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# Micromechanical deformation processes in toughened and particle filled semicrystalline polymers. Part 2: Model representation for micromechanical deformation processes

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Toughening mechanisms occurring in various toughened and particle filled semicrystalline polymers have been investigated by several cursive electron microscopic techniques. In the previous work (Part I) it has been shown that the toughening mechanisms involved in different blend systems are influenced decisively by the phase morphology of modifier particles and the phase adhesion between matrix and modifier particles, which in turn lead to different micromechanical deformation processes. Form these results six different schematic models for micromechanical deformation processes are proposed. To simplify the explanation of micromechanical deformation processes it has been described in form of three-stage-mechanism. Finally, the results of micromechanical deformation processes are discussed with the concept of energy dissipation and stress states. © 1998 Elsevier Science Ltd. All rights reserved.

**(Keywords: semicrystalline polymers; micromechanical deformation processes; *in situ*-electron microscopy)**

## INTRODUCTION

Mechanical properties of a polymer can be controlled by the incorporation of well-defined modifier particles in the polymer matrix. Improved toughness of polymer blends without significantly impairing other desirable engineering properties may become a decisive factor of material selection for many structural applications[1,2]. To produce polymers with improved toughness, it is extremely helpful to understand the structure–property relationship, which can be deduced from the micromechanisms of deformation and fracture. In heterogeneously modified polymer systems two major toughening mechanisms are generally accepted, crazing and shear yielding. In most rubber-toughened glassy polymers, such as high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS)[1–4], the toughening mechanism has been interpreted in terms of multiple crazing, while in the impact modified polyamide (PA) and polypropylene (PP) the main source of toughness is shear yielding of the matrix[2,5–8]

Recently, the effect of cavitation of rubber particles comes into a considerable attention for toughening mechanism in many rubber-toughened polymers, rubber-modified PA[5–10], PP[7,8,11], polycarbonate (PC)[12–14], epoxy resins[15–17], poly(vinyl chloride) (PVC)[18–22]. 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. In the previous work [Part 1], micromechanical deformation processes in various toughened and particle filled semicrystalline polymers have been characterized in conjunction with the phase morphology of modifier particles and the degree of adhesion between the modifier particle and the matrix. It has been found that the different phase structures of various modifier particles lead to different micromechanical deformation processes. Additionally, microvoid formation is a operating mechanism for the initiation of plastic deformation. This microvoid formation can be caused either by cavitation in the stretched rubbery shell (core-shell particles), inside particles (pure rubber particles) or by debonding at the interface between particle and matrix. The contribution of cooperative microvoid formation is minor in terms of enhanced toughness, but this process plays an important role in initiating the toughening mechanism, which facilitates energy absorption by shear yielding of the matrix during the deformation. From these experimental results we have proposed schematic models of micromechanical deformation processes involved in different polymer blend systems.

## MODEL REPRESENTATION FOR MICROMECHANICAL DEFORMATION PROCESSES

The results of the *in situ* electron microscopic investigation of micromechanical deformation processes in various toughened and particle filled semnicrystalline have been described as a three-stage-mechanism[7,8]:

- *Stage 1: stress concentration*. The modifier particles act as stress concentrators, because they have different elastic properties from the matrix. The stress concentration leads to the development of a triaxial stress in the rubber particles and to dilatation.

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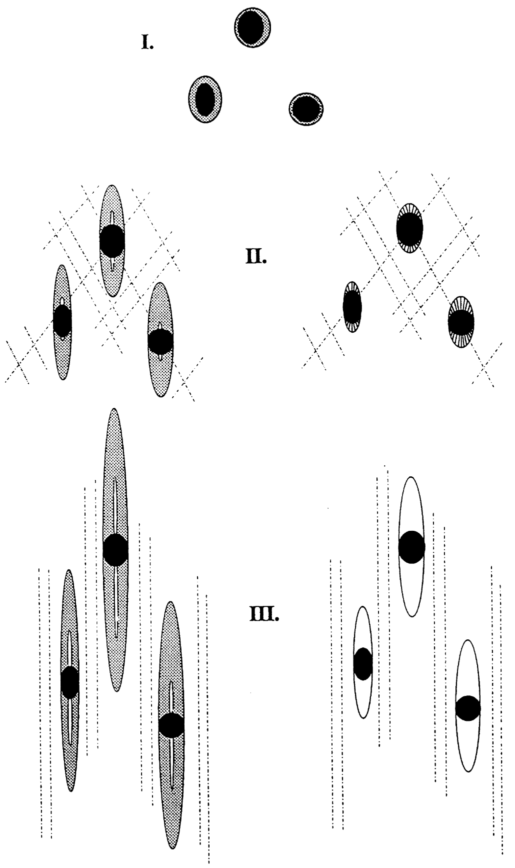

Figure 1 Single cavitation process in ternary blend systems: (a) PP/EPR block copolymer with low content of ethylene; and (b) PP/PA/SEBS-g-MA Blend

- *Stage 2: void and shear band formation*. Due to the stress concentration, a higher hydrostatic or triaxial stress builds up inside particles and gives rise to void formation through cavitation inside particles or debonding at the particle matrix interface. With continuous growth of voids, simultaneously, weak shear bands are formed in the matrix between the voids under an angle of about 45° to the direction of the maximum principal tensile stress.
- *Stage 3: induced shear yielding*. Once the voids caused by cavitation or debonding have occurred, the triaxial tension can be locally released in the surrounding of voids corresponding to an increase in the shear component. Thereby the yield strength is lowered. As a consequence, the further shear yielding is greatly induced in the matrix.

In the following, this general mechanism will be more appropriately modified for the models describing the micromechanical deformation processes of individual blend systems.

### *Single cavitation process in ternary blend system*

*Figure 1* shows a schematic model of micromechanical deformation process in ternary blend systems (PP/EPR block copolymer, PP/PA/SEBS-g-MA blend). In these blends the modifier particles possess only one inclusion and are relatively fine dispersed in the matrix. At first (Stage 1) stress concentration takes place around the modifier particles. Second (Stage 2), the modifier particles deform together with the matrix, and void formation appears in form singular cavitation with or without fibrils at the interface between the modifier particles and the matrix. This process depends essentially upon the inherent properties of rubbery shell. Simultaneously with the growth of voids, shear bands form in the matrix between the modifier particles. Third (Stage 3), when the polymer specimen will be further strained, shear yielding will be induced in the matrix. As a result, plastic deformation of matrix will be significantly enhanced. In the case of PP/EPR block copolymer the voids grow gradually with the straining of specimen, whereas in the case of PP/PA/SEBS-g-MA blend the fibrils break down at the interface.

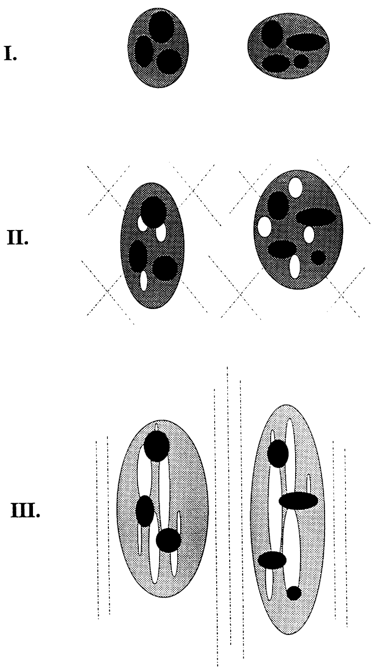

Figure 2 Multiple cavitation process in ternary blend systems: (a) PP/EPR block copolymer with middle content of ethylene; and (b) PP/LLDPE/SEBS-g-MA blend

### *Multiple cavitation process in the ternary blend systems*

In *Figure 2* the micromechanical deformation process in ternary blend systems is presented schematically. In these blends, the modifier particles (PP/EPR block copolymer) possess several inclusions with one rubbery shell, or they are close to each other, forming aggregates in appearance (PP/LLDPE/SEBS-g-MA).

In the first stage, stress concentration takes place around the modifier particles. In the second stage microvoids form around the inclusions in the plastically stretched rubbery shell. At the same moment, the shear bands form in the matrix between the modifier particles. In the third stage, the size of the voids grows gradually as increase of the strain, as a result shear flow in the matrix will be accelerated.

### *Single cavitation process in binary blends systems*

In the case of PA/BA blend, in which the modifier particles consist of only one rubbery phase, the micromechanical deformation process can be followed in the form of single cavitation process (*Figure 3*). In the first stage the stress concentration occurs around the modifier particles the same as in other blend systems. In the second stage, the modifier particles can be slightly stretched, and microvoids are formed inside the plastically stretched modifier particles. With void formation inside the particles, shear bands form in the matrix between the modifier particles. With further straining of specimen, the voids will be more

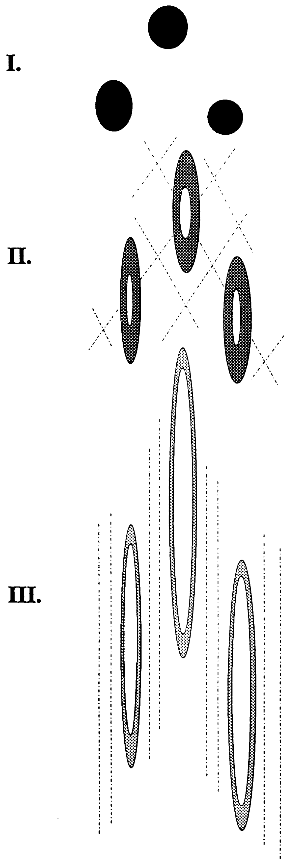

**Figure 3** Single cavitation process in binary blend systems: PA/BA blend

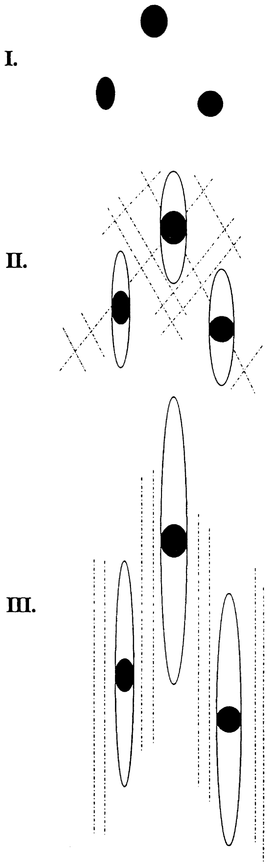

**Figure 4** Single debonding process: (a) PP/EPC mechanical blend; and (b) PP/Al(OH)$_3$ polymer composite

elongated, and the matrix will be further deformed through shear yielding.

*Single debonding process*

*Figure 4* shows the schematic micromechanical deformation process of single debonding process. This process takes place in the blend systems, in which the phase adhesion between the modifier particles and matrix is poor as in the cases of particulate polymer composites or PP/EPC mechanical blend systems. In the first stage, stress is concentrated around the particles. In the case of particulate polymer composite (PP/Al(OH)$_3$) its maximum lies in the polar regions of particles. Due to the poor phase adhesion, debonding can easily take place on the both polar regions of filler particles in the perpendicular external stress direction. Additionally, simultaneous shear bands form in the matrix (in the second stage). In the next stage, with combination of debonding process the matrix strands between the filler particles deform throughout the shear flow processes.

*Fibrillized debonding process at the interface*

This process is schematically shown in *Figure 5*. When a certain phase adhesion between the modifier particle and the matrix exists, deformation occurs through a debonding process with fibrillation at the interface between modifier particles and matrix. In the first stage stress concentration occurs around the particles. The modifier particles will be slightly stretched due to the stress concentration. Due to the existence of a certain amount of phase adhesion, fibrils form at the interface between modifier particles and matrix and simultaneously shear bands form in the matrix. With increasing the strain of the specimen the fibrils break down at the polar regions of particles (i.e. at places in parallel direction of external stress), only a few fibrils remain in the area of equator regions of particles. In the third stage, the further shear flow of matrix is considerably enhanced.

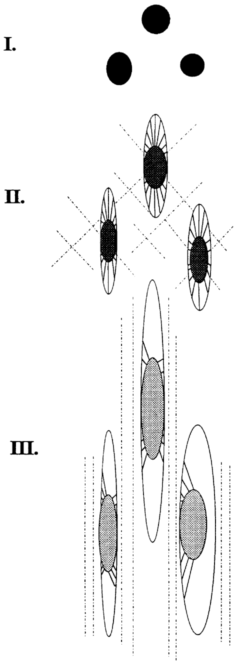

**Figure 5** Fibrillized debonding process at the interface: PP/EPDM blend

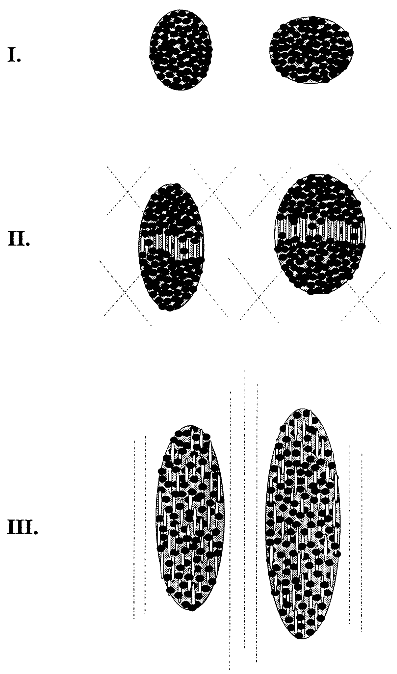

**Figure 6** Multiple debonding process: PE/SiO$_2$ polymer composite

*Multiple debonding process*

When the filler particles form large aggregates such as in a polymer composite system (PE/SiO$_2$), the specimen deforms in a multiple debonding process. This process is shown in *Figure 6*. In the first stage, stress concentration takes place, as usual, around the particles. The maximum stress concentration occurs in the equatorial region of aggregates, because the aggregates act as large soft particles during the deformation processes, although each filler particles inside the aggregates consist of rigid inorganic filler particles. There is a very small interparticle distance between the particles in the aggregates, so that shear flow process and fibrillation can be easily activated in the thin matrix strands between the filler particles. Therefore, well developed craze-like structures inside deformed aggregates are shown as in *Figure 6*. At the same time, the matrix between the aggregates deform plastically with the formation of shear bands. In the last stage, if the matrix distance between the aggregates is sufficiently small, the matrix material can be further deformed through the shear flow.

DISCUSSION

In *Figure 7* the deformation process in uniaxial tensile tests is schematically illustrated respect to a concept of energy dissipation and stress state. Successive deformation processes are divided into two regions:

- the elastic region;
- the plastic region.

Once the uniaxial tensile stress is applied to the specimen, the stress concentrates around the modifier particles. Due to the differences of the Poisson ratio and the bulk modulus between the matrix and the dispersed modifier particles the maximum stress concentration is placed at the equator or at the poles of modifier particles (rubbery modifier particles or inorganic rigid filler particles, respectively). This stress concentration leads to local transition from uniaxial to triaxial stress state. This triaxial stress causes a small volume dilatation in the interior of rubber particles or in the

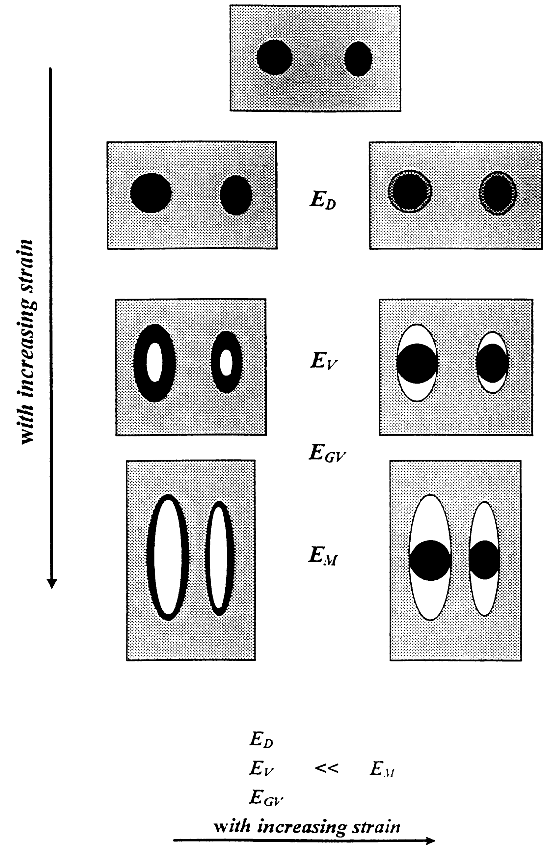

**Figure 8** Schematic representation of qualitative estimation of energy dissipation

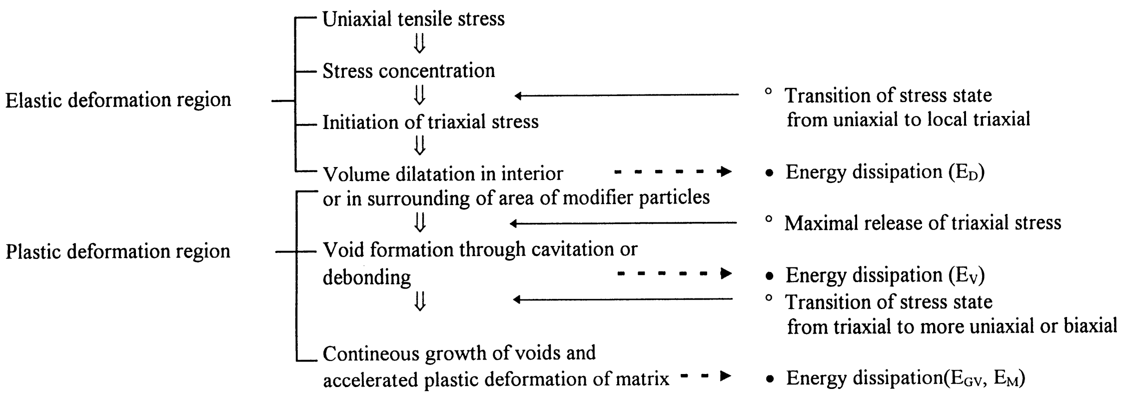

**Figure 7** Schematic illustration of energy dissipation and stress state during uniaxial tensile test

surrounding area of inorganic rigid filler particles, where some applied energy ($E_D$) is dissipated. Up to this point, these successive events take place within the elastic region, because on removal of the external load the specimen fully recovers. Until the maximum triaxial stress is reached, the microvoid formation occurs in the specimen, which is caused by either cavitation or debonding processes depending on the types of modifier particles. Through the initiation of microvoids, the extra additional applied energy ($E_V$) in the specimen is dissipated. Once the microvoids are formed in the matrix, the hydrostatic stress caused by stress concentration is released, with the stress state in the ligaments of matrix material between the voids being converted from a triaxial to more biaxial or uniaxial tensile stress state. This stress state is significant for the initiation of shear bands. The microvoids gradually grow in the applied stress direction with increasing strain in the specimen. Through the continuous plastic growth of voids, the triaxial stress will be further released, by which the plastic deformation of the ligaments of matrix material is considerable accelerated. For these processes the applied energy through the growth of voids ($E_{GV}$) and the plastic deformation of matrix material ($E_M$) is dissipated.

The study of micromechanical deformation processes and deformation structures in tensile tests allows one to estimate the order of energy dissipation in each process. The result of qualitative estimation is illustrated in schematic presentation in *Figure 8*. Although void formation followed by cavitation or debonding process itself is a secondary factor contributing to toughness (in other words, only a small part of energy dissipation may contribute to toughness), it plays an important role for the activation of further plastic deformation of matrix material during the micromechanical deformation process.

## SUMMARY

Different types of models for micromechanical deformation processes responsible for the toughening mechanisms in various toughened and particle filled semicrystalline polymers have been proposed in the form of three-stage-mechanism, from the results of a cursive electron microscopic investigation. Depending on the phase morphology of modifier particles and the phase adhesion between matrix and modifier particles, six different schematic models for micromechanical deformation processes are classified. As main initiation site of plastic deformation the microvoid formation is considered. According to where the microvoids take place, two kinds of processes are defined: the one is cavitation with or without fibrils, which can be caused by internal cracking of rubbery shell in core-shell modifier particles or pure rubber particles, the other is debonding with or without fibrils, which occurs at the interface between the matrix and rubber or rigid filler particles. Occurrence of fibrils depends essentially upon the phase adhesion between matrix and modifier particles. In addition, taking into account the number of inclusions in one modifier particle and the efficiency of agglomeration of particles, single or multiple processes are caused. In combination with irreversible plastic growth of microvoids shear bands with a certain angle form in a specimen simultaneously. In the ‘all blend’ systems studied, the considerable enhancement of toughness or major part of energy dissipation results from the shear yielding (flow processes) of matrix material triggered by microvoid formation. It has been shown that the mechanical deformation processes and its deformation structures of impact modified heterogeneous thermoplastics will be decisively influenced by the morphology of modifier particles.

The results from the present work may be considered as a map for the micromechanical deformation processes of modified semicrystalline polymers.

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