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# CONTROLLING DUAL SCALE MORPHOLOGIES OF EPOXY AND POLY(ETHERIMIDE) TOWARDS IMPROVED INTERLAYER TOUGHENING OF COMPOSITES

U. Farooq, J. Teuwen and C. Dransfeld

Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, Delft, The Netherlands
Email: c.a.dransfeld@tudelft.nl

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## Abstract

A common approach to toughen epoxy matrix systems is to dissolve a thermoplastic phase, in the uncured thermosetting monomers. These can interdiffuse within the thermoplastic, followed by reaction-induced phase separation, leading to intricate graded morphologies with a high fracture toughness. Here, we first architect the thermoplastic phase, made of poly(etherimide) films as a macroscopic layered scaffold, and infiltrate it by an epoxy system, leading to dual-scale morphologies with distinct spatial control of morphological feature at the microscopic and macroscopic scale. The fracture toughness of the modified epoxy system is investigated as a function of varying cure temperature (120–200 °C) for interphase formation and poly(etherimide) film thickness (50–120 µm). Results show that the fracture toughness of the heterogeneous system is mainly controlled by the macroscopic feature, the final PEI layer thickness. Remarkably, as the PEI layer thickness exceeds the plastic zone around the crack tip, around 60 µm, the fracture toughness of the dual scale morphology surpasses the property of bulk PEI. Additionally, decreasing the gradient microscale interphase morphology triggers higher crack tortuosity, which seems to be the dominating mechanism for the synergistic toughening. Ultimately, this knowledge will lead to novel toughening approaches to increase the damage tolerance of fibre reinforced composites by suppressing delamination damage modes.

## 1. Introduction

In structural applications, fibre reinforced polymers are subjected to high static and dynamic loadings that call for a high damage tolerance and fracture toughness. However, epoxy-based thermosetting matrix systems have high cross-link densities to achieve sufficiently high glass transition temperatures, which generally leads to low fracture toughness. Therefore, many methods are thought of to improve its fracture toughness. Bulk resin modification is the process of adding a second phase—such as rubber, inorganic nanoparticles, or thermoplastics—to the epoxy matrix via a variety of techniques [1]. During the epoxy curing step, these tougheners typically create morphologies that improve the system's fracture toughness. Unfortunately, adding a tough phase to the epoxy system can limit the system's end-use temperature and lower the system's total modulus for elastomeric tougheners. In addition, bulk resin modification—mainly through thermoplastics—may also cause the resin system's processing viscosity to drastically rise, rendering them inappropriate for liquid composite moulding.

Various approaches have been explored to toughen brittle materials on different scales: One macro-scale approach consists of introducing ductile interlayers into brittle materials, leading to toughening through the *inhomogeneity effect*. This effect involves spatial variations in material properties influencing crack propagation. Ductile interlayers act as crack arresters, significantly increasing fracture toughness without a substantial loss in strength. Studies by Sistaninia et al. [2] demonstrate the effectiveness of this approach, emphasizing the importance of heterogeneous materials architectures to enhance fracture toughness.

At the microscale, toughening of epoxy systems is mostly achieved by adding an amorphous thermoplastic like poly(etherimide) (PEI) or poly(ethersulfone) (PES). This addition leads to the dissolution, followed by phase separation induced morphologies within the epoxy, resulting in a significant increase in fracture toughness by the intrinsic contribution of the tougher thermoplastics and also by crack deflection in the phase-separated systems. Alternatively, using a thermoplastic film or discrete powder deposition as an interlayer in prepregs allows for the diffusion of reactive monomers into the thermoplastic with spatial control, inducing phase separation and creating a gradient morphology in the interfacial zone [3], thus overcoming processability constraints.

The aim of this study was to investigate heterogeneities of PEI at the macro and microscale in a brittle epoxy system to deconvolute their respective effects on fracture toughness. With this objective PEI scaffolds with periodic arrangement of film were infiltrated with a brittle epoxy system and subjected to different cure cycles leading to varying degrees of dissolution and micro-scale gradients. The cured sample here is characterized through a single edge notched beam test.

## 2. Materials and Methods

Films of poly(etherimide) (ULTEM 1000, SABIC, Saudi Basic Industries Corporation), with a molecular weight 55,000 g/mol, and a glass transition of Tg = 217 °C, with thicknesses of 50, 60, 90, and 120 µm), were used as the tough phase. The epoxy systems was formulated as a blend of M-(2,3-epoxypropoxy)-N,N-bis(2,3- epoxypropyl)aniline (TGMAP, Araldite MY 0610 CH), and bisphenol-F epoxy resin monomer (DGEBF, Araldite PY 306 CH). 3,3′-sulfonyldianiline (DDS, Aradur 9719-1) all supplied by Huntsman Advanced Materials, Switzerland, resulting in a high Tg (around 200 °C).

First, PEI scaffolds were prepared by stacking the PEI films periodically in a 1:2 ratio of equal thickness as obtain scaffolds with 33 vol % fraction of PEI, respectively, with a porosity of 66% to be infiltrated by the epoxy system. Then, the epoxy system was then infused into the PEI. Infiltration occurred dominantly spontaneously through capillary action. Once the infiltration step was completed, samples were placed in a preheated oven at a selected cure temperature. The dimensions of the scaffolds were as follows: length = 120 mm, width = 26.4 mm, and thickness = 6 mm. Each scaffold allowed to extract nine samples, which were used for further analysis.

The experimental principle is represented in Figure 1 and shows an arrangement of the scaffold in respect to principal crack direction. Table 1 lists all configurations between original film thickness and curing cycles, note that the PEI volume fraction was kept constant for all experiments.

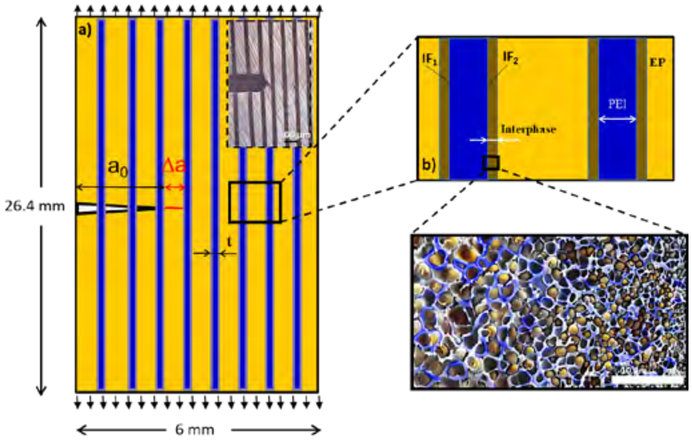
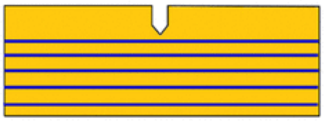
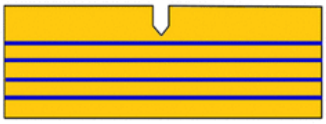
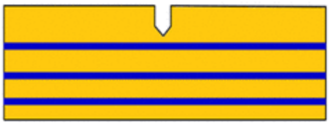
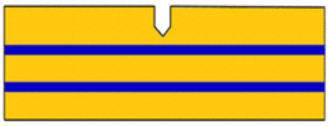


Figure 1 – (a) schematics of the experimental variables, including original PEI film thickness t with a constant pitch of 3t, and cure depending on interphase dimensions and morphology. (b) representation of different regions in the multilayered sample; PEI = poly(ether imide) (blue) EP = epoxy (yellow), IF1 = interface 1, and IF2 = interface 2.

The fracture toughness of the specimens was determined by single-edge notched bending (SENB) testing according to the ASTM D5045-99 standard. The dimensions of the SENB sample had a length = 26.4 mm, a width = 6 mm, and a thickness = 3 mm.

Table 1 Scaffold and curing parameters investigated [4]

| *PEI Thickness (µm)* | *Cure Temperature (°C)* | *Sample ID* | *Number of PEI layers* | |
|---|---|---|---|---|
| 50 | 120 | 5P12 | 40 |  |
| | 140 | 5P14 | | |
| | 160 | 5P16 | | |
| | 180 | 5P18 | | |
| | 200 | 5P20 | | |
| 60 | 120 | 6P12 | 33 |  |
| | 140 | 6P14 | | |
| | 160 | 6P16 | | |
| | 180 | 6P18 | | |
| | 200 | 6P20 | | |
| 90 | 120 | 9P12 | 22 |  |
| | 140 | 9P14 | | |
| | 160 | 9P16 | | |
| | 180 | 9P18 | | |
| | 200 | 9P20 | | |
| 120 | 120 | 12P12 | 17 |  |
| | 140 | 12P14 | | |
| | 160 | 12P16 | | |
| | 180 | 12P18 | | |
| | 200 | 12P20 | | |

Specimen features, such as crack path and phase morphology were investigated with confocal laser scanning microscopy (CLSM) and scanning electron microscopy (SEM) at higher resolutions.

## 3. Results

CLSM and SEM were used to study the interphase development of epoxy and PEI at various cure temperatures. Figure 3 illustrates a multilayer sample with a 90 µm PEI layer that was cured at 160 °C (1st dwell temperature). The sample's CLSM image (Figure 3a) shows that the brittle epoxy contains parallel PEI layers that are uniformly dispersed. Simultaneously, Figure 3b displays a magnified SEM picture of two successive PEI layers and two interphase regions, each with a thickness of roughly 61 µm. Figure 3c shows a noticeable gradient in morphology between the pure epoxy (left) and pure PEI (right) interfaces. A noticeable morphological gradient has formed in Figure 3c between the interface of the epoxy system (left) and PEI (right). It shows the occurrence of epoxy-rich droplets in a continuous PEI matrix near the pure epoxy interface. They shrink gradually near the pure PEI region due to the rise in PEI concentration. Similar results were also obtained for the other temperatures.

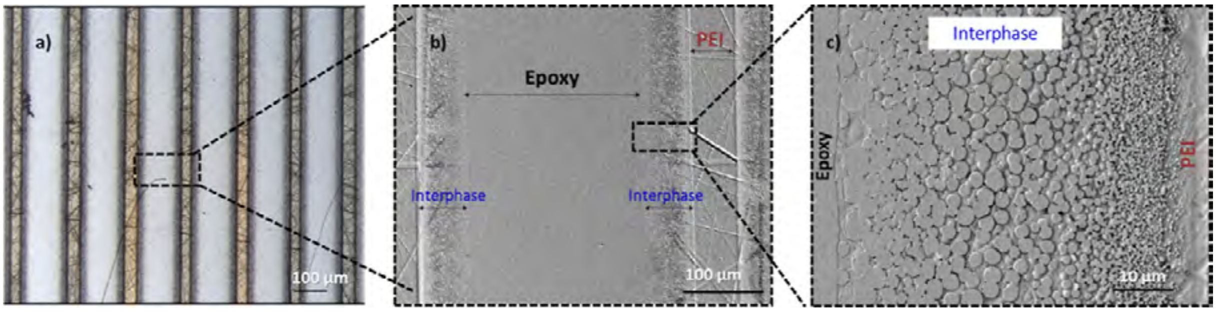


Figure 2 – Microscopic analysis reveals the dual-scale heterogeneous architecture at various scales [4]

The fracture toughness of the SENB samples is reported in Figure 3a, the low toughness of the pure epoxy system seems to be independent of the examined cure temperatures. However, the toughness of the heterogeneous systems seems to decrease with increasing curing temperature. A correlation to the initial film thickness seems less conclusive. Interestingly, samples cured at lower temperatures seem to surpass the fracture toughness values of the tougher constituent, pure PEI. All reported values seem to be above a linear rule of mixture between the brittle epoxy system and the tough PEI.

These observations lead to an interest in the scaffold geometry after interphase formation: For a given scaffold film thickness, increasing the curing temperature leads to an increased diffusion and interphase dimension, resulting in a reduction of the remaining (final) PEI film thickness, as can be seen in Figure 3b. It also became apparent that the rate of dissolution vs temperature seems larger at lower temperature and seems to somewhat saturate at higher temperatures. The very thin PEI films of 50 µm do, however entirely dissolve at a curing temperature of 200°C.

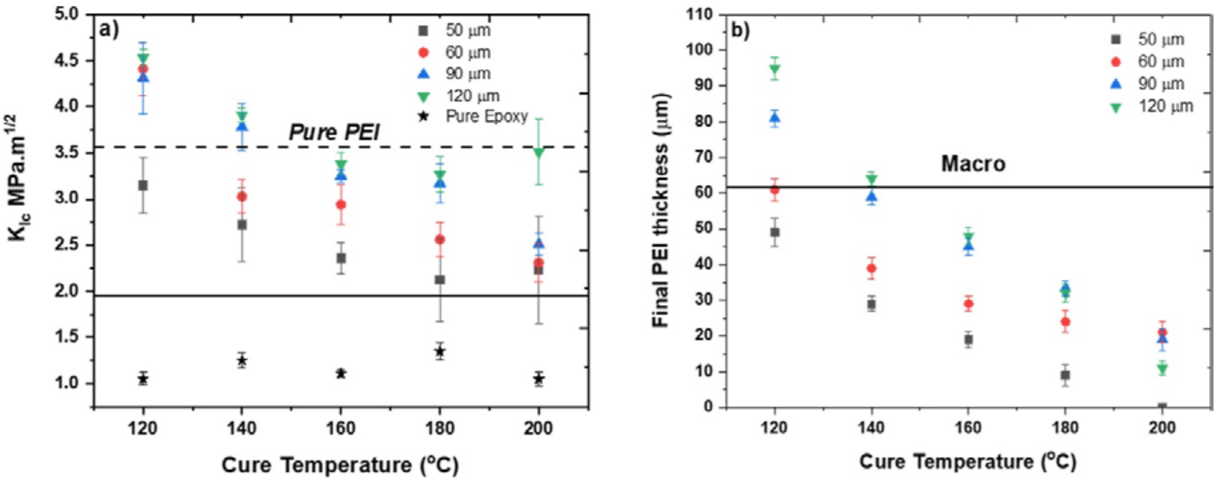


**Figure 3** – Left: Fracture toughness (KIc) of SENB specimen made from different PEI film thickness with varying cure temperature, the dashed line represents the fracture toughness of pure PEI, while the solid line represents the corresponding target value in a simple rule of mixture. Right: Resulting PEI film thickness after partial dissolution as a function of cure temperature, the solid line represents the size of the plastic zone for pure PEI [4]

## 4. Discussion

To better understand the effect of scales of the heterogeneous architecture, the size of the plastic zone of the tough PEI phase was estimated, according to Irwin, for plane strain conditions to be about 62 µm

$$Plastic\ zone\ size = \frac{1}{6\pi}\frac{k^2}{\sigma^2} \qquad (1)$$

Assuming a stress intensity factor $k$ of 3.45 MPa.m$^{1/2}$ and a yield stress $\sigma$ of 105 MPa for PEI. Representing the fracture toughness versus the macroscopic feature of the heterogeneity, the remaining (final) PEI films thickness, as shown in Figure 4, a clear trend emerges: The fracture toughness seems to correlate to the dimension of the tougher phase. Already at small final PEI thickness, the fracture toughness seems to exceed a simple rule of mixture expected for a homogeneous blend. It is hypothesized that the phase separated micro-scale heterogeneity is already contributing to the dissipative mechanism here. More interestingly, when the PEI film thickness exceeds the size of the plastic zone, the system fracture toughness exceeds the fracture toughness of the pure bulk PEI. The fracture path undergoes macroscopic change, which was captured by determining the crack tortuosity $\tau$, which is a dimensionless expression of crack pat length with respect to its shortest path.

$$\tau = \frac{macroscopic\ crack\ length}{sample\ height} \qquad (2)$$

With the final PEI thickness exceeding the size of the plastic zone, as shown in Figure 5, the macroscopic crack morphology gradually evolves to very high crack tortuosity values $\tau$ up to 2, the significant extension of the crack path is the root of the synergistic toughening effect leading to a higher fracture toughness than its tougher constituents.

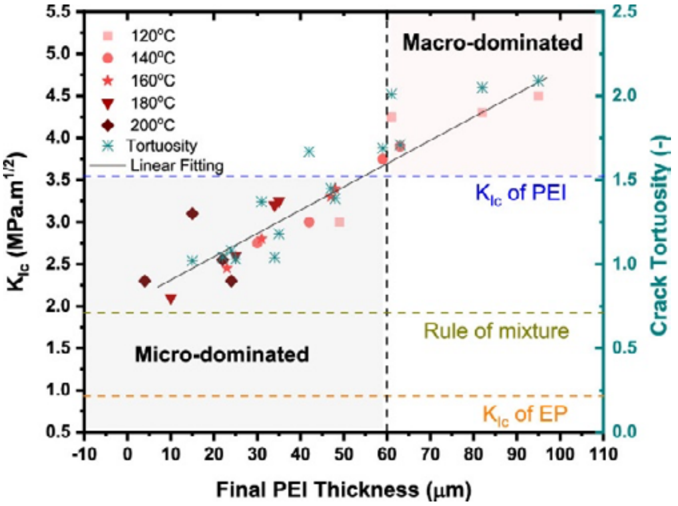


Figure 4 - Fracture toughness (KIc) and crack tortuosity as a function of the final PEI thickness obtained after curing. The vertical dashed line represents the size of the plastic zone (rp = 62 µm) of PEI; the horizontal blue and orange lines represent the fracture toughness of the bulk PEI and Epoxy systems, respectively [4]

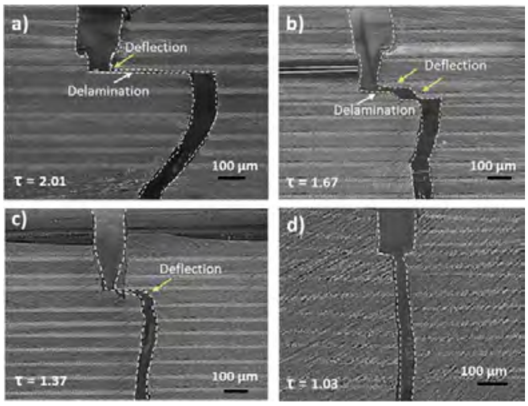


Figure 5 – Crack tortuosity analysis: CLSM images of a PEI/epoxy system with a 60 µm PEI layer cured at (a) 120 °C, (b) 140 °C, (c) 160 °C, and (d) 180 °C, corresponding to reducing final PEI thickness. Yellow arrows represent deflection, and white arrows show delamination. τ is the crack tortuosity [4]

## 5. Conclusion

It has been observed in nature, that principles of tailoring heterogeneous brick and mortar systems [5] allow to reach significant synergies in strength and damage tolerance. However, these effects refer to the contrasting stiffness of the brick and the soft mortar. Here, we have demonstrated that systems have the very similar elastic modulus but contrasting fracture toughness, interesting architecting option can be put into practice.

In choice of architecture, the size of the fracture process zone of the tougher phase is a relevant dimension and dictates the scale of the dominant heterogeneity. In a layered heterogeneity, the penetrating work of fracture must be high enough to promote deviatoric or delamination work of fracture, leading to significant crack tortuosity. Hence, further controlling the balance of these failure modes will require more attention in future work.

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