# CHARACTERIZATION OF THE FRACTURE RESISTANCE OF HIGH TOUGHNESS COMPOSITES AND BLENDS: PROBLEMS AND LIMITATIONS OF CURRENT TEST METHODOLOGIES

*ANDREA LAZZERI*
Università di Pisa

*ABSTRACT*

*The limitations of current fracture mechanics approach in the case of high toughness composites and blends are discussed. Possible solutions are also suggested.*

## *1. INTRODUCTION*

Despite the current level of development of fracture mechanics (FM) of polymers, simple Izod and Charpy tests are still currently widely used in both industry and academia for R&D purposes and materials selection. The success of these rather naive test methods is only in part due to their simplicity and ease of interpretation. There are also other explanations which are related to current limitations of modern FM, and in particular to its historic development. Although often the first study in fracture mechanics is considered that of Griffith on glass, what really motivated the advancement of FM was the problem of fracture in structural steel. In this material, cracks had been observed to develop and grow in a catastrophic manner under stress conditions well within the elastic range. So the initial focus of FM was that to understand the conditions for crack initiation in structural materials. Fatigue crack propagation is another fundamental aspect that was dealt with by FM. This area of research is particularly critical in aerospace applications, so much effort has been devoted to this branch of FM.

Since its infancy, FM benefited from the large body of knowledge that had been built on metals from the 1950s to the 1970s (1). As a consequence of this origin, state of the art FM of polymers tends to focus more on crack initiation rather than crack propagation, which is very relevant in most applications of plastics, especially under impact conditions. As an example, the critical parameters that can be measured experimentally, like $K_{IC}$, $G_{IC}$ in linear elastic fracture mechanics (LEFM) or $J_{IC}$ in elastic plastic fracture mechanics (EPFM), all deal with crack initiation. Another consequence of the historical origin of FM of polymers is that current FM standards involve a range of specimen thickness that is neither realistically achievable nor representative of industrial manufacts. This is, in fact, a practical major limitation of FM which substantially limits its use in both industry and academia.

The purpose of the paper is to review the main shortcomings encountered when trying to use FM on toughened plastics or short fiber reinforced polymer composites. Also possible solutions will be envisaged and suggested.

## *2. AN EXAMPLE OF FM RESULTS ON FILLER TOUGHENED PLASTICS*

As discussed above, current FM has strong limitations when applied to tough behaviour under impact conditions. In this paragraph several examples of the limitations encountered when using FM in research and development of new materials will be examined.

The first example is taken from recent results obtained in our laboratory in a research oriented to toughening polyolefins with rigid fillers (2). In this work, very fine particles (70 nm) are used which have a strong tendency to form large agglomerates that cannot be broken during melt compounding. The consequence is a brittle behaviour since agglomerates behave as large cracks or crazes. This problem can be overcome by the addition of a suitable quantity of stearic acid (SA) which covers the individual particles, lowering the surface tension between the polymer and the inorganic surface, and enabling a rather good level of dispersion to be reached. It is clear that when SA is added above a critical threshold, some reduction in the overall properties can be found.

The purpose of the work was in fact to determine the optimum level of SA. The fracture characterization has been performed by means of a series of impact tests according to both standard Charpy and LEFM (3). Figure 1 to 3 show the experimental results obtained.

A sharp decrease in Charpy impact strength can be observed in Fig. 1 when 10% vol. of uncoated CaCO3 is added to HDPE. Upon increasing the SA content, the energy to break the sample progressively increases, although only at SA contents over 9% the PCC/HDPE composites show a higher value in impact strength respect to pure HDPE. For a stearic acid content of 12% (wt%) a maximum in impact energy can be observed; this fact is due to a better dispersion of the filler in the matrix, reducing the average size of the agglomerates. When these data are compared with LEFM values of $K_{IC}$ and $G_{IC}$ (Fig. 2) the picture is quite different[1]. In terms of $K_{IC}$ there is only a minor drop in fracture toughness upon adding uncoated PCC particles. The addition of SA has the effect of moderately increasing $K_{IC}$, with a maximum around 10%.

---

[1] As discussed in the next paragraph, neither of the results shown in this paper are valid plane strain fracture toughness values. Some suggest the use of, say, $K_q$ could be used instead of $K_{IC}$ in these cases.

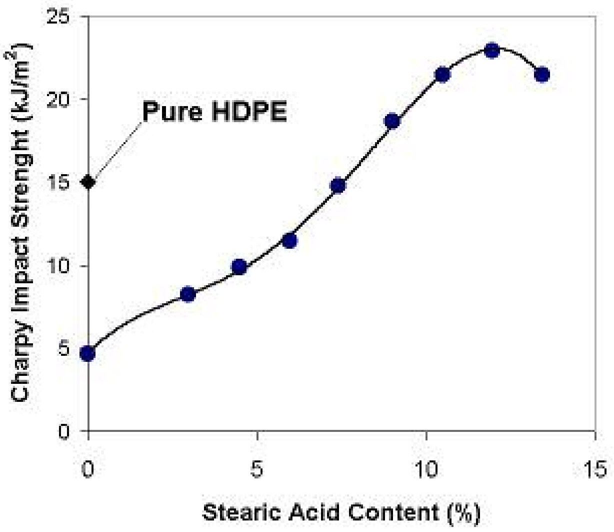


Figure 1 – Charpy impact strength vs. SA content for 10 vol% PCC/HDPE composites.

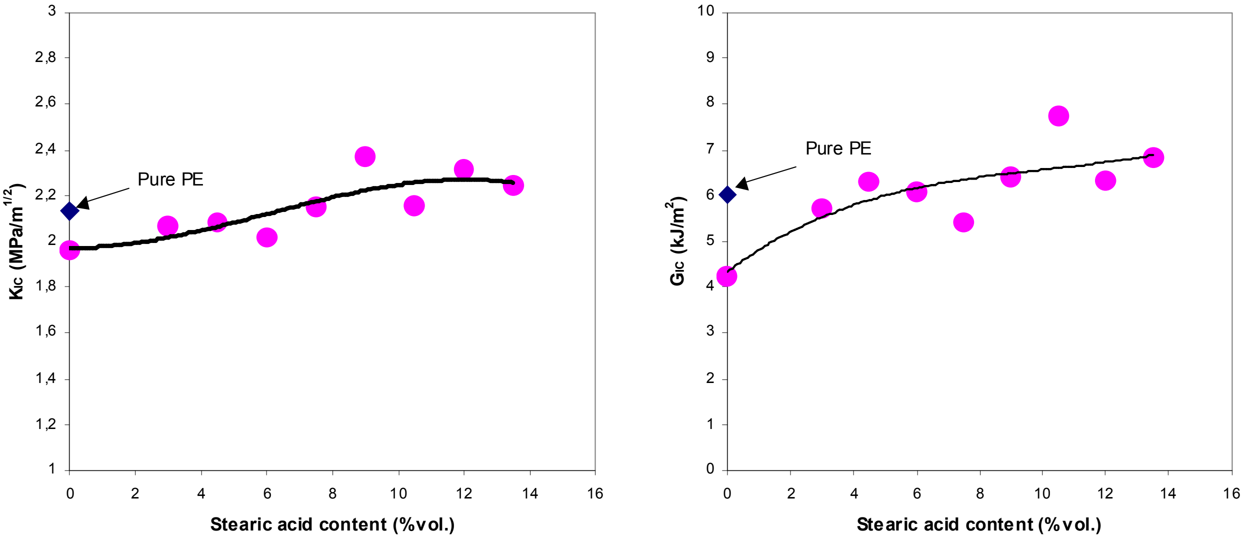
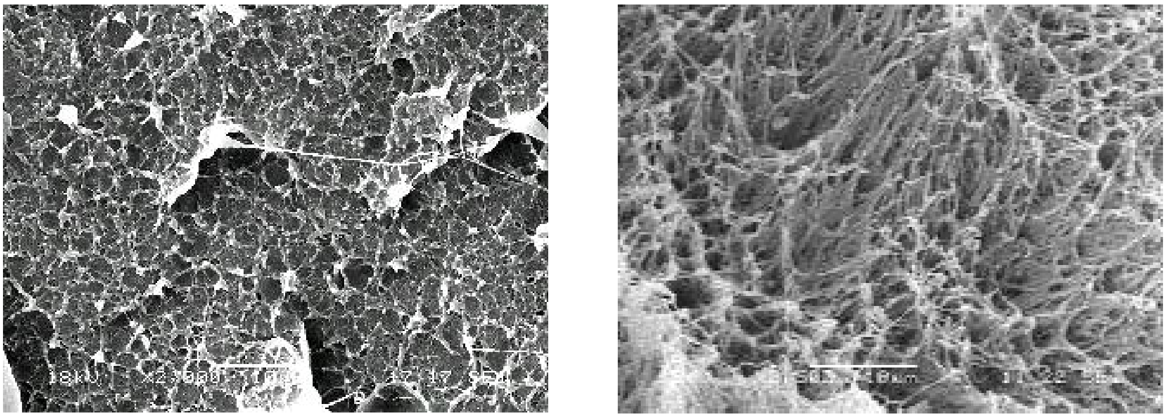


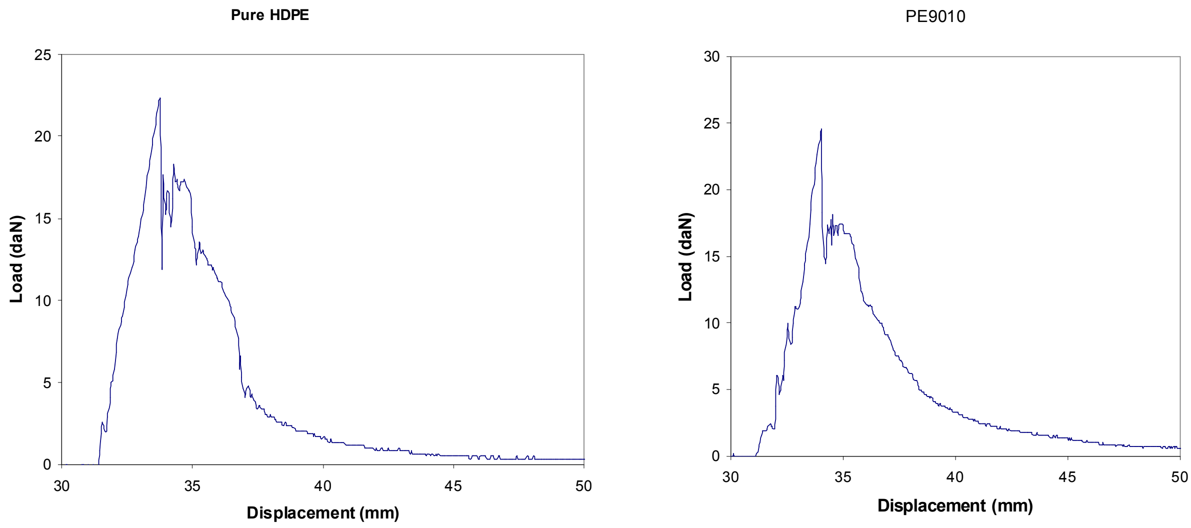
Figure 2 – $K_{IC}$ and $G_{IC}$ vs. SA content for 10 vol% PCC/HDPE composites.



***(a)*** ***(b)***

Figure 3 – Charpy fracture surface for (a) pure HPDE and (b) for 10 vol% PCC/HDPE composite with 12% SA.

Similar comments can be made on the graph showing $G_{IC}$ vs. SA content (Fig. 2b). Despite the scatter in the data, it seems that all composites have, more or less, the same fracture resistance than pure HDPE. This is contradicted by the SEM morphological analysis on the fracture surface of the tested Charpy specimens. Figure 3 compares the Charpy fracture surface for pure HDPE samples with those of PCC/HDPE composites. While for the pure material the surface appears quite brittle, in the case of the composite, it is possible to see a fibrillar structure, that is a clear sign of ductility. This observation explains why the Charpy test seems to be more sensitive to the chemical modification of the interface. In fact, the Charpy impact strength accounts for both the initiation and propagation stages of fracture. Improving the particle dispersion has a moderate effect on the peak stress and on the corresponding energy at crack initiation, while it a strong effect in inducing local plasticity ahead of the crack during propagation.



(a) (b)

Figure 4 – Load vs. displacement curves for (a) HDPE and (b) 10 vol% PCC/HDPE composite with 9% SA during impact tests.

This is clearly shown in Fig. 4 where the load vs. displacement curves for pure HDPE and for the 10 vol% PCC/HDPE composite with 9% SA during impact tests, are compared. Both curves present a sudden drop of the load after the peak but to continue to grow the crack continues to absorb energy. What make the PCC/HDPE composite different from the matrix, a part a slight variation in the peak load, is a larger energy absorption during the crack propagation stage, probably thanks to the dedonding and fibrillation phenomena shown in Fig. 3b. This characteristic feature is quite important in energy-absorbing manufacts like bumpers and computer cases to name just a few possible applications. The conventional FM parameters are of little use when comparing materials in this type of use.

## 2. THE $B_{MIN}$ QUESTION

A more general problem when testing polymer toughness according to LEFM protocols is the minimum thickness for plane strain testing, $B_{min}$:

$$B_{MIN} = 2.5 \cdot \left(\frac{K_{Ic}}{\sigma_y}\right)^2 \tag{1}$$

For tough polymer blends and composites this conditions is very rarely met. An example comes from the same data plotted in Fig. 2. For these composites, the minimum thickness is reported in Tab. 1.

Tab. 1 – Fracture toughness and $B_{min}$ for PCC/HDPE composites.

| PCC content | SA content | $K_{IC}$ MPam$^{1/2}$ | B min (mm) |
|---|---|---|---|
| 0 | 0 | 2,1 | 31,3 |
| 10 | 0 | 2,0 | 20,4 |
| 10 | 3,0 | 2,1 | 24,0 |
| 10 | 4,5 | 2,1 | 26,2 |
| 10 | 6,0 | 2,0 | 24,3 |
| 10 | 7,5 | 2,1 | 28,9 |
| 10 | 9,0 | 2,4 | 34,1 |
| 10 | 10,5 | 2,2 | 29,0 |
| 10 | 12,0 | 2,3 | 33,4 |
| 10 | 13,5 | 2,2 | 31,5 |

As it can be seen, the minimum thickness is in the order of 24-34 mm, which is not possible to achieve in practice. Current injection machines cannot mold such thick samples, yet it would be absurd to use hypothetical fracture results obtained on samples of such thickness for designing manufacts of much smaller size. The structure of the blend (particle size and morphology) and the crystallization conditions would be totally different from those of the material molded to the typical industrial thickness (few millimeters). This means that if one tries to use LEFM to evaluate this type of materials, the measured $K_{IC}$ and $G_{IC}$ cannot be considered valid. On the other hand, the specific fracture behaviour of such composites, as shown in Fig. 4, with an initial fast crack propagation (which gives rise to the observed load drop) followed by a slower pattern of crack propagation rules out completely both EPFM and the Essential Work of Fracture (EWF) method.

An endemic problem when dealing with rubber toughened polymers is that, upon increasing rubber content, the materials become progressively tougher, and the conditions for linear elastic fracture mechanics (LEFM) are no longer met. As an example, a series of rubber toughened blends based upon a copolymer grade PP at different rubber content were tested according to the ESIS protocol to obtain $K_{IC}$ (4). For the two blends with higher rubber content, J-testing was performed, still according to the ESIS protocol, making use of a multispecimen technique to measure the J-resistance curves and fracture toughness, $J_{IC}$ (considered here to be equivalent to $J_{0.2}$) at room temperature. The corresponding $K_{IC}$ value has been estimated by using the usual formula:

$$K_{IC} = (E\ J_{IC})^{½} \qquad (2)$$

Table 2 reports fracture toughness at different values of the volume fraction of rubber, $\phi$.

Tab. 2 – Fracture toughness and $B_{min}$ for PP/rubber blends.

| $\phi$ | Kic MPam$^{1/2}$ | $\sigma_y$ (MPa) | E (GPa) | B min (K) | $J_{Ic}$ (kJ/m$^2$) | B min (J) |
|---|---|---|---|---|---|---|
| | | | | | | |
| 0,00 | 1,90 | 24,90 | 1,30 | 14,56 | 2,78 | 2,79 |
| 8,34 | 2,10 | 22,15 | 1,24 | 22,47 | 3,57 | 4,03 |
| 16,62 | 2,80 | 20,00 | 1,08 | 49,00 | 7,27 | 9,08 |
| 20,70 | 3,40 | 18,00 | 0,99 | 89,20 | 11,70 | 16,25 |

As it can be noted, at rubber volume fractions when the material shows a brittle behaviour the minimum thickness for plane strain fracture toughness determination, according to ELFM, would be larger than 15 mm. On the other hand, when the rubber content is high enough that the blend shows a ductile behavior, and testing according to EPFM can be carried out, the minimum thickness required to achieve plane strain exceeds 9 mm. To summarise, neither testing brittle, low rubber content, nor ductile, high rubber content materials can meet the minimum size for valid fracture toughness determination. The specimens are certainly in plane stress near the surface and in some mixed mode in the core where a certain degree of plastic constraint exists. One ends up with a series of mixed mode values which are of little use since it cannot be easily determined which fraction of plane strain has been achieved during fracture. Presumably the degree of constraint also varies with rubber content thus making comparison among materials very difficult. This is quite a frustrating result taking into account that FM testing involves much more care and time compared with standard Charpy or Izod tests. Moreover, an additional issue is the need to change standard when, in this case, varying rubber content, especially because, in most cases, it cannot be predicted, *a priori*, whether a new blend or composite will be better tested according to LEFM or EPFM. Thus there is a need for a preliminary series of tests to judge the response of the material. Also there is the necessity for operators which must be both skilful and knowledgeable with fracture mechanics.

All these difficulties may also explain why in the polymer industry and somehow even at academic level, FM testing has failed to become the standard for materials selection and quality control.

## *4. DILATATIONAL PLASTICITY IN MULTIPHASE POLYMERS*

When a multiphase polymer is subjected to an external load, during the earlier stages of deformation, the hydrostatic component of the stress in the material starts to build-up and at a certain point, when some critical condition is met, some particles will start to debond from the matrix or to internally cavitate. In this initial stage, voids will appear randomly but their presence significantly affects the yielding and fracture behaviour of polymers. Lazzeri and Bucknall (5-7) proposed a yield function to account for the effects of cavitation on the yielding behaviour of polymers showing debonding or cavitation:

$$\sigma_e(\phi_R, f) = \sigma_o(\phi_R, 0)\sqrt{\left(1-\frac{\mu\sigma_m}{\sigma_o(\phi_R,0)}\right)^2 - 2fq_1\cosh\left(\frac{3q_2\sigma_m}{2\sigma_o(\phi_R,0)}\right) + q_3 f^2} \qquad (3)$$

where $\Phi_R$ is the disperse phase volume fraction, $\sigma_e(\Phi_R, f)$ is the effective (von Mises) yield stress and $\sigma_o(\Phi_R, f=0)$ is the matrix yield stress when the mean normal stress $\sigma_m$ and the void content $f$ are both zero, while $\mu$ is the pressure coefficient of yielding. Factors $q_1$, $q_2$ and $q_3$ assume the values 1.375, 1.010 and 2.988, respectively.

According to Eq. (3), the main consequence of debonding or cavitation of second phase particles is a lowering of the macroscopic yield stress that is more evident at higher levels of triaxiality, as near a crack tip where it leads to an enlarged plastic zone. This effect is particularly important in rubber and filler toughened polymers because in these systems the measured impact strength is proportional to the volume of the plastic zone.

A first order approximation of the size and shape of the plastic zone in a dilating polymers has been calculated on the basis of the yield function by considering an elastic analysis (7).

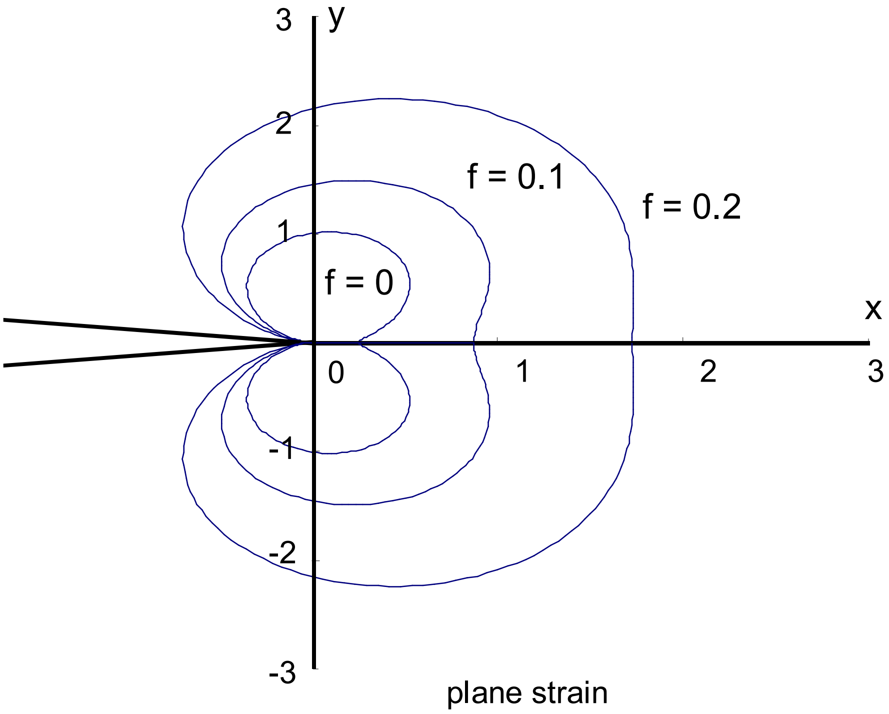


Figure 5 - Approximate shape of the plastic zone at different void contents in adimensional coordinates (from ref. 7).

Figure 5 compares the shape of the plastic zone near a crack tip for a rubber toughened polymer in condition where the particles have not cavitated ($f = 0$) with that of the same polymer at two different levels of microvoid content ($f = 0.1$ and $f = 0.2$) in plane strain. As it is evident from the figure, the size of the plastic zone increases considerably with the volume fraction of microvoids. Since, during an Izod or Charpy impact test, most of the energy is dissipated within the plastic zone, it can be anticipated that a polymer with rubber particles which are not able to cavitate will develop a small plastic zone and will show a low value of impact strength.

This is a consequence of the highly non linear dependence of the yield stress on the hydrostatic stress for a polymer with cavitated or debonded particles (eq 3). The effect of microvoids is quite limited in the tensile test (low triaxiality), so that the yield strength of the polymer is not reduced excessively, while the nucleation and growth of voids has a dramatic effects on the yield stress near a notch or a crack tip (high triaxiality) leading to the formation of a large plastic zone and hence to a high value of fracture resistance.

Figure 5 also shows that moderate levels of cavitation or debonding substantially mitigate, even if without suppressing completely, the effects of plastic constraint on the central portion of thick notched bars. The practical consequence is that the $B_{MIN}$ requirements should be probably relaxed in the case of multiphase polymers.

## ***5. POSSIBLE DEVELOPMENTS IN FRACTURE MECHANICS OF POLYMERS***

As discussed above, a fundamental issue is the fact that most commercial polymers are multiphase materials which show dilatational yielding. Therefore elastic-plastic fracture mechanics of polymers should be further developed since post yield behavior is largely responsible for energy dissipation during fracture in this class of materials. Since many applications of polymer blends and composites involve shock absorption FM should consider crack propagation and not only crack initiation. Maybe a two parameter fracture mechanics should be developed with some critical parameter accounting for crack growth. This issue is especially important when polymers are to be used for impact resistant applications.

In the author’s view, there is a strong need to use impact testing methods for polymers which are more scientifically more meaningful than Charpy and Izod. On the other hand current FM protocols are rather elaborate can only be used safely by highly skilled technicians and scientists. Therefore there is a need for the development of a “pratical” fracture mechanics approach in polymer testing, and especially the elaboration of simpler procedures for quality control and R&D of new polymer blends and composites. This means, for example, designing new standard specimen configurations with intrinsic higher degree of constraint. Instead of the small unnotched or V-notched Charpy or Izod samples a new protocol for impact testing might suggest the use of bigger samples, with dimensions similar to those used in current fracture mechanics, and maybe with more complex shapes to achieve higher levels of triaxiality. Just as a tentative example for the purpose of clarity, a single edge notched specimen with side grooves might be used. Such sample could be easily injection moulded and would need only a razor to sharpen the notch tip to be ready for testing.

Another possible approach could involve the development of new correlation and/or extrapolation procedures to allow critical parameters to be evaluated from specimens with REALISTIC thickness and geometry. This would enable to estimate the plane strain fracture resistance of the material even if the maximum available specimen size is sensibly smaller than minimum thickness for achieving plane strain conditions.

## *6. CONCLUSIONS*

Despite their naivety, simple Izod and Charpy tests are still currently widely used in both industry and academia for R&D purposes and materials selection. This success is due to their simplicity and ease of interpretation.

State of the art FM of polymers focuses more on crack initiation rather than crack propagation, which is very relevant in most applications of plastics.

Current FM standards for tough polymer blends and composites involve specimen thickness that are either non-realistically achievable or non representative of industrial manufacts.

In this work problems and limitations of current test methodologies have been reviewed, as well as practical aspects concerned with fracture testing. A few possible solutions have also been suggested.

## *REFERENCES*

1. *JG Williams, Fracture Mechanics of Polymers, Ellis Horwood, London, 1984.*
2. *A Lazzeri, SM Zebarjad, M Pracella, K Cavalier, R Rosa, submitted to Polymer.*
3. *DR Moore, A Pavan, JG Williams, Fracture Mechanics Testing Methods for Polymers, Adhesives and Composites, Elsevier Science, Oxford, 2001.*
4. *SM Zebarjad, R Bagheri, SM Seyed Reihani, A Lazzeri, "Deformation, Yield and Fracture of Elastomer-Modified Polypropylene". J. Appl. Polym. Sci. 90, (2003) 3767.*
5. *A Lazzeri, CB Bucknall, J. Mater. Sci. 1993, 28, 6799.*
6. *A Lazzeri, CB Bucknall, Polymer, 1995, 36, 2255.*
7. *A Lazzeri, CB Bucknall, "Recent Developments in the Modeling of Dilatational Yielding in Toughened Plastics" in Toughening of Plastics, (R. Pearson, H.-Y. Sue and A. Yee Eds.), ACS Symposium Series 759, Oxford University Press, London-New York, 2000, pp. 14-34.*