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Towards phase transformation toughened semicrystalline polymers

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Dedicated to Prof. József Varga on the occasion of his 60th birthday*

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ABSTRACT

Phase transformation toughening (PTT), characterized by a transition from a metastable to a stable crystalline phase and associated with volume expansion, is widely used for toughness improvement of metals and ceramics. The essential prerequisites of this toughening concept are met also for semicrystalline polymers since they are polymorphous and capable to undergo transformation from one crystalline phase to an other under mechanical stresses. The transition is, however, mostly connected to volume contraction, i.e. just the opposite what is being exploited in toughened steels and ceramics. It was argued that an irreversible transformation from a less dense crystalline phase to a more dense one could also be beneficial for toughness upgrading in polymers. This transition is combined with changes in lamellar and molecular level resulting in a "strain-hardened" microstructure, that can be considered as the best possible response of the polymer upon mechanical loading ("adaptive" toughening). The main advantage of the PTT concept is that toughness improvement is achieved without incorporation of foreign materials which is the guarantee of easy recycling.

1. INTRODUCTION

Fracture toughness of solids can be enhanced through various crack tip shielding mechanisms, grouped into crack deflection, zone and crack tip shielding ones ([1] and references therein). Phase transformation toughening (PTT) belongs to the zone shielding mechanisms. PTT is featured by a stress-induced transformation of an unstable crystalline form to a more stable one. Since this transition is accompanied with dilatation (i.e. volume increase or decrease in the crystallographic density), the transformation zone becomes under a compressive residual stress field (cf. Figure 1). By this way the resistance to crack growth of the materials is improved very efficiently. This PTT mechanism is working well in steel alloys and engineering ceramics.

High strength steel of high ductility and toughness are produced according to the above concept and are often called to TRIP (acrynim for transformation-induced plasticity) steels. The transformation in their case is the γ–α' or martensitic transition being associated with 3 % volumetric expansion [1-2]. It was concluded that toughness enhancement is due to the followings: a) energy absorption required to the phase transformation, and b) dilatation-caused stress relief at the crack tip (cf. Figure 1).

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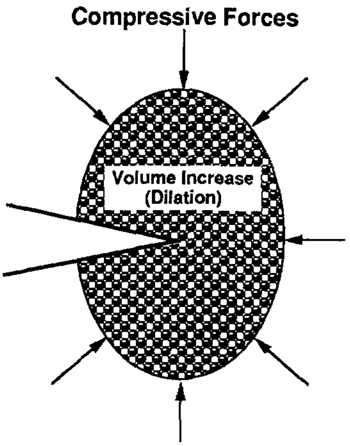
Analogously, stress-induced volume expansion is the toughening method in zirconia (ZrO_2) containing ceramic materials (Figure 1). In this case particles of the metastable tetragonal ZrO_2 are embedded in a cubic zirconia or alumina matrix (PSZ-ceramics; containing partially stabilized zirconia). The stress-induced martensitic transformation of the tetragonal ZrO_2 to the monoclinic cyrstalline form is related to a 3 to 5 % volume increase [1-2].

Specific characteristics of PTT can be summarized as follows:

- transition from an unstable to a more stable crystalline form, and
- dilatation due to the phase transformation from a more dense to a less dense crystalline modification.

Considerable efforts are nowadays focused on the adaptation of the above concept for polymers. Aim of this paper is to contribute to this topic and to outline some useful rules to be followed.



Transformation Characteristics:
- localized
- transformation from higher toward lower crystalline density (dilation)
- transformation results in a more stable crystalline modification
- transformation is athermic

Result (Toughening Mechanism)
Crack tip "shielding" (compression stress field acts on the crack tip)

Figure 1
Phase transformation toughening in engineering ceramics and their main features schematically

2. PHASE TRANSFORMATION IN SEMICRYSTALLINE POLYMERS

Essential prerequisites of PTT are given also for semicrystalline polymers. They are namely polymorphous in nature and microstructural alterations, including changes in the crystalline phase can be triggered by mechanical stresses. Based on these facts one can put the question: whether crystalline transformations with volume expansion can be provoked in semicrystalline polymers? In this connection the author would like to give credit to Saraf and Porter [3] who first classified the semicrystalline polymers in respect to their solid state deformation behavior. Considering their data ([3] and references therein), one can recognize that a decrease in the crystalline density caused by deformation is likely an exception and, in addition, it is mostly relied on a reversible transition from a stable to an unstable crystalline form. The best example for demonstration of this claim is given by poly(butylene terephthalate) (PBT). PBT undergoes a reversible α (helix)-β (planar zig-zag) transformation upon loading [3-5]. Since for the densities of the α- and β-form 1.40 and 1.29 g/cm^3 were reported (e.g.[4]), this transition may be associated, indeed, with a nominal dilatation of 9 %. This reversible transition, however does not reflect in the macroscopic toughness of

PBT, that is toughened by the usual way (i.e. embedding of solid polymer particles, core-shell type rubbery particles and the like).

Kim and Robertson [4] quoted recently that the unexpected high toughness improvement in cured epoxy (EP) resins toughened by PBT dispersion may be related to the aforementioned volume expansion. Although the authors could not evidence this hypothesis, bearing in mind the analogy with toughened ceramics and the fact that the first failure step in toughened EPs is always cavitation (e.g. [1]), the explanation given by the authors seems to be reasonable.

It should be emphasized that drawing, orientation of semicrystalline polymers gives rise to an increase in crystalline density. This may occur also simultaneously with an unstable-to-stable crystalline transformation. The overall outcome is, however, volume contraction, i.e. just the opposite what we were looking for. Should be therefore the concept of PTT abandoned? Not at all. It will be shown next that increasing crystallinity, or more exactly, increasing crystallinity due to a local rearrangement in the crack tip, might be an efficient tool for toughness improvement in semicrystalline polymers.

3. EFFECTS OF CRYSTALLINITY ON THE TOUGHNESS

It is generally accepted that crystalline polymers are superior to amorphous ones with respect to their toughness performance. This is due to their folded or extended chain conformation in the lamellae and microfibrillar structures, respectively. Nevertheless, in the literature one can find lots of papers claiming for a toughness deterioration with increasing crystallinity. Attention should be paid to the fact that in these papers generally no clear difference was made between effects of crystallinity and supermolecular structure. On the other hand, it can be assumed in the first approximation that the toughness of semicrystalline polymers goes through a maximum in function of crystallinity (Figure 2).

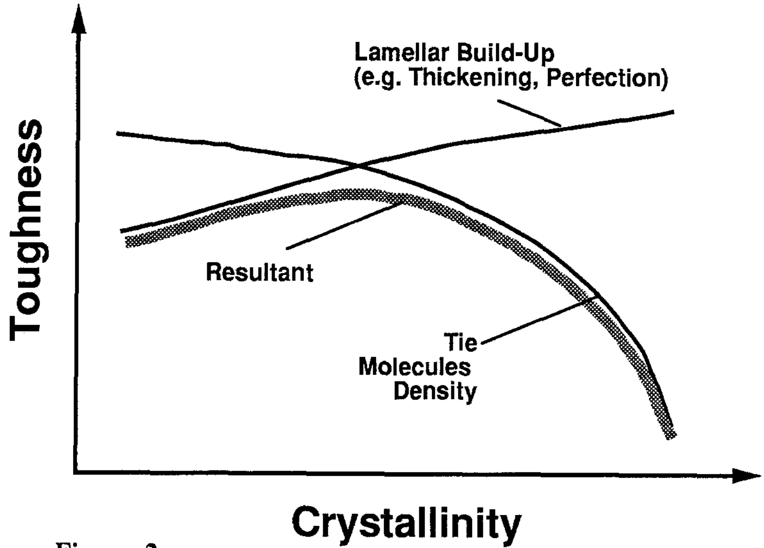


Figure 2
Scheme of the change in toughness as a function of crystallinity and its contributing terms

The resultant curve in Figure 2 can be attributed to competitive effects of the lamellar build-up (beneficial) and tie molecule density (the decrease of which with increasing crystallinity is detrimental for the toughness). The position of the more or less pronounced toughness maximum depends on both testing parameters (measuring frequency of the toughness determination) and inherent microstructure controlling the phase tranformation process (in which lamellar rearrangement, defolding of lamellae and chain alignment may be involved [6]). It is most likely that this microstructural rearrangement occurs simultaneously with the phase transformation (cf. later).

It was shown on the example of unfilled poly(ether ether ketone) (PEEK) that the fracture toughness at high crosshead speed ($K_Q \approx 1.5$ MPam$^{1/2}$) can substantially be enhanced ($K_Q \approx 6$ MPam$^{1/2}$) when the compact tension (CT) specimen is slightly prestressed prior to the high speed loading test. It was evidenced by scanning electron microscopy (SEM; Figure 3) that preloading of the specimen resulted in a morphologic rearrangement ("stress-" or "strain hardening" or crack tip blunting) that was made responsible for the toughness increase.

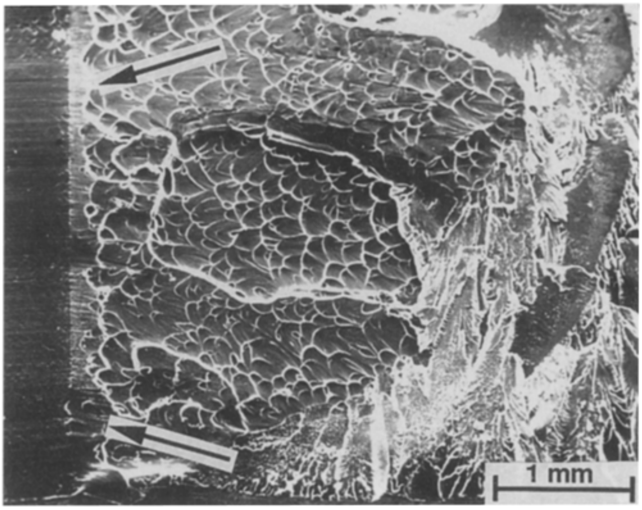


Figure 3
SEM microphotograph taken on the fracture surface of PEEK
(Note: arrows indicate for the "stretched" zone due to plastic deformation at the crack tip)

4. ADAPTIVE TOUGHENING CONCEPT

Figure 4 depicts schematically the proposed scenario of PTT in semicrystalline polymers. The attribute "adaptive" is relied on the fact that phase transformation occurs at stress concentration sites (e.g. in the crack tip; cf. Figure 4), or with other words there where a toughness enhancement is locally required ("healing" effect). The main advantage of this concept that toughness improvement is achieved by making use of the polymorphy and related irreversible transformation from an unstable to a stable crystalline modification, instead of incorporation of a hard or soft modifier phase (which is the present state of art).

Preliminary investigations on isotactic polypropylene (iPP) [7-8] by exploiting its mechanical loading-induced β(hexagonal)-α(monoclinic) transition ([9] and references therein) corroborated the viability of the above concept. The crystallographic densities of the β- and α-iPP modifications are 0.921 and 0.936 g/cm^3, respectively [10], indicating that the β–α transition is connected to volume contraction. The toughness enhancement is illustrated in Figure 5 by comparing the stress-strain behavior of α-iPP and β-iPP with the same molecular characteristics. During deformation the β-iPP undergoes the aforementioned β–α transition, as evidenced by differential scanning calorimetry (DSC) [7-9].

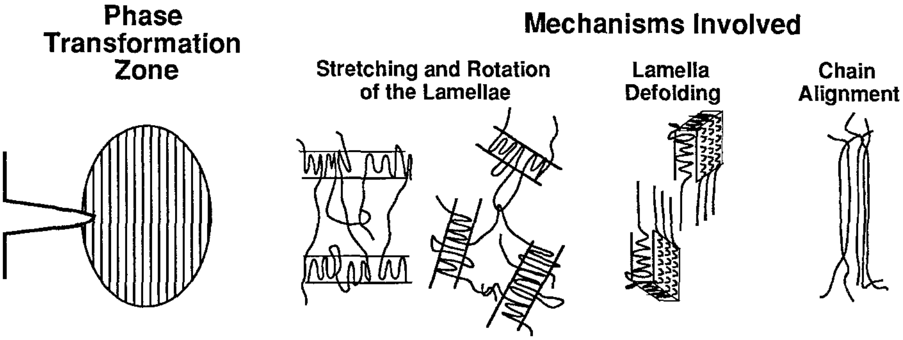


Figure 4
Scheme of the proposed adaptive toughening
(Note: this figure shows those failure mechanisms according to [6] that are likely to occur during PTT)

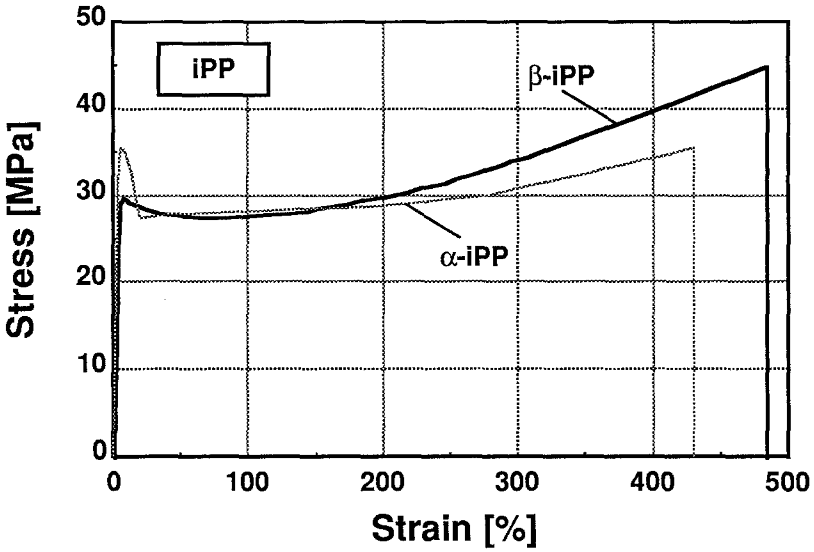


Figure 5
Stress-strain behavior of α- and β–iPP, respectively
(Note: the work of fracture, represented by the area beneath the curves, is higher for the β-iPP undergoing β–α transition during stretching)

5. CONCLUSIONS

It was shown that phase transformation toughening (PTT) via volume expansion is not likely to be a viable mechanism for toughness improvement of semicrystalline polymers. Instead of that, efforts should be focused on stress-induced phase transformations from a less to a more dense crystalline structure with concomitant volume contraction. This is just the opposite to the toughening mechanism practised for some steel alloys and engineering ceramics. The only common feature between the toughening behavior of the latter materials and polymers is that the transition occurs from a metastable to a a stable crystalline form.

Further investigations are needed in order to find the most suitable polymers and related crystalline transitions that could be activated and exploited for adaptive toughening.

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