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Micromechanical deformation processes in toughened and particle-filled semicrystalline polymers: Part 1. Characterization of deformation processes in dependence on phase morphology

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Relationships between morphology and micromechanical deformation processes in various toughened and particle-filled semicrystalline polymers with different types of modifier particles have been investigated by high voltage electron microscopy and scanning electron microscopy using *in situ* tensile techniques. From the study of phase structure of modifier particles, two morphological standard types are classified: the binary system (homogeneous modifier particles are dispersed in the matrix), and the ternary system (heterogeneous modifier particles are dispersed in the matrix). Taking into account these categories and the phase adhesion between the modifier particles and the matrix, micromechanical deformation processes have been characterized. As initiation sites of plastic deformation the microvoid formation is considered, which plays an important role for the activation of further plastic deformation of matrix material during deformation processes. According to the morphology of modifier particles this microvoid formation is caused by either cavitation in the stretched rubbery shell/inside particles or debonding at the interface between particles and matrix. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

For many applications of polymeric materials mechanical properties are decisive or at least of non-negligible importance. Improvement of toughness is of particular interest, since the toughness of polymeric materials is an important selection criterion for many applications. Impact toughness or toughness of a material in general reflects the degree of energy absorption from the beginning of mechanical load to final fracture. By incorporating well-defined moderate amounts of dispersed modifier particles with different physical properties in a polymer matrix, its toughness can be improved[1]. Toughness is, however, one of the most complex properties and difficult to control, because it is greatly influenced by many morphological and micromechanical parameters[2–4]. Therefore, it is of fundamental importance for the development of polymer systems with improved mechanical properties and toughness, in particular, to understand the relationship between the morphology and deformation behaviour of modified polymer systems. Tremendous efforts towards understanding and revealing the mechanisms responsible for the improvement of toughness in modified polymer systems have been made in the last two decades[1,4–18]. A currently suggested and commonly accepted view on the role of modifier particles is that these inclusions alter the stress state in the material around the particles and induce extensive plastic deformation in the matrix, such as multiple crazing[1,4,19], shear yielding[9,11,20], crazing with shear yielding[5–7] and rubber particle stretching or tearing and debonding at the inorganic filler particles[14,17,21] etc. Because the stress condition around the particles is particularly important in activating matrix plastic deformation, the effects of rubber size[1,4,22–24], interparticle distance[25–30] and particle cavitation behaviour[30–36] have received considerable attention. Although a considerable amount of experimental work has confirmed the presence of rubber cavitation and the sequence of cavitation/shear yielding, the necessary condition of cavitation prior to shear yielding for toughness is still in debate. It is well known that the phase structure of the modifier particles plays a decisive role in the toughening mechanism. However, the effects of these different morphologies in the modified heterogeneous polymer blends upon the toughening mechanism are far from clear at present. In the present work, the influence of the morphology of various modifier particles in different semicrystalline polymers on the micromechanical deformation processes has been studied. In particular, micromechanical deformation processes are investigated in relation to

- the type of modifier particles
- the phase morphology of modifier particles
- the variation of interfacial adhesion between modifier particle and matrix.

To study the phase structures, the morphological parameters and the micromechanical deformation processes, various electron microscopes (TEM, transmission electron microscope; SEM, scanning electron microscope; HVEM, high voltage electron microscope) were used. It is to be noted that higher acceleration voltage in the HVEM

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(1000 kV) leads to a lower inelastic scattering of the electrons. Consequently, the thickness of the specimens can be increased, and less irradiation damage occurs. There is, however, a much discussed problem involving the *in situ* tensile experiments in electron microscope. That is the applicability of results from electron microscopical investigations on semi-thin sections to the bulk materials. Although the stress–strain state in semi-thin sections is different from that in bulk materials even under the same external loading condition, the character of deformation (the deformation mode) cannot be changed, because the semi-thin sections are representative of the morphology. Only the degree of plastic deformation, i.e. the degree of elongation should be changed. Therefore, it is difficult to compare the degree of elongation between semi-thin sections and bulk material, but the character and type of deformation, that is, the micromechanical deformation mechanism are comparable in both cases[2,37].

EXPERIMENTAL

Materials

In the present work, different types of semicrystalline polymer matrix were chosen to study the micromechanical toughening mechanisms (*Figure 1*). The main object of investigation was impact-modified polypropylenes (PP), which were modified with different types of rubber. To compare the results from the impact-modified PP with the other heterogeneous polymer systems, impact-modified PA 66 with butyl acrylate and particulate polymer composites were also investigated.

At first, PP modified with ethylene–propylene-block copolymer (EPR) were used with varying concentrations of ethylene (6 and 20 mol%). These blends are so-called reactor blends, produced in a two-stage polymerization process similar to those described in the literature[39,40]. The matrix phase is produced here in the first reactor in liquid propylene, while the EPR phase is produced in a second reactor in the gas phase. The EP-copolymerization, which takes place in the second reactor is a statistical process, yielding a mixture of crystalline and amorphous phases[30]. Secondly, mechanical blends by injection moulding were studied. In these blends, two different types of modifier particles were used: the one modified with 15 vol.% amorphous ethylene–propylene-copolymer particles (EPC), the other with 20 vol.% ethylene–propylene–diene-terpolymer (EPDM). Thirdly, the two kinds of injection-moulded polymer combinations with compatibilizer consisted of maleic-anhydride–grafted polystyrene-block-poly(ethene-co-but-1-ene)-block-polystyrene (SEBS-g-MA) were used. One was PP (67.5 vol.%) modified with polyamide 6 (PA 6, 30 vol.%) mixed compatibilizer (2.5 vol.%), and the other was PP (72 vol.%) modified with linear low-density polyethylene (LLDPE, 18 vol.%) mixed 10 vol.% compatibilizer. In order to compare the results of impact-modified PP with other polymer systems, the impact-modified polyamide (PA 66) with 22 vol.% butyl acrylate (BA) and particulate polymer composites were also investigated. Particulate polymer composites were PP modified with $Al(OH)_3$-filler particles (10 wt%), and polyethylene (PE) modified with SiO_2-filler particles (7 wt%).

Study of morphology

To study the morphology, three preparation and investigation techniques were used:

(1) The rubber phase of the samples was chemically selectively stained with chlorosulphonic acid and osmium-tetroxide or ruthenium-tetroxide. Ultra-thin sections about 0.1 μm thick were microtomed at -80°C and investigated in the conventional TEM.
(2) Semi-thin sections (up to a few μm thick) were prepared by ultramicrotomy at -80°C. They were studied in a 1000 kV high HVEM, revealing clearly larger particles and thus showing the true particle diameter distribution.
(3) Brittle fracture surfaces were prepared at low temperature and investigated by SEM, showing preferentially larger particles.

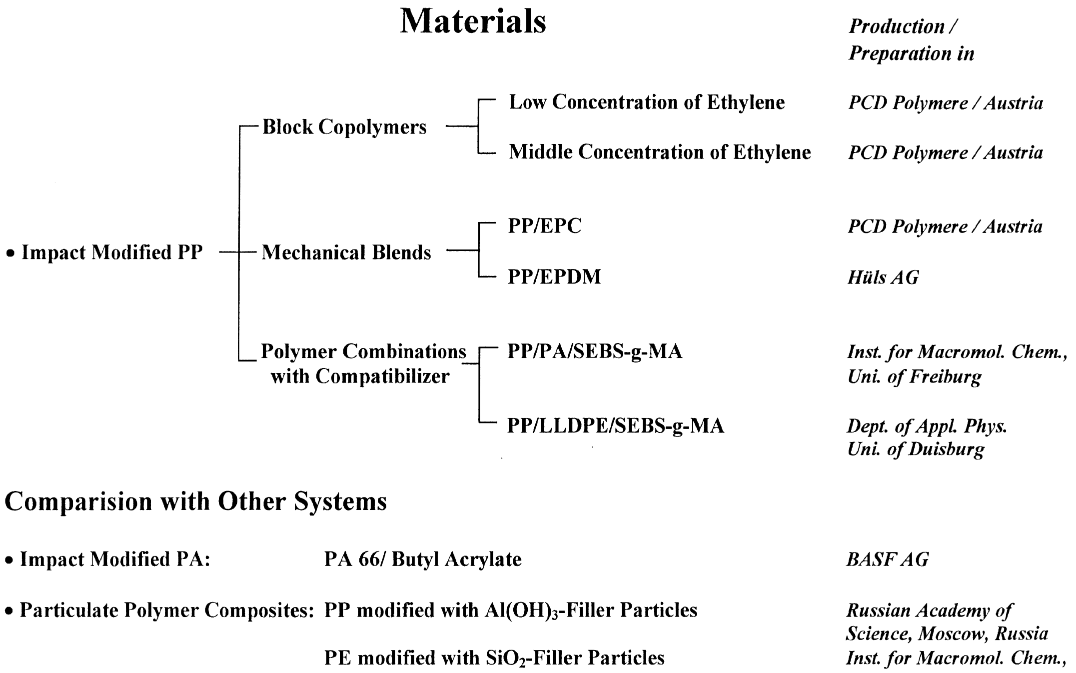

Figure 1 The materials investigated

The particle size, particle size distribution and centre-to-centre distance between the particles were quantitatively analysed with the help of a computerized image analyser using SEM-micrographs from low-temperature brittle fractured surfaces.

Investigation of micromechanical deformation processes

To study micromechanical deformation processes, samples were deformed and investigated *in situ* by 1 MV HVEM and SEM. All deformation tests under the microscope were performed at room temperature. The specimens for HVEM and SEM investigations were microtomed at $-80°C$, containing thickness of about 1–2 μm.

RESULTS AND DISCUSSION

Morphology

There are morphological differences in the PP/EPR block copolymer systems. *Figure 2a* shows a TEM micrograph of PP/EPR block copolymer with low ethylene content (6 mol%). The phase structure corresponds to the one of core-shell particles, in which three characteristics are clearly visible:

- the matrix of semicrystalline PP containing lamellae;
- a structureless dark boundary region appearing around the particles, which consists of an amorphous ethylene–propylene rubbery phase;
- one inclusion in the particles, which consists of semicrystalline PE, revealing lamellae.

Figure 2b is taken from PP/EPR block copolymer with middle ethylene content (21 mol%). In this system the modifiers (EPR-particles) possess several PE-inclusions with a surrounding EP-rubbery shell. From these results, it is clear that, as the ethylene concentration in the PP matrix increases, particles become greater and possess several inclusions surrounded by a single EP-rubbery shell. *Figure 3a* shows a typical phase structure from PP/EPC mechanical blend. The PP-matrix shows a spherulitic structure, in which the EPC-particles are dispersed[38–41]. The modifier particles consist of amorphous ethylene–propylene-copolymer without a shell, therefore the

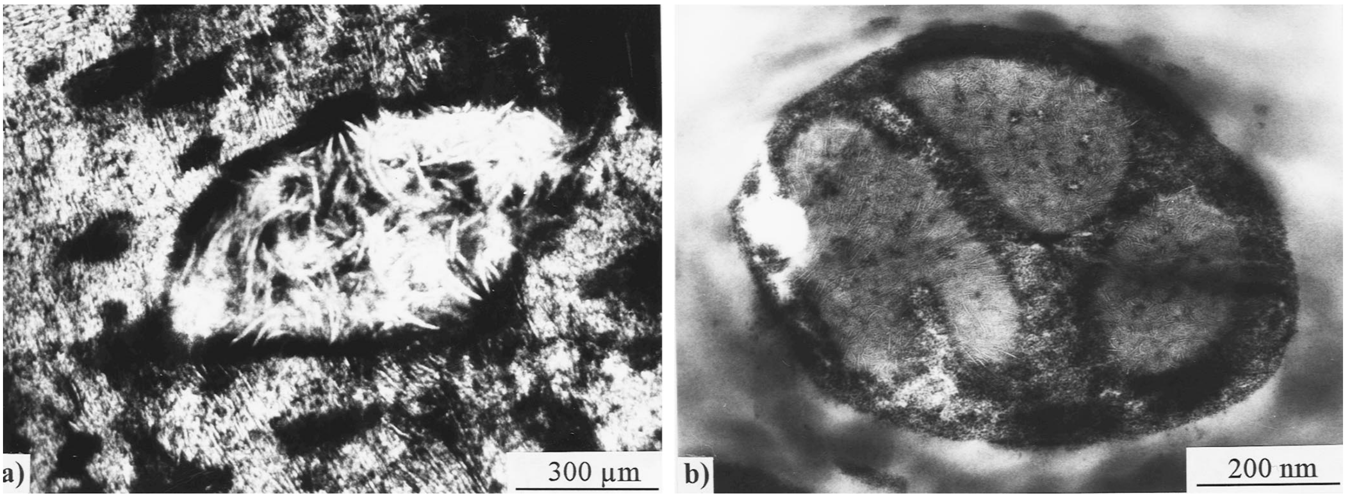

Figure 2 Transmission electron micrographs of the PP/EPR block copolymer: (a) 6 mol% ethylene; (b) 21 mol% ethylene

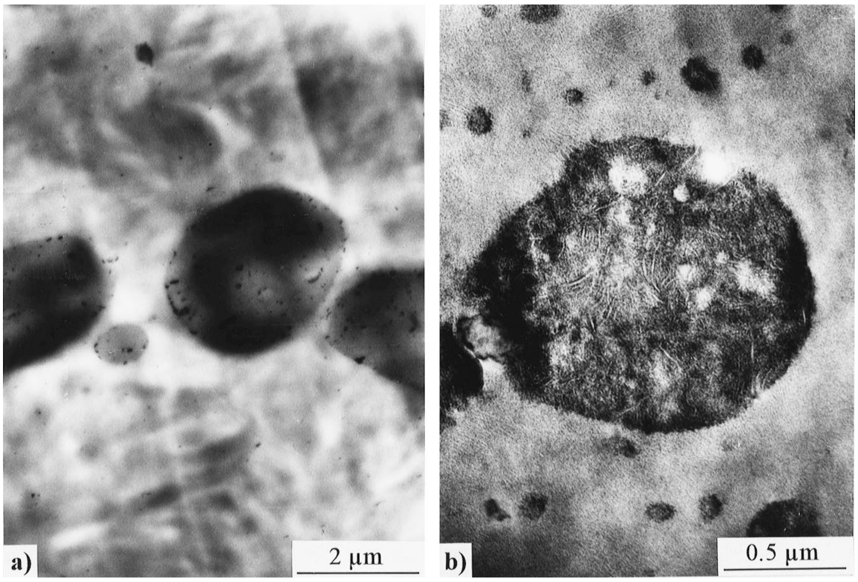

Figure 3 Transmission electron micrographs: (a) PP/EPC mechanical blend, (b) PP/EPDM blend

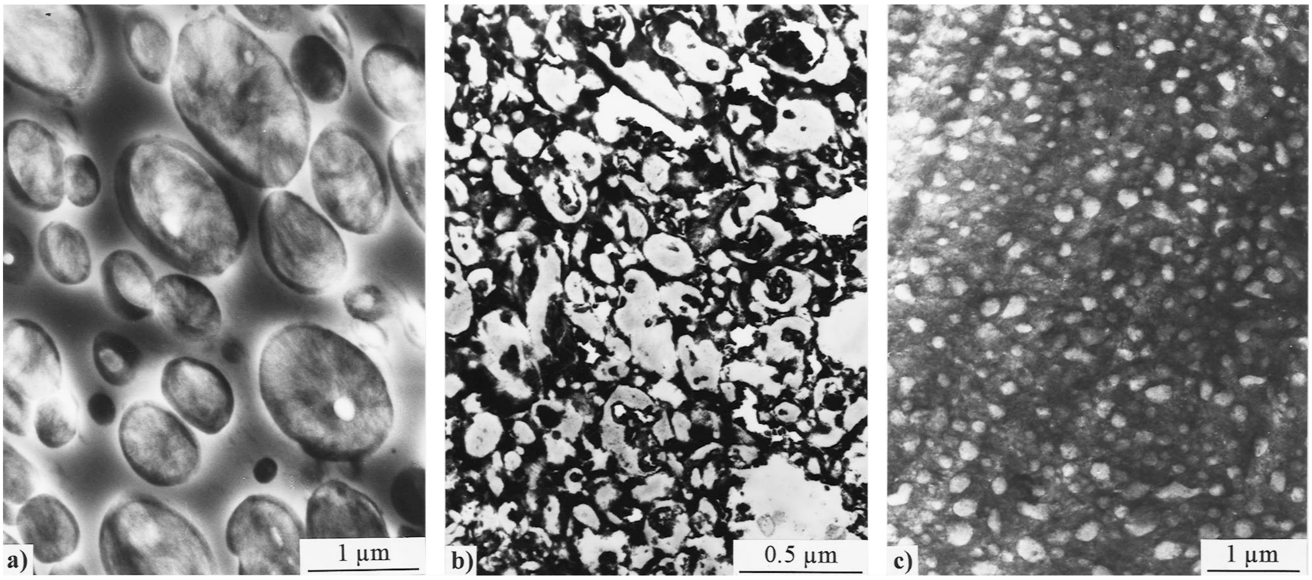

Figure 4 Transmission electron micrographs of polymer blends: (a) PP/PA/SEBS-g-MA; (b) PP/LLDPE/SEBS-g-MA; (c) PA/BA

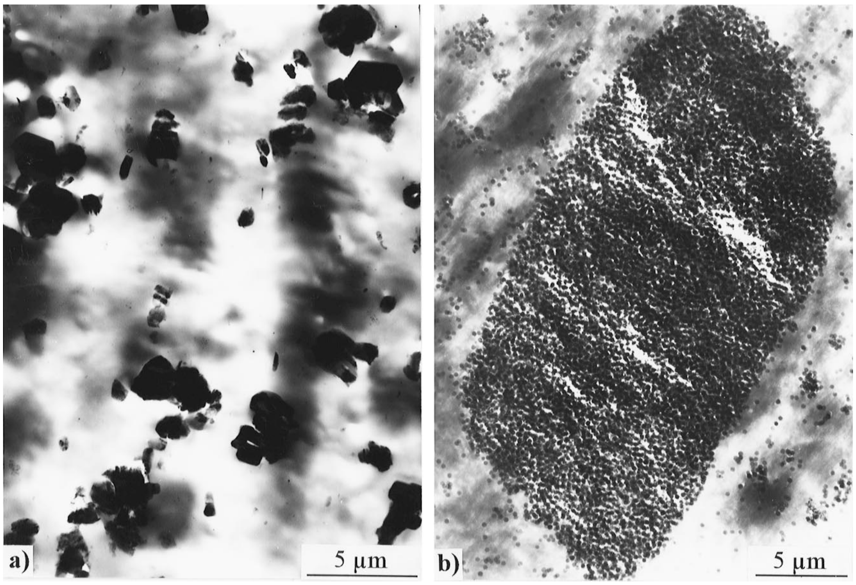

Figure 5 High voltage electron micrographs of polymer composites: (a) modified with $Al(OH)_3$; (b) modified with SiO_2

TEM-micrographs show neither PE- nor PP-lamellae in the modifier particles[40,42].

A typical phase structure of PP/EPDM blend is present in *Figure 3b*. Inside the modifier particles there are a few lamellae, since the EPDM particles possess little crystallinity[43]. *Figure 4a* shows a phase structure from a PP/PA/SEBS-g-MA blend. The micrograph clearly shows that the PA phase forms a separated microphase in the PP matrix[44]. In the same manner as in the PP/EPR block copolymer, the phase structure shows a type of core-shell-particles: semicrystalline PP exhibiting lamellae as matrix, semicrystalline PA exhibiting lamellae as inclusion and triblock SEBS-g-MA phase as amorphous shell. *Figure 4b* shows a phase structure from PP/LLDPE/SEBS-g-MA blend. The compatibilizer phase of SEBS-g-MA is stored on the interface between the matrix, and the inclusions consist of LLDPE. In this blend, it is particularly interesting that these dispersed modifier particles are partially agglomerated in the matrix. The phase structures of modifier particles from PP/EPR block copolymers, PP/PA/SEBS-g-MA and PP/LLDPE/SEBS-g-MA blends will be defined in the present work as mandu-particles[45], in contrast to the salami-particles in HIPS[46]. These types of phase structure belong to ternary systems, in which heterogeneous modifier particles including semicrystalline inclusions with lamellae surrounded by amorphous shells are dispersed in the matrix. The TEM-micrograph in *Figure 4c* shows a typical phase structure from the PA 66/butyl acrylate (BA) blend. Modifier particles are dispersed relatively finely in the matrix.

Figure 5 shows typical HVEM-micrographs of the particulate polymer composites. In the polymer composite PP/$Al(OH)_3$ the particles are relatively finely dispersed in the matrix (*Figure 5a*). In the polymer composite with SiO_2, the inorganic filler particles are not finely dispersed in the matrix but locally form agglomerates of the order of 10–50 μm in size, although the filler particles are nearly monomodal and spherical, of the order of about 250 nm (*Figure 5b*).

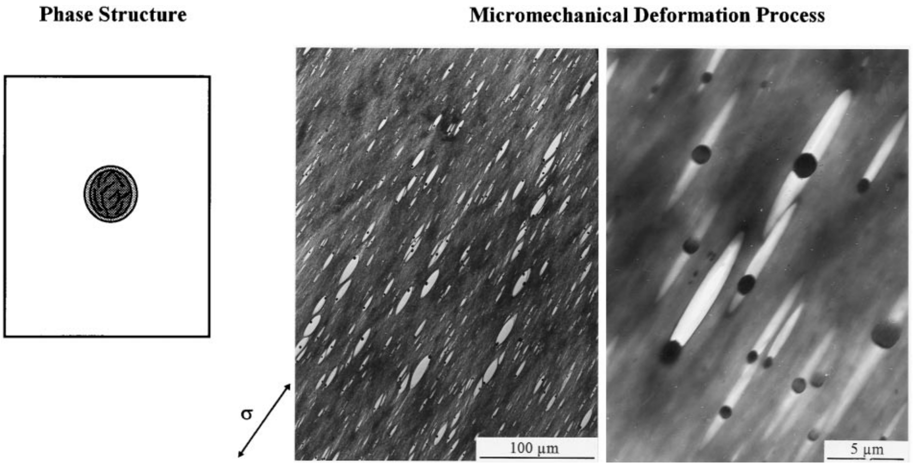

Figure 6 Characteristic deformation structure depending on the phase structure of EPR-modifier particles (6 mol% ethylene)

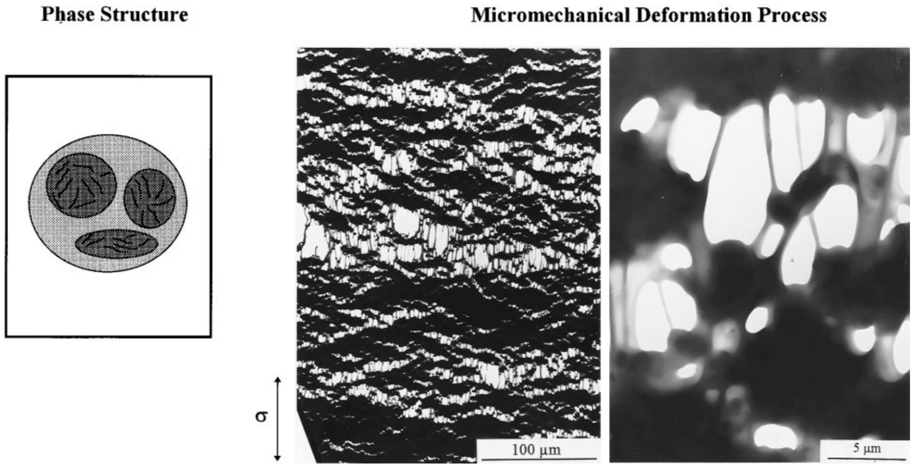

Figure 7 Characteristic deformation structure depending on the phase structure of EPR-modifier particles (21 mol% ethylene)

Characterization of micromechanical deformation processes in dependence on the phase morphology of modifier particles

In the following figures, the characteristic deformation structures from *in situ* tensile tests in HVEM (on the right side) in dependence on the phase structure of modifier particles for individual blends (which is illustrated schematically on the left side) will be discussed in more detail. From the study of morphology, two different morphological standard types are classified for the analysis of toughening mechanisms, namely a binary system (homogeneous particles) and a ternary system (heterogeneous particles). In the following these two categories will be discussed.

Ternary blend systems

PP/EPR block copolymers. PP/EPR block copolymers are ternary systems. According to the content of ethylene, the modifier particles exhibit one or several semicrystalline polyethylene inclusions surrounded by single EP-rubbery shell (*Figures 6 and 7*, respectively). The shell, consisting of an amorphous ethylene–propylene-block copolymer, increases the interfacial adhesion between the PP- and PE-phase. *Figure 6* shows HVEM micrographs taken during *in situ* deformation tests of ethylene–propylene block copolymer containing lower ethylene content. In the early stage of the deformation process the modifier particles deform together with the matrix. When the stress reaches a certain critical value, void formation appears in the plastically deformed EP-rubbery shell. In combination with successive void formation and continuous growth of voids themselves, weak shear bands form in the matrix ligaments between particles. With further increase in strain, a more intense shear yielding occurs in the whole specimen. In previous work[3,30,45], this toughening mechanism was defined as a single cavitation process.

Figure 7 shows HVEM micrographs taken during deformation of ethylene–propylene block copolymer containing middle ethylene content. The deformation structure reveals well-developed fibrils in the deformed specimen, which resembles a craze-like deformation structure. It is clearly visible that void formation occurs predominantly in the plastically strong deformed EPR particles at the interface of PE inclusions. When the voids begin to interact with each other, simultaneously, the shear yielding of matrix takes place.

The following can be concluded from the remarkable differences in the deformation structures. When the modifier particles possess only one inclusion, the deformation will be followed by a single cavitation process; when the particles possess several inclusions, the deformation will be followed by a multiple cavitation process, which is described in the previous papers[3,30,45].

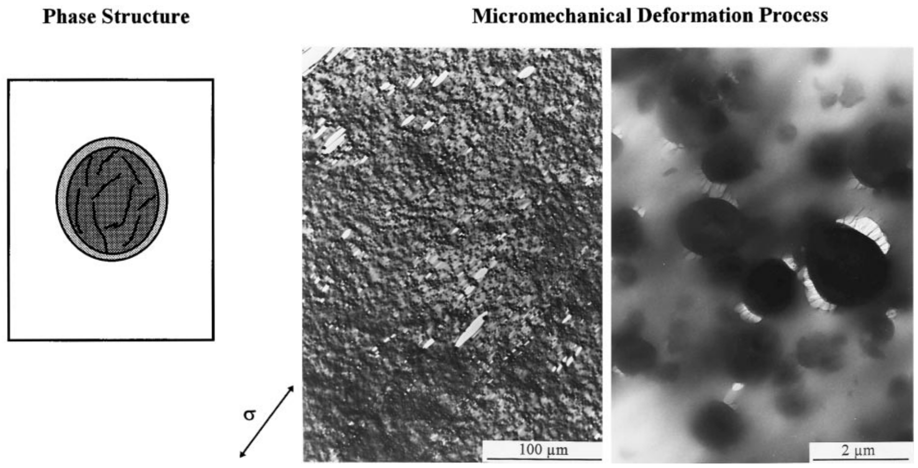

Figure 8 Characteristic deformation structure depending on the phase structure of PP/PA/SEBS-g-MA blend

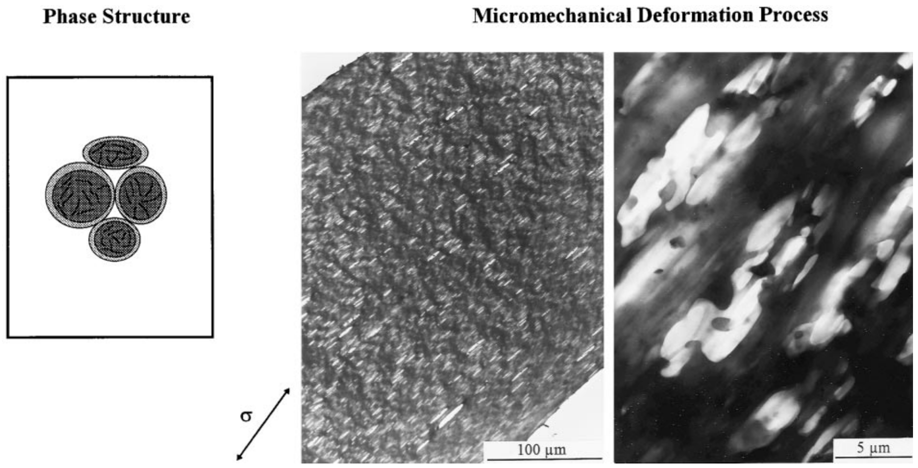

Figure 9 Characteristic deformation structure depending on the phase structure of PP/LLDPE/SEBS-g-MA blend

PP/PA/SEBS-g-MA. The study of morphology shows that each modifier particle has one inclusion, which consists of a semicrystalline PA-phase surrounded by an amorphous triblock SEBS-g-MA phase (*Figure 8*). Micromechanical deformation processes are shown in *Figure 8* on the right-hand side. During the deformation process, the shell, consisting of SEBS-g-MA, is first stretched in the tensile direction. Once the strain of the shell has reached a certain critical value, fibrils form at the interface between the PA inclusion and the matrix (fibrillized cavitation). These fibrils appear at the polar region of modifier particles and are aligned in the direction of applied stress. It is to be noted that this fibrillized cavitation begins preferentially at larger particles and jumps to smaller particles in the neighbourhood with an increase of strain. The prerequisite for this kind of cavitation is a relatively strong phase adhesion between the PA inclusion and the matrix.

PP/LLDPE/SEBS-g-MA. *Figure 9* shows a schematic phase structure and the micromechanical deformation processes from the *in situ* uniaxial tensile test in HVEM. The SEBS-g-MA compatibilizer acts as an effective dispersing agent, resulting in a reduction in size as well as an interfacial adhesion promoter. Consequently, the finely reduced and dispersed LLDPE particles form agglomerates. Numerous voids can be seen, as well as the plastically deformed matrix between the voids. The voids are distributed homogeneously in the matrix and are somewhat the same order of size. During the deformation processes, these agglomerates play the same role as modifier particles, with several inclusions encapsulated by rubbery shell. Therefore, numerous voids surrounding plastic deformed modifier particles are revealed.

Binary blend systems

PP/EPC mechanical blend. *Figure 10* shows a schematic phase structure on the left-hand side and typical deformation structures during the *in situ* tensile tests in HVEM. During the deformation processes, the stress concentration occurs first in the vicinity of the particles. When the stress concentration reaches a critical value, void formation takes place by a debonding process at the interface between modifier particle and matrix, which appear at both sides of the particles parallel to the direction of applied stress. The voids are aligned with a certain angle in the deformed specimen. This occurrence can be considered to be dilatation bands, which was suggested by Lazzeri and Bucknall[32]. It is to be noticed in deformation structure that the intersection points of these dilatation bands are always positioned at the local larger particles. The larger particles generate a wide stress field, and as a consequence the orthogonality of dilatation bands can be distorted.

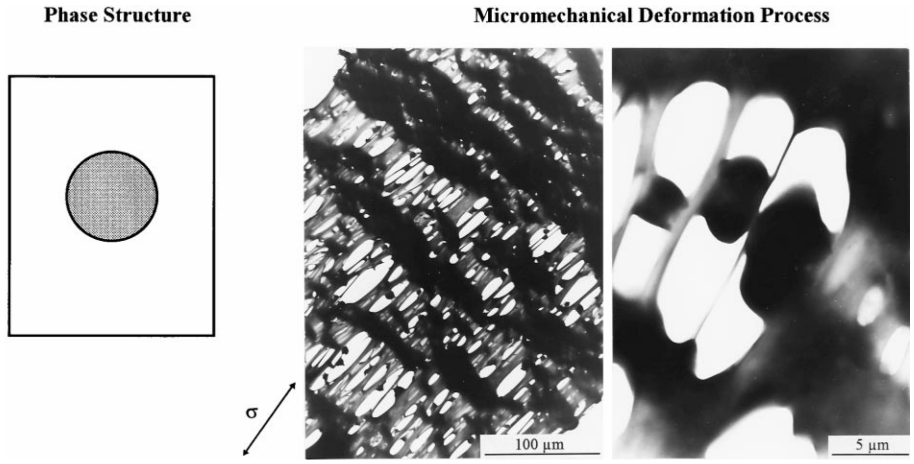

Figure 10 Characteristic deformation structure depending on the phase structure of PP/EPC mechanical blend

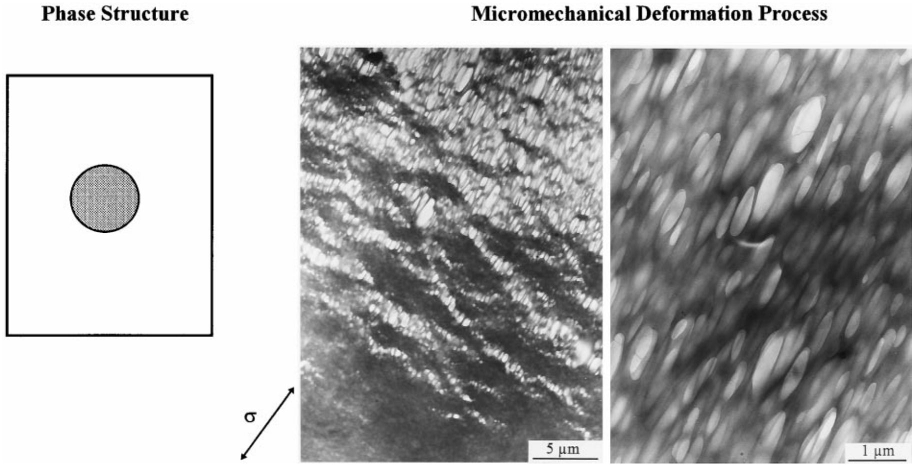

Figure 11 Characteristic deformation structure depending on the phase structure of PA/BA blend

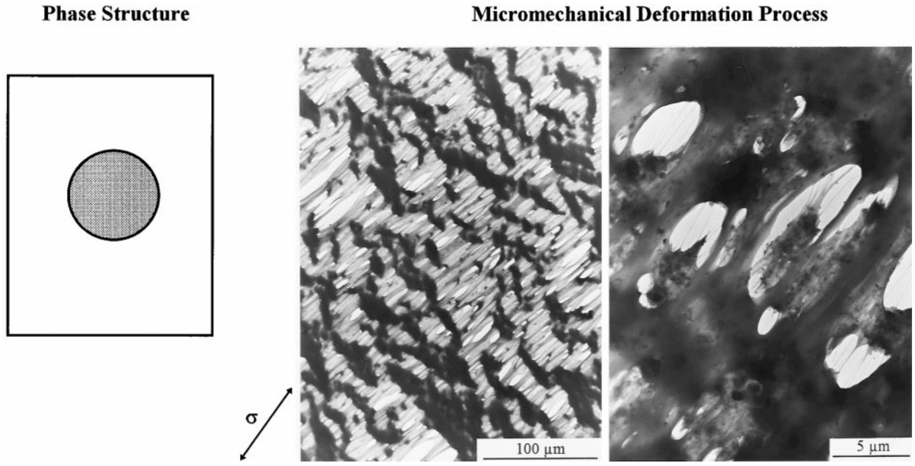

Figure 12 Characteristic deformation structure depending on the phase structure of PP/EPDM blend

PA/BA blend. The modifier particles consist of an amorphous butyl acrylate without shells and are dispersed densely in the matrix. *Figure 11* shows deformation structures in different magnification from *in situ* deformation tests in HVEM. The plastically deformed specimen in lower magnification reveals band-like deformation structures. Within the deformation bands, the numerous voids as well as plastically stretched modifier particles can be seen. Void formation occurs inside plastically elongated particles after reaching a critical strain within the specimen. As the strain is increased, the voids are elongated gradually in the applied stress, and as a result shear yielding in the matrix will be induced. It also should be emphasized that the intersection points of deformation bands are positioned at the

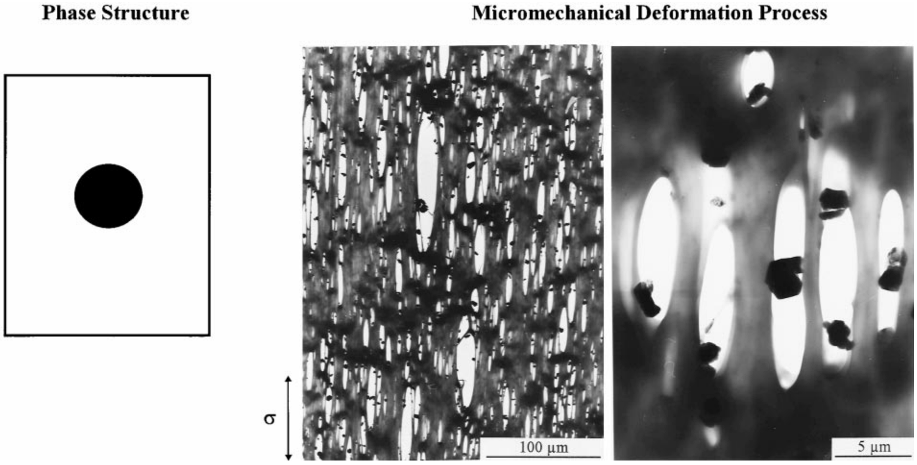

Figure 13 Characteristic deformation structure depending on the phase structure of PP/Al(OH)$_3$ polymer composite

larger particles. We assume that when the developing deformation bands meet at a larger particle, they will branch and propagate to the adjacent particles with a certain angle with increasing strain.

PP/EPDM. *Figure 12* shows the schematic phase structure from this blend and the HVEM micrographs of typical deformation structures. The particles dispersed in the matrix consist of an ethylene–propylene–dine terpolymer rubber. Numerous plastically stretched EPDM particles and voids surrounding them can be seen. At the beginning of plastic deformation, the EPDM particles elongate together with the matrix in the direction of applied stress. When the strain reaches a critical value, debonding processes take place at the polar region of EPDM particles (parallel to stress direction). While this blend has some degree of interfacial adhesion compared with most other mechanical blends, here the fibrils are connected at the interface between particles and matrix. With the formation of voids, simultaneously, shear bands form in-between the plastically stretched EPDM particles/voids and the matrix. In this way, the applied load can be transmitted in the matrix in the same manner as crazes do in amorphous polymers. This micromechanical deformation process is comparable to the particle bridging mechanism[8,47]. Over a certain specific strain of specimen, the failure of fibrils develops at first on the polar region propagating to the equatorial region of elongated EPDM particles. Finally, only a few fibrils remain in the equatorial region. It can be concluded that, although modifier particles possess few polyethylene lamellae, these lamellae do not have any influence on the deformation processes.

Particulate polymer composites

Particulate polymer composites studied here can be classified as binary systems, because they possess no interface treatment (i.e. are without shells).

PP/Al(OH)$_3$. Because of the rigidity of inorganic filler particles, they cannot be deformed by external stress in the specimen but act only as stress concentrators during deformation processes. Due to poor adhesion between the Al(OH)$_3$ filler particles and the matrix, the debonding process takes place easily at both sides of the particles in a parallel direction to the applied stress, while the maximum stress concentration is positioned at the poles for the rigid modifier particles (*Figure 13*). In this polymer composite modified with 10 wt% Al(OH)$_3$ filler particle, the matrix strands in-between the particles are sufficiently large so that the contraction of specimen in the direction perpendicular to the applied stress occurs following necking. In connection with these debonding processes, the matrix material between the voids deforms more easily to achieve a shear yielding.

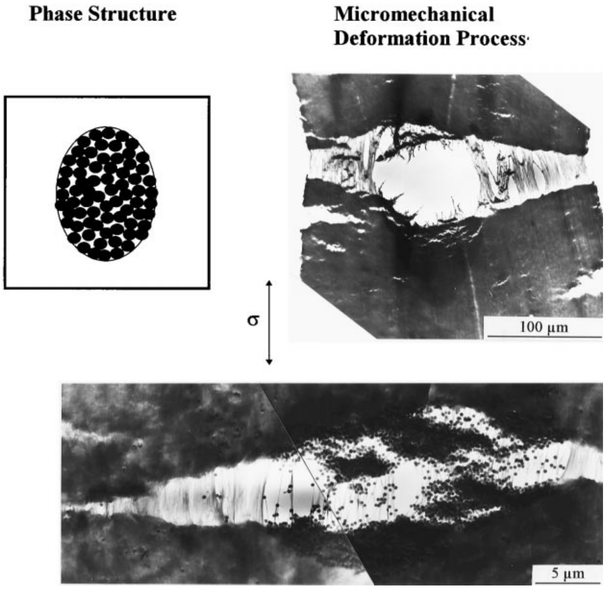

Figure 14 Characteristic deformation structure depending on the phase structure of PP/SiO$_2$ polymer composite

PE/SiO$_2$. *Figure 14* shows the deformation structures of this polymer composite with 7 wt% SiO$_2$ filler particles, It can be seen that, during the deformation, the agglomerates are torn at their equator. In the neighbourhood of torn agglomerates, the matrix material is also strongly plastically stretched in the direction of the applied stress. When the filler particles form agglomerates, these agglomerates play a different role during the deformation. Although the agglomerates consist of numerous small rigid filler particles, they act on the whole similar to rubber modifier particles during the deformation processes. At the beginning of deformation, the stress concentration takes place at the equatorial region of agglomerates, so that here the plastic deformation is initiated. Owing to insufficient phase adhesion between the filler particles and the matrix, debonding also occurs more easily. Moreover, the interparticle distance in an agglomerate is too small, so that the matrix strands inbetween the filler particles are fibrillized during the stretching of voids. Thus, the craze-like deformation structure inside deformed agglomerates is exhibited. With increasing strain in the direction of the applied stress, the fibrils break down in the equatorial region of agglomerates (transparticular fracture), and the matrix material in these regions is further deformed plastically.

SUMMARY

In the present work it has been shown that the toughening mechanisms involved in different blend systems are influenced decisively by the phase structure of modifier particles, which in turn leads to different micromechanical deformation processes. As an initiation site for the plastic deformation, the microvoid formation is considered. This microvoid formation can be caused either by cavitation in the stretched rubbery shell/inside particles or by debonding at the interface between particles and matrix. From the analysis of different micromechanical deformation processes, a few morphological standard types are derived for the toughening models, namely binary and ternary systems. In the ternary blend systems, because of the specific inherent properties of the interface, cavitation processes occur with or without fibrillation in the plastically deformed rubbery shell. Depending on the number of inclusions in a modifier particle, the modified polymers deform through the multiple or single cavitations in a rubbery shell. In the binary blends modified with rubber or inorganic filler particles, the phase adhesion has a great significance for the course of events in micromechanical deformation processes. When the phase adhesion between the modifier particles and the matrix is good, the plastic deformation occurs via single cavitation processes inside modifier particles, whereas when there is no or poor phase adhesion, the micromechanical deformation processes are followed by debonding. According to the efficiency of agglomeration of filler particles, single or multiple debonding processes are caused during plastic deformation of polymer specimens.

In a further paper (Part 2), from the experimental results we propose the models of the micromechanical deformation processes.

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