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Dependence of the Fracture and Fatigue Performance of Polyolefins and Related Blends and Composites on Microstructural and Molecular Characteristics

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ABSTRACT

This article surveys the influence of microstructural, morphological and molecular variables on the fracture and fatigue behavior of polyolefins, related blends and composites. The effects of major parameters of the structural hierarchy on the fracture mechanics (FM) response were considered and the related model descriptions reviewed. Emphasis was put on how important is to select the right FM approach for the toughness determination. It was pointed out that a clear distinction between crack initiation and growth is the essential prerequisite to differentiate between effects of the initial structure and its alteration due to mechanical loading. Although the microstructural dependence of the fracture and fatigue properties in reinforced, filled and impact modified polyolefins is quite well explored, this information is still missing for the neat polymers. This is due to a strong interlinking among molecular and morphological variables in neat polyolefins. Recommendations were given how to overcome this difficulty.

1.INTRODUCTION

Toughness is a key property for many applications of polymers and polymer-based systems. The standardized test methods usually adopted for the toughness assessment differ from one another in the local stress state (uni-,bi- or triaxial), loading mode and rate, test configuration, notching etc., so that the related results cannot be compared if not exactly the same standard and specimen preparation technique were used. On the other hand, it is sound to raise the question whether or not the toughness is an inherent material property. Assuming the latter, the toughness should rely on the supermolecular and molecular build-up of polymers. In order to shed light on this issue the first task is to find suitable toughness determination methods the outcome of which does not depend either on the specimen configuration or on the testing frequency (at least in a given range) under the same type of loading. It is believed that the above premises are met by the methods of fracture mechanics (FM). The reader may disagree

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with this note by arguing that FM cannot be adopted for polymers due to several reasons, including gross yielding, damage growth, and viscoelasticity. It will be shown later that these aspects can be considered by using methods of the elastic-plastic (EPFM) and post-yield fracture mechanics (PYFM) instead of the the linear-elastic version (LEFM). In order to elucidate the microstructural, morphological and molecular dependence of FM parameters, tests should be performed on series of samples in which only the structural parameter to be studied is changing. Though this requirement is obvious, it cannot be easy fulfilled in semicrystalline polymers since the effects of molecular and morphological parameters are strongly interrelated. It is well known for example that changes in the molecular weight (MW) affect the crystallinity, the lamellar build-up, the density of the tie molecules etc. - so, which one of them should be considered as controlling parameter? The scenario becomes even more complex due to processing, the effects of which (e.g. skin-shear-core structure, molecular segregation) may overwrite the initial molecular arrangement. Needless to say, that in case of filled and reinforcd systems we are faced with additional complexities. So, what to do? The most straightforward action is to figure out the control parameters on molecular, supermolecular (morphological) and microstructural levels, respectively, by using suitable polymer samples. This contribution is aimed at supporting this task by giving an overview based on both open literature and also the data of the author. Figure 1 lists the domains influencing the FM response of polyolefins and related composites and serves at the same time as an outline for this contribution. The shadowed area in Figure 1 emphasize the interrelation among the areas listed.

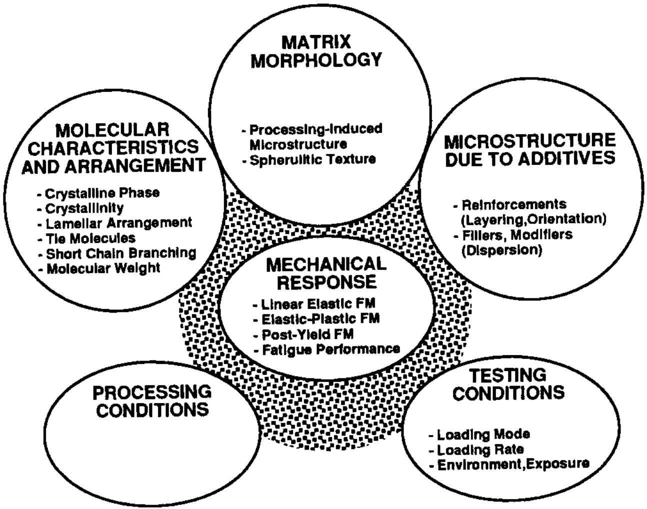

Figure 1

Factors influencing the fracture and fatigue behavior of neat, filled, and reinforced polyolefins

The presentation follows a "deductive" way. It starts with reinforced and filled systems in which matrix characteristics less affect the fracture and fatigue performance and ends up with listing the interlinked molecular parameters which control the FM response in plain polyolefins. A major goal of this contribution is to point out open questions and encourage the cooperation between polymer chemists, physicists and engineers in order to solve them accordingly.

2. FRACTURE TOUGHNESS AND FATIGUE TESTING (METHODS AND METRICS)

The techniques are grouped into standardized and FM methods. This distinction is reasoned by the fact that until now no standard FM method exists for polymers. It should be kept in mind that for the determination of the fracture and fatigue resistance some other methods than those listed below may also be used (e.g. work derived from the stress-strain curve for the toughness or hysteresis change during cycling for the fatigue evaluation).

2.1.Standardized Tests

2.1.1. Fracture Behavior

The widely used standardized tests are as follows:

- uniaxial tensile impact with and without notches (DIN 53 448)
- flexural beam tests with and without notches (Izod- ISO 179; Charpy- ISO 180). It is worth noting that FM data can be derived from notched Charpy and Izod tests.
- falling weight impact or puncture tests on films,plates or boxes (ISO 6603), Gardner impact (ASTM D3029).

By using instrumented impact devices a deeper understanding of the fracture history of the specimens can be reached. Further, it is possible to differentiate between the force and energy required for initiation and those needed for propagation, respectively. Nevertheless, the data from different tests cannot be converted to one another. In addition, the results in one test may also differ as a function of the allowed alternatives in test configuration and specimen preparation (e.g. injection or compression molded specimens, molded or mechanically introduced notch).

2.1.2. Fatigue Behavior (Static and Cyclic)

Though standardized tests methods are available for both static (creep tensile-ISO 899, creep:tensile,flexure,compressive - ASTM D2990) and cyclic fatigue (tensile fatigue- ASTM D 3479, reciprocating flexure - ASTM D 671), the related data are generally not disclosed in the technical literature (product brochures). The outcome of these tests is mostly the endurance limit (fatigue lifetime), i.e. the maximum allowed stress below which no failure occurs within a given time interval (creep) or number of cycles (fatigue). Though this threshold value is of great practical importance for design, it relies on alterations in the microstructure (e.g. crazing, shear deformation, morphological rearrangement) rather than on the initial structural order. This is the right place to emphasize that the control parameters of the fracture and fatigue response can only be established if the crack initiation step (related to the initial structure) can be clearly divided from the propagation step (depending on possibilities of loading-induced morphological changes). If these steps are superimposed on each other, the toughness or the fatigue responses can not be represented by a single parameter (as desired) but must be represented by a curve (e.g. crack resistance curves - see sections 2.2.2 and 2.2.3).

2.2. Fracture Mechanics (FM)

The basic premise of FM is to acknowledge the existence of cracks or flaws in materials. Flaws of various origins can be found in polymers (density or orientation fluctuations, microvoids, foreign particles, weld lines) which justify the use of FM. On the other hand, the inherent material flaw size does not correspond to a notch. The failure of neat polymers is stress controlled1). Thus the question arises: what does FM measure? FM is aimed at determining the response of a cracked material to applied loads and offering methods to measure the toughness. Each FM method defines, however, its own version for the resistance of the material to fracture (called "fracture toughness")2). The beauty of these approaches is that they give values which either are equivalent to each other (under given conditions) or can be converted to one another in the knowledge of additional material properties. Based on the latter, various FM results can be collated - this is a great advantage over the standardized test methods listed in section 2.1. Since in the whole paper the mode I loading (crack tip opening) is reviewed, the usually used subscipt I will be omitted. For a detailed description of the various FM methods given below, the interested reader is addressed to Refs.2-9).

2.2.1. Linear-Elastic Fracture Mechanics (LEFM)

The LEFM works for brittle materials which fail by catastrophic crack propagation after reaching a threshold stress value. The related criteria rely either on the stress field ahead of the crack tip (stress intensity factor or fracture toughness, K_c) or on the energy release during crack extension (strain energy release rate or fracture energy, G_c). Both of these criteria found application for polymers and polymeric composites showing limited ductility. LEFM works well for highly filled or reinforced systems, for plain or modified polyolefins at low temperatures and/or at high testing frequencies (i.e. cold impact). Draft standards for the K_c and G_c determination of polymers and polymeric composites are available by the ESIS TC-4 and ASTM D-20 committees.

2.2.2. Elastic-Plastic Fracture Mechanics (EPFM)

For polymers and related composites the J-integral and the crack tip opening displacement (CTOD) are mostly used. The former represents a path-independent integral around the crack tip and thus considers also the plastic deformation at the crack tip. The J-integral can well be determined by the multiple specimen technique (J_R-curve, where R stays for resistance), as depicted schematically with the physical meaning of the critical J value (J_c, full crack tip blunting prior to crack growth) in Figure 2.

Draft for the determination of J_c was elaborated by the ESIS TC-4 group. The problems with this technique are as follows:

- full blunting is an exceptional phenomenon since the crack tip of polymers may experience crazing or yielding. Therefore, no universal expression (given by $2\sigma_y\Delta a$, where σ_y is the yield stress and Δa is the crack advance - see Figure 2) holds for the blunting. Several workers follow the alternatives given by the ASTM E813 (valid for metals) from 1981 (J_c determination by linear extrapolation as shown in Figure 2) and 1987 and 1989 (description of the J_R curve by a power law function), respectively. Others determine J_c as the direct intercept with the y (J)-axis. The latter treatment is argued to overcome the ambiguity with the blunting.
- one can see in Figure 2 that J is surface-related. On the other hand, the deformation zone in the crack tip region extends also in the bulk (see Figure 3). This volume-related energy component remains unconsidered.
- Δa can hardly be determined in polymers and polymeric composites experiencing "strain hardening" via various deformation processes.

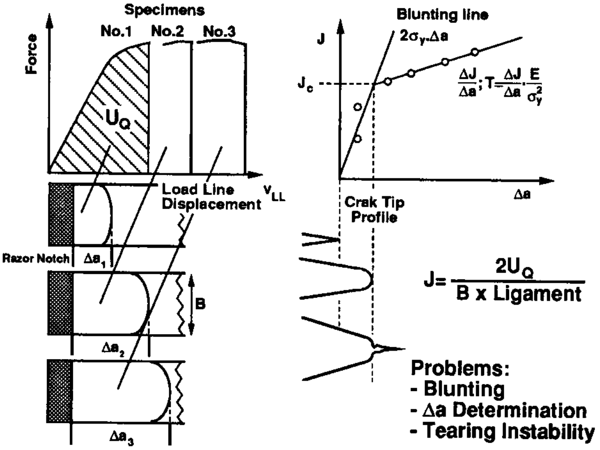

Figure 2

Schematic determination of the J-integral by the multiple specimen technique

Irrespective of these problems the J-integral technique has been succesfully applied for many polymers, including polyolefins.

The CTOD criterion is linked to the crack opening prior to extension. CTOD thus also considers the plastic flow capablity of the polymer. The problem is again that many polymers tend to craze or flow instead of exhibiting homogeneous plastic deformation. The CTOD is a very straighforward technique reflecting the effects of the initial structural order. Unfortunately, it is rather seldom adopted for polymers possibly due to instrumentation/crack inspection problems.

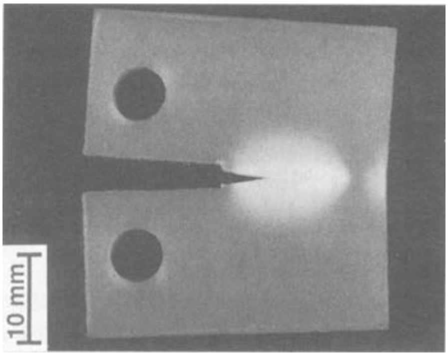

Figure 3

Damage zone formed (see stress-whitened region) in a static loaded compact tension (CT) specimen of a PP copolymer

2.2.3. Post-Yield Fracture Mechanics (PYFM)

Here attention will be paid to the essential work of fracture (EWF) method which is analogous to the J-integral since both of them represent a type of the resistance curves (R-curve). The biggest benefit of EWF over the J-technique is a clear distinction between surface (essential part) and volume-related (non-essential part) work is made. The basic prerequisite of this method is that the ligament (l) of the specimen should be fully yielded before the crack propagation starts. This is again rather seldom the case since in many of the polymers tested ligament yielding occurred simultaneously with a more or less pronounced crack growth. A draft on how the EWF should be performed (see schematics in Figure 4) was also elaborated by the ESIS TC-4 group.

2.2.4. Remarks

The reader will find in the literature several reports claiming that one or another of the aforementioned FM approaches did not work. Less information is available on the question why. The reason behind this fact is that FM is pushed forward mostly by mechanical engineers with less knowledge on the structure-property relationships of polymers. On the other hand, polymer chemists and physicists do not trust the FM to solve the complex problem of structural dependence of the toughness. Therefore caution is required in respect to categoric statements especially on the inapplicability of the FM methods. The simple reason in many cases that the "wrong" approach was adopted for a "wrong" (from the viewpoint of the required behavior) polymer. The author of this review hopes that some topics of dispute will be seen in a different light after reading this paper and the cited works within.

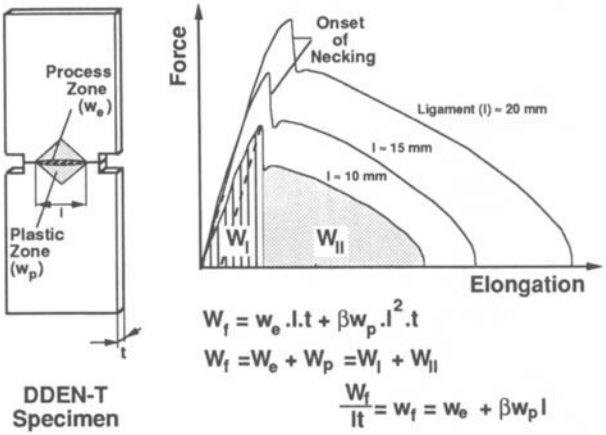

Figure 4

Determination of the essential and non-essential work of fracture by using specimens of various ligament length

3. EFFECTS OF MICROSTRUCTURE ON THE FRACTURE MECHANICAL PROPERTIES

3.1. Definition of the Microstructure

By the word "microstructure" we mean the structural order of reinforcements, fillers and modifiers in the polyolefin matrix and that of the polymer itself (spherulitic structure). This category covers also the processing-induced changes both in the filler structuring (layering and orientation, segregation etc.) and in the matrix morphology (skin-core structure, higher-order structures).

3.2. Processing-Induced Microstructure

3.2.1. Discontinuous Fiber-Reinforced Composites

The shear and elongational flow in the cavity during injection-molding result in a peculiar structuring of short and long discontinuous fibers as depicted schematically in Figure 5. This resembles a multiply composite structure in which each distinct layer can be characterized by a given planar orientation pramater (f_p). The layering and orientation depend on a number of factors such as fiber volume fraction (V_f), mold thickness (B), processing conditions etc.; the most relevant of them are summarized in Figure 5 10). Based on Figure 5 it is obvious that the fracture and fatigue performance of specimens notched along (L-notched, or according to ASTM E616 T-L-notched) the mold filling direction (MFD) differ from those notched transverse to the MFD (T, or L-T notch). How to consider this microstructure? The recomendation of the ESIS TC-4 takes into account only the relative fiber layering (cf. C/B or S/B in Figure 5) and thus can be treated only as a very rough estimation of the microstructure.

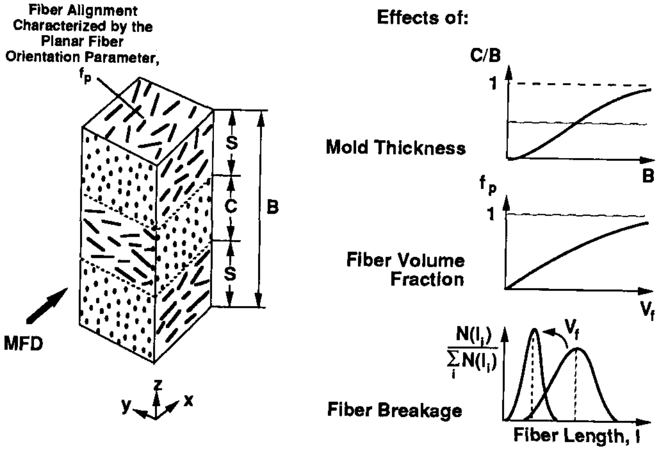

Figure 5

Microstructural parameters of discontinuous fiber-reinforced injection-molded polymer composites, schematically

The microstructural efficiency (M) concept, originally introduced by Friedrich 11) and later improved 12) is far more advanced:

$$K_{C,c}=MK_{C,m}=(a+nR)K_{C,m} \qquad (1)$$

where $K_{C,c}$ and $K_{C,m}$ are the fracture toughness of composite and matrix, respectively, a is the matrix stress condition factor, n is the energy absorption ratio and R is the reinforcing effectiveness parameter. Equation 1 considers via R the contribution of V_f, the reinforcement structuring (layering+orientation) with respect to the notch, the effective aspect ratio and its distribution11-13). The suitability of this concept was demonstrated on a large number of injection-molded composites 13), among others also for composites of polypropylene (PP) and PP-based blends both under static 14-15) and dynamic conditions 16). An attempt was also made to use this M concept to predict the J-integral results 13-14). Though the trend was well predicted, some deviation was observed in the curves J vs. R. This can be explained by disregarding the volume-related work. It is obvious that the effect of the latter becomes more pronounced with increasing aspect ratio of the reinforcement.

The fatigue crack propagation (FCP) usually obeys the Paris-Erdogan power law function:

$$\frac{da}{dN}=A(\Delta K)^m \qquad (2)$$

where da/dN is the crack growth per each cycle, A and m are constant and ΔK is the stress intensity amplitude. It was found that the FCP response can well be described by the M-concept when assumed that the terms a and n of Equation 1 are taken as equal to those derived from static loading tests 13). The FCP-rate at a constant ΔK value as a function of M or R resulted in a fair linear regression 13,17-18). With the knowledge of M and its constituents, both fracture toughness and FCP can be described or predicted. As quoted earlier, the effect of microstructure on the fatigue response is likely better reflected by the ΔK threshold below which no FCP occurs. Unfortunately no such data are available for reinforced polyolefins. The alternative criterion may be related to the changeover from the stable decelerated to the stable accelarated crack growth. Such a changeover was observed not only for chopped GF reinforced PP 19-20), but also for neat PP 21). Its onset was attributed to the full development of the crack tip damage zone, which should reflect the effects of the initial microstructure more correctly. This aproach can also be used for the creep response, during which an analogous threshold between stable deceleration and acceleration was found 17).

As surveyed above, the LEFM approach is usable for the description of the fracture and fatigue responses of chopped fiber-reinforced polyolefins. Prerequisite is that the matrix influence is marginal in comparison to those of the reinforcement. This is met in composites having high V_f and/or relative low-ductility matrices. In case of semiductile, ductile failure the use of the maximum crack growth resistance ($K_{R,max}$) may extend the applicability of LEFM (see section 3.2.2.).

3.2.2. Filled Systems

The fracture performance of injection- or compression molded polyolefin systems can be adequately characterized by the methods of LEFM, especially under impact conditions 17). According to the present state of knowledge, both K_c and G_c decrease with increasing V_f. The run of the related curves (which may show also some increase at very low V_f) depends on further terms such as the type and amount of the coupling agent, and the presence of rubbery modifiers. This, on the other hand, affects the dispersion state of the fillers. It should be emphasized again how problematic is to distinguish among the superimposed effects of dispersion, coupling, encapsulation, interfacial morphology, molding-induced morphology and molecular characteristics. Friedrich and Karsch 22) proposed a constitutive model to describe the G_c vs V_f function for silica filled PP, which proved to work also for highly filled

PE systems. In more ductile systems some modification of LEFM or use of EPFM approaches are required.

In case of LEFM usually the R-curve concept is followed. $K_{R,max}$ is determined by computing the K_c values as a function of the crack extension (Δa) in the stable crack propagation range. $K_{R,max}$ usually goes through a maximum (located at low V_f) as a function of V_f. This hints at the crucial importance of the interparticle distance 23). The alternative approach is based on the J_R-curve by which the importance of the interparticle distance was also corroborated 17,23). A refined model based on the works of Lauke 24-25) which involves the J- and CTOD criteria was introduced and verified for chalk-filled HDPE at high impact speed 26). This model considers the damage zone as composed of process and plastic zone constituents. Recall, that exactly these terms are used in the EWF method of the PYFM. Results achieved on kaolin filled HDPE showed that the high extent of the volumetric work is the reason why the LEFM fails 27). On the other hand, the EWF approach was well suitable for the same type of composite 28). Results from kaolin filled HDPE 28) and glass sphere (GS) filled PP with and without rubber modifiers 29) can be generalized as depicted in Figure 6. Figure 6 indicates for effects of the interparticle distance. Mouzakis et al. 29) succesfully demonstrated that the formation of the surface plastic zone can be described by Wu's criterion 30).

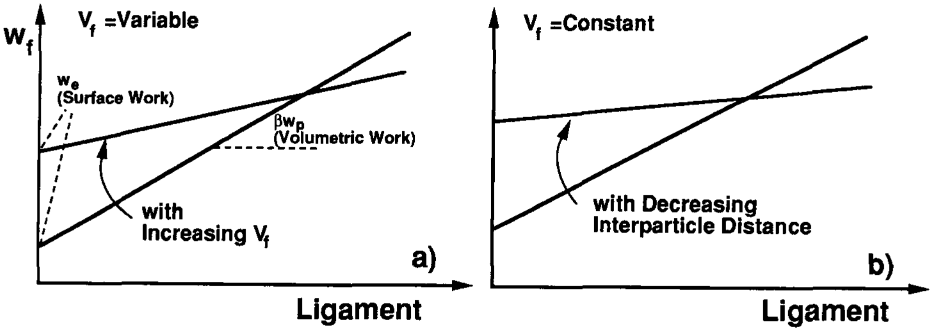

Figure 6

Specific work of fracture (w_f) vs ligament (l) curves for filled systems at constant particle size with increasing V_f (a) and at constant V_f with decreasing particle size (b)

The EWF theory is the best tool for the fracture assessment of rubber-toughened polyolefins 31-33). Caution with this technique is required in the case of molded items with pronounced skin-core morphology. The complex anisotropic deformation of the skin may blur the distinction between the process and plastic zones and yield useless data. This can, however, be recognized early during the tests, since the load-displacement curves at various ligaments are not self-similar, i.e. they do not coalesce by normalization 33). The toughness of such anisotropic systems cannot be assessed, or more exactly can be determined only if no or little morphology rearrangement takes place during testing (for example under impact). The latter aspect indicates that morphological effects can be clarified by means of low frequency tests, i.e. in creep or fatigue tests.

Surprisingly, much less information is available on the FCP behavior of filled polyolefins. The possible explanation for this is the very complex form (especially from the point of view of the subsurface pattern) of the advancing crack front. In many cases no crack propagation but only a change in the surface and bulk plastic zone can be observed. Due to this behavior, the LEFM theory cannot be applied. In other cases both the crack size and shape are changing with crack growth; this can be followed and treated for example by the crack layer theory 34-35). Nevertheless, this theory was mostly applied for unfilled polymers such as PP 36).

3.2.3. Neat Polymers

The injection-molding-induced complex morphology (termed the skin-shear-core structure) makes the fracture and fatigue response direction-dependent (anisotropic). This was revealed by K_C values established on CT-specimens of PP loaded along and perpendicular to the MFD 14). However, as mentioned above the fatigue tests are more appropriate to figure out the morphology effects. Figure 7 shows the effect of MW and relative orientation of the skin and

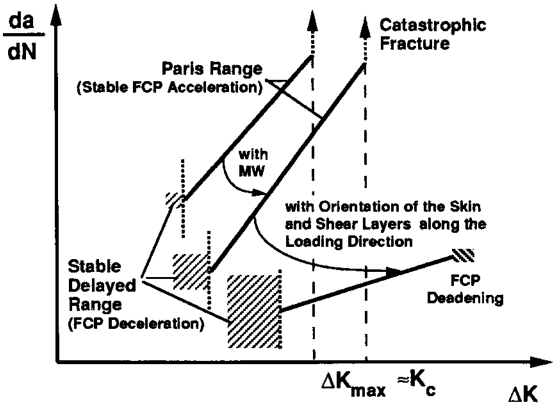

Figure 7

Effects of molecular weight and orientation of the skin-core structure on the FCP response of injection-molded PP shear layers on the FCP response of molded PP [17-18,21]. The stable deceleration range indicated in Figure 7 is due to a crack tip blunting proess associated with stress- or strain induced lamellar rotation, lamellar break-up, molecular orientation etc. Obviously the possibility of this deformation is linked to the relative orientation and build-up of the skin and shear layers with respect to the loading. During cyclic loading, the outer skin layer may be transformed into hard elastic (springy) bands which bridge the crack flanks so efficiently that the FCP stops [17-18,21]. This is an excellent evidence that the loading-induced microsructural changes may strongly affect the FM response and limit the applicability of FM. This supports the earlier claim that attention should be paid to the initiation stage in order to discard the above strain-hardening effects caused by morphological restructuring.

3.3. Disperse Structure

The methods for determination of the toughness and resistance to crack growth of polymer blends and composites of dispersed structure, however without molding-induced supermolecular structure, are essentially the same as surveyed in section 3.2. For ductile polymer blends, the method of Vu-Khanh [37-38] can also be used. This approach assumes that the fracture energy varies linearly with the crack extension and the energy is mostly dissipated in the process zone (i.e. no volumetric work as in the case of EWF is considered). It is obvious that this R-curve variant works well for the interpretation of high-impact tests on notched specimens where less energy is dissipated in the plastic zone.

3.4. Spherulitic Structure

Aspects of the spherulitic structure were topics of investigations for both PEs and PPs in the 1980s. The interest for PE was triggered by its moderate environmental stress cracking (ESC) behavior [eg. 39], and for PP by its morphology-related toughness improvements [e.g. 17,40]. The outcome of these studies was that both toughness and crack growth resistance strongly decrease with increasing spherulite size. This conclusion holds also for rubber-modified polyolefin blends. The reason behind this is a change from plastic deformation towards interspherulitic boundary fracture with increasing spherulite size [17]. The next logical step was therefore to increase the density of interspherulitic tie molecules. For this purpose PP grades with high atactic PP (aPP [41]) were introduced and tested [42]. This philosophy is followed now with a more advanced aPP-containing polymer, viz. elastomeric PP (ELPP) [43]. The ELPP is a stereoblock PP version composed of aPP and crystallizable isotactic PP blocks (iPP) and thus a new member of the semicrystalline thermoplastic elastomers [44-45]. The "interspherulitic bonding" concept suggests that neither the spherulite size, nor its texture, but a more complex interaction between molecular and morphological parameters directs the FM performance.

4. EFFECTS OF MOLECULAR AND CRYSTALLINE CHARACTERISTICS ON THE FRACTURE MECHANICAL BEHAVIOR

4.1. Crystalline Phase and Structure

Several works reported that the toughness of the β-phase PP (β-PP) is superior to the α-form e.g. 46-48). It was also demonstrated that β-PP undergoes a mechanical-loading induced β-to-α transformation in both static and dynamic tests above the glass transition temperature ($T_g \approx 0°C$)49-50). The author of this contribution termed this behavior "phase transformation toughening" 49-51). Recently both LEFM 52-53) and PYFM (EWF 49-50)) approaches were followed to quantify the toughness difference between β- and α-PP. One of the striking observations of the static mechanical tests was that the essential work of fracture is identical for both α- and β-PP, whereas the slope (i.e. the non-essential work constituent) of the related w_f vs. l curves is three times higher for β-PP compared to α-PP 49). The former finding can be attributed to the fact that the same grade of PP was used, however, β-PP was produced by adding a selective β-nucleant in 0.1. wt.%. By this method the molecular characteristics remain essentially the same, but the crystalline state becomes different. No effect of the latter could be found, however, by the linear extrapolation procedure of EWF on the essential work of fracture term. This is a hint that for some polymers the toughness can hardly be described by a single parameter. The alternative is that the whole resistance curve should be considered. The change in the slope of the w_f vs l curve is due to a large volumetric work in the plastic zone of β-PP, the size of which was considerably larger than in α-PP 49-50). The author is still not aware why the outstanding toughness performance of β-PP can also be detected below the Tg, where the β-α transition is less likely to occur. It was speculated 53) that this is an effect of the morphology and related damping.

The revolutionary metallocene polymerization technique allowed the production of ELPP, which became the subject of a recent PYFM study 54). It was established that the essential work increased, whereas the non-essential work decreased with decreasing crystallinity. This tendency was explained by a synergistic effect of the molecular entanglement in the amorphous phase and the physical network structure, in which crystalline PP aggregates form the "knots". Since ELPP is a special kind of semicrystalline thermoplastic elastomers, it is not surprising that the molecular entanglement does play an important role.

4.2. Crystalline Fraction, Order and Orientation

The application of PE for pipes, especially in gas-piping, initiated strong interest for lifetime prediction, determination of the brittle-ductile transition temperature, failure analysis, etc. The FM approach was followed in many cases from the early beginning. Reports on the effects of crystallinity (density) on the fatigue and fracture behavior are controversial. For PEs it was shown for example that the toughness increases with increasing crystallinity [55], whereas for PP the opposite tendency was observed [56]. This is due to the fact that variation in the crystallinity is associated with changes both in the spherulitic structure (size) and within the spherulites (lamellar thickness, orientation, amorphous layer, tie molecules) which have not been always considered. One can assume, however, that both fracture toughness and resistance to FCP go through a maximum with increasing crystallinity if all other parameters are constant. It is obvious that deformation and rearrangement in the crystalline structure (lamella rotation and break-up, formation of fibrils etc. - cf.model of Peterlin [57]) are associated with substantial energy consumption. Thus enhanced crystallinity yields improved fracture toughness. Why is the opposite tendency expected when passing a threshold crystallinity? The author argues that this occurs by crack tip "sharpening" due to increased crystallinity which restricts the stress relief in the amorphous phase. With increasing crystallinity the amorphous layer thickness reduces when the other molecular parameters (e.g. lamellar thickness, tie molecule density) are kept constant. As analogy the restriction of the damage zone in advanced composites composed of plies of unidirectionally (UD) aligned continuous fibers with increasing V_f should be considered [58]. Unfortunately no direct evidence is available on this topic due to the aforementioned complex interaction between the molecular parameters. Based on FCP tests Runt and Jacq [59] demonstrated a competing effect between degree of crystallinity and tie molecule density.

The outcome of a J-integral study on pipe-grade HDPEs was that the initiation value (J_c) depended on the thickness of lamellae, side chain concentration and degree of order in the crystalline region. The thicker the lamellae and the more ordered the crystalline region the greater is the resistance of HDPE to crack initiation. On the other hand, the crack growth changed adversely with increasing concentration of short side chains [60]. It is supposed that by making use of the metallocene synthesis, polyolefins with the required changes in molecular paremeters can be produced and thus give a deeper insight in this aspect.

The fracture and fatigue responses as a function of orientation (both crystalline and amorphous) are more clear. Increasing orientation (by whatever means achieved) results in upgraded toughess and resistance to FCP when the loading direction agrees with that of the orientation. Applying stress perpendicular to the orientation direction results in a much smaller toughess value. This anisotropy can easily be explained by formation of a strongly UD oriented (e.g.fibrillar) crystalline structure. By biaxial orientation, the anisotropy can be tailored. Thus, introduction of molecular orientation increases the fracture resistance [61]. This may strongly limit, however, the application of FM approaches. In case of UD-oriented notched specimens loaded in L-T direction delamination ahead of the crack tip may occur [61]. This is a clear experimental evidence for the strong anisotropy in the FM response. Recall that the weak interface perpendicular to the anticipated crack growth is due to molecular orientation. This mechanism (termed Cook-Gordon mechanism 62)) can be exploited in self-reinforced polyolefins accordingly 63). It is the right place to point again the analogy of UD-oriented polyolefins with UD-reinforced advanced composites. FM tests were performed on cold-rolled (J-integral 64)) and roll-drawn (LEFM 65)) PPs and showed the aforementioned structural anisotropy accordingly.

4.3.Short Chain Branching and Tie Molecule Density

Comparison of the FM response of LDPE and linear low density polyethylene (LLDPE) showed a superior toughness of the latter 66). Based on this finding several studies were devoted to the effects of short chain branching (SCB) on the FM properties of LLDPE. Comparing the fracture behavior of ethylene/1-olefin copolymers with similar molecular characteristics but with varying length of SCB (copolymers of 1-octene, 1-hexene and 1-butene yielding SCB length form 6 to 2 carbon atoms), the authors found that the toughness of LLDPE increases with increasing SCB length 67). The longer SCB was believed to inhibit the chain folding of the molecules which would have increased the number of interlamellar tie-molecules. Note that again the parameter under focus of investigations (i.e. SCB length) involved another parameter, viz. tie-molecule density. The latter was assessed by the Brown-Ward equation 68) and increased with increasing SCB length, indeed. A refined treatment of the high-speed impact FM results showed a further hidden effect, viz. SCB distribution (SCBD), based on which the related ethylene copolymer becomes a special kind of blend. Broader SCBD correlates with higher toughness 67). The author suggests that this is the reason why PE manufacturers offer grades with bimodal molecular weight distribution (MWD).

Studying the fatigue fracture of medium density ethylene copolymers, improvement in the resistance to crack initiation and growth was found with increasing length of the SCB. Unfortunately the authors did not disclose further useful molecular details that would allow a deeper understanding 69). Similar conclusions on effects of branching and tie molecule density were derived by Channel and Clutton 70) in a profound LEFM study focused on the high-impact performance of HDPE and LLDPE grades. The authors used PEs with various M_W and polydispersity (P) values and found that G_C linearly increases with increasing M_W. Since the increase in the molecular weight is accompanied by an increase in the number of tie molecules in the amorphous region 68,71), the above linear relationship should hold also as a function of the tie molecule density.

4.4. Molecular Weight and Tie Molecule Density

It was observed in high-speed impact tests of PP that both K_C and G_C increase linearly with M_W in a broad temperature range (-100...+40) 72). It is worth noting that for amorphous polymers the G_c vs. M_w function followed an s-type curve in double-logarithmic scale 7). Other authors reported that K_c correlates with $\sqrt{M_w}$ for PP 73). This result validated the molecular theory of Kramer 74) deduced for low molecular weight polymers. In a recent fundamental study 75) the authors considered the effects of the following variables on the LEFM of HDPE grades: MW (M_n,M_w), SCB, and thickness of the amorphous and crystalline layers. The results were validated by an extensive statistical analysis (backward stepwise regression) which considered possible interactions among the above parameters. The authors summarized the outcome of this analysis in correlation matrices. It was claimed that the decisive control parameter of the toughness is M_w. As with increasing M_w the toughness improves but the processability of HDPE becomes more dificult, it was recommended to improve the toughness at the same M_w by introducing SCB (copolymerization with 1-olefins). A further relevant finding of this study was that decreasing crystalline and increasing amorphous thicknesses do upgrade the toughness. Increasing amorphous thickness implies a high tie molecule density which was, however, not explicitely considered.

Fatigue tests on various polyolefins showed that M_w is, indeed, the key parameter. Lu et al. 76) demonstrated by a very elegant method (using fractionated PE resin which was sandwiched between PE holders prior to static fatigue) that there is a critical M_w above which the resistance to fatigue is strongly improved. This critical value was linked to the formation of tie molecules. It was reported by Huang and Brown 77) that the probability of forming tie molecules depends on both MW and the long period (sum of the crystalline and amorphous layer thicknesses). Since the long period is linked to the density of SCB (because the lamella thickness is governed by the mean distance between branches), it is expected that the tie molecule forming critical M_w will decrease as the average density of SCB increases.

Yeh and Runt 78) interpreted the FCP response of HDPE samples (varying MW at the same crystallinity and supermolecular structure) by considering the tie molecule density. The latter was estimated from the brittle fracture stress 68) and computed also according to a modified model based on that of Huang and Brown 77). The FCP resistance was strongly enhanced by increasing tie molecule density. The crack tip became enlarged and "blunted" in the presence of the tie molecules. This process was accompanied with a high energy consumption during the test, resulting in low FCP rates. Interestingly, the authors did not find a significant difference in the FCP response when HDPE samples with the same crystallinity and tie-molecule density but different spherulitic size were tested 78).

The above note on the crack tip blunting hints for the important role of the tie molecules in stress transferring and distribution. Since the blunting process in polyolefins is usually associated with crazing, it is worthwhile to consider the state of knowledge of the molecular dependence of crazing 79-82). For PP it was shown that the craze fracture is caused by failure of the tie molecules. The craze strength of PP was argued to depend on M_n and to be independent of M_W, which needs experimental verification [83]. The toughness prediction of Wu [84] considering the entanglement and molecular dimension fits also in this scenario.

5. OTHER DESCRIPTIONS OF THE FRACTURE MECHANICAL RESPONSE

The author in this overview focussed on the microstructural dependence of the facture and fatigue response of polyolefins and related systems. This is definitely not the only way. The alternative description of Brostow et al. [85-87] is based on the chain relaxation capability and thus linked to the free volume concept. This description may be an alternative to estimate the fracture and fatigue behavior.

6. OUTLOOK

The microstructural parameters which control the FM response of discontinuous fiber-reinforced, particulate-filled and impact modified polyolefins are well known. The related models require some refinement. Attention should be paid in this respect to the use of an FM approach "adjusted" to the failure mode of the polymer tested. In case of the plain polyolefins, however, only a combined effort of polymer physicists, chemists and engineers could contribute to solve the open questions which can be summarized as follows:

i) interrelation between molecular and morphological parameters

It is of paramount importance to perform tests on well characterized polymers showing the change in the variable to be studied and adopt suitable statistical analysis to deconvolute the results from superimposed effects. It can be prophecied that samples meeting the above requirements can be produced by the metallocene synthesis.

ii) fracture and failure mode and their description

It is indispensable to perform mechanical tests with in-situ inspection of the microstructure. This may occur by use of synchrotron X-ray radiation [88-89], microbeam FT-IR, high-voltage electron microscopy [90], atomic force microscopy and the like. The use of these techniques would contribute to separate the effects of the initial microstructure from those caused by mechanical loading.

iii) direct determination of the tie molecule density

Recall that the tie molecule density is usually an estimated value. On the other hand, direct techniques(electron microscopy, neutron scattering etc.) would yield useful results when sampling takes place in a representative probe dimension.

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