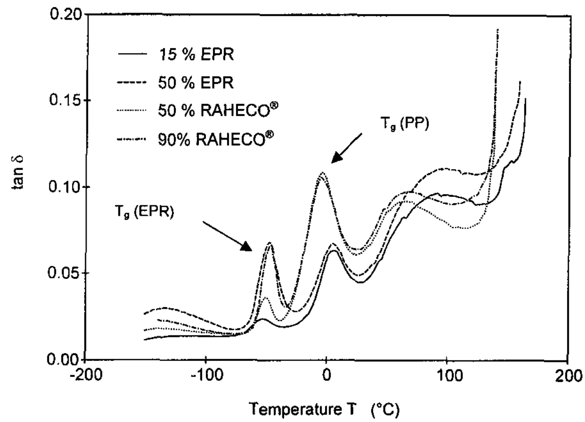

Fig. 6: Loss factor tan δ as a function of temperature

The maximum in the tan δ versus temperature curves for PP does not shift with increasing EPR content. The glass transition temperature of PP is, consequently, not affected by blending or copolymerization processes. The differences between the glass transition temperatures of the blends and the copolymers are caused by different PP materials.

RESULTS AND DISCUSSION

Figure 7 shows the J_R curves of the PP/EPR blends. The technical crack initiation values $J_{0.2}$ show a strong decrease between 30 % and 45 % of EPR. The brittle-to-tough transition of these materials was determined at 15 % of EPR[13)]. That means, a second transition region exists, but the processes which cause this second transition are not clear. Comparable results were found for different copolymers (Figs. 8 and 9). The copolymers have different PP matrix materials with a different crystallinity, melt index, etc., and, therefore, different toughness properties, and a different particle morphology. However, the effect of a "tough-to-tougher" transition can be found in all materials at different test temperatures (see Fig. 9).

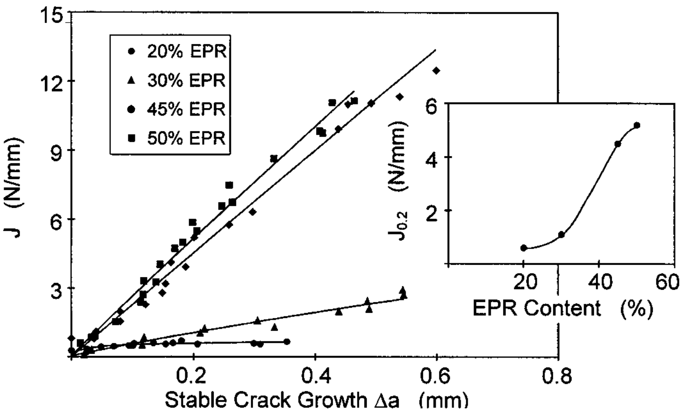

Fig. 7: J_R curves of PP/EPR blends; technical crack initiation values $J_{0.2}$ versus EPR content

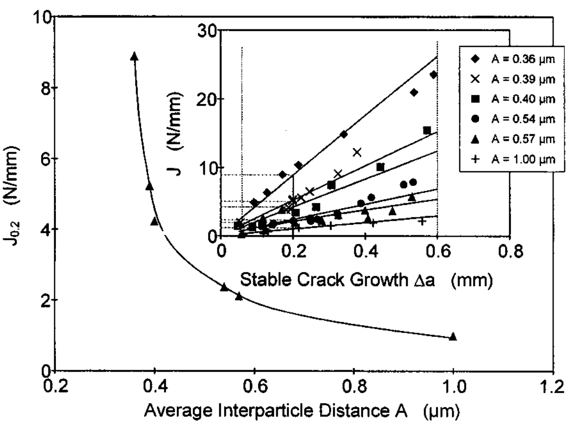

Fig. 8: Critical technical crack initiation value $J_{0.2}$ versus average interparticle distance; J_R curves of the material RAHECO®

The influence of the test temperature is comparable with the results in unstable crack growth. With increasing test temperature, the transition shifts to higher interparticle distances and at room temperature, the transition is not so strongly marked. From this theoretically similar behaviour of fracture mechanical values quantifying different proportions of the crack growth process, one can conclude that different processes must be occurring.

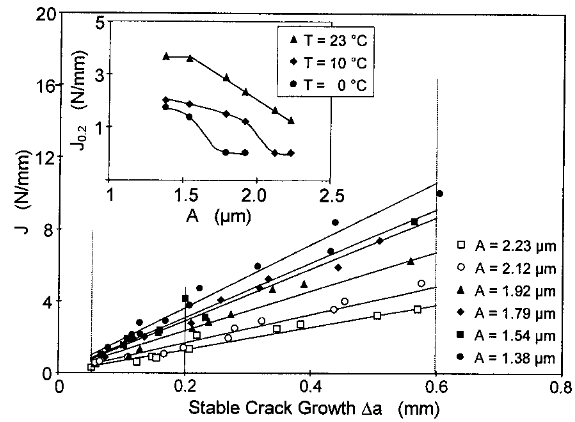

Fig. 9: J_R curves of the heterophasic copolymer HECO (T = 23 °C); critical technical crack initiation values as a function of average interparticle distance at different test temperatures

It is well known that the toughness behaviour is slightly affected by the stress state of the specimen. It is also known that the plane strain state favours the process of stable crack growth. On the other hand, the results from literature[7-9] are based on conventional impact tests. In conventional impact tests, specimen fracture must occur otherwise no values can be determined. That means only a part of stable crack growth is included in the value "notched impact strength". On the basis of the conventional notched impact strength, it is not possible to separate the stable and the unstable part of the crack growth process.

The aforementioned theories[7-11,15,16] about the nature of transition from brittle to tough are based on conventional notched impact strengths. There is a possibility that the controversial discussion is due to the fact that the crack growth behaviour is unknown. The results of the fracture mechanics tests indicate a validity of Wu's percolation theory[7] if crack growth is predominantly unstable. In the region of predominantly stable crack growth, the theory of Margolina et al.[15,16] is valid. This theory is based on the consideration that changes from plane strain to plane stress conditions in thinner matrix ligaments (i.e., decreasing interparticle distance) reduce the critical stress for matrix yielding.

In all theories[7-11,15,16], the matrix deformation processes are primarily considered. As can be proved for example in[12], the particles, especially in the copolymers, play a decisive role in the deformation process. It is therefore necessary to include the deformation processes of the particles in the discussion. All these considerations must be specified and their validity must be checked on other materials.

OUTLOOK

The results of the present study show that fracture mechanical material testing is an important contribution to the development of polymers. Quantitative investigations of the correlations between toughness and morphology should be performed to enable an effective material design. These investigations should be carried out under consideration of the damage and micromechanic models. For this, additional investigations into the influence of the structural parameters on the crack initiation behaviour and systematic investigations into the links between structure and property are necessary.

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