Dissipating mechanical mechanisms and their link to morphology in polyamide toughened carbon-epoxy UD laminates

Emmanuel Baranger
LMT Cachan, ENS Cachan, CNRS, Université Paris-Saclay, 61 avenue du Président Wilson, 94235 Cachan cedex, France
E-mail: baranger@lmt.ens-cachan.fr

Abstract. Toughened carbon/epoxy laminates include thermoplastic particles. Depending of the curing cycle, the morphology of the thermoplastic phases can differ. This strongly impacts the degradation scenario of the composite. In the present paper, such reinforced laminates are evaluated. Different morphologies are studied. Classical experiments are used to evaluate the impact of the morphology on the damage and plasticity evolution laws at the scale of the ply. Some elements to model the toughening mechanism at the inter-ply scale are given and limitations are discussed.

1. Introduction
Carbon/epoxy UD laminates have relatively limited performances regarding damage tolerance as they are prone to delamination. The toughness of epoxy matrices being relatively low regarding thermoplastics, some authors proposed to improve their performances by adding thermoplastic phases such as PES [1] or PA [2]. These two examples modify the composite morphology at different scales, PES is used at the submicron scale while PA is used at inter-plies and therefore for scale-lengths about 10 microns. This kind of intrinsic toughening strategy [3, 4] does not necessary lead to improved macroscopic properties as shown in [2, 5]. For example, different scenarios of degradations are observed during mode I or mode II macroscopic delamination tests. This extrinsic part of the toughening strategy may play a major role and be modified by the processing conditions of the material. In this work, we focus on the curing cycle of prepregs. This study has been conducted during the French ANR project: PROMORPH. The objective of this paper is to give some insight of the toughening scenarios and their relation to the morphology of toughened carbon/epoxy UD laminates. For that, an extensive literature survey has been conducted associated to micro-mechanical models. Based on that understanding, the modelling of the toughening mechanisms by PA at interfaces is then studied at the inter-ply scale. The local constitutive relations and their identification as well as their use in a finite element framework describing a simplified geometry are detailed. In particular, limitations of the different parts of the model are tackled such as localization. This modelling study is accompanied with an experimental campaign at the mesoscale conducted on different materials. In fact, modifying curing conditions can lead to different phase morphologies at the scale of the thermoplastic reinforcement. Five morphologies have been produced, the associated mechanical properties
are compared using the mesomodel developed at LMT-Cachan [6, 7]. An understanding of the underlying mechanisms is proposed to explain the differences observed. The material manufactured in this paper is relatively close to the one used by [2] i.e. a carbon/epoxy laminate toughened by poly-amide (PA) particles of about 20µm. Depending on the impregnation and curing cycle parameters, several morphologies have been obtained:

1 - un-toughened material;
2 - intra-ply particle dispersion, melted particles;
3 - intra-ply particle dispersion, phase separated particles;
4 - inter-ply particle dispersion, melted particles;
5 - inter-ply particle dispersion, phase separated particles.

The first three configurations have been mainly evaluated for the moment.

2. Literature survey

A wide literature exists on the toughenability of polymers [Argon and Cohen, 2003] using different methods. For example, [1] shows the influence of PES modification on epoxy toughening by phase separation, modifying the crack path. This phase separation introduces inclusions of characteristic size of 1 micron. It also modifies the viscosity of the matrix and therefore the processability of the laminate. These studies on pure polymers are not always relevant. [8] shows that, the addition of fibers to the polymers may modify the polymer blend morphology and thus lead to an unexpectedly poor toughening. Thus, the composite should be studied. This as been done extensively for non toughened composite in [9] but also by Kinloch [10]. In [9], many composites were characterized whatever the matrix, the fibers, the sizing, or the process. The objective of this study is to show the correlation of the raw matrix properties on the composite ones regarding delamination. Two regimes are demonstrated driven by the size of the plastic zone at the crack tip versus the thickness of the inter-ply region. Note also that adjacent plies modify the local stress field leading to a shielding effect (the stress wavelength in front of the crack tip is longer and smoother). [11] studied the formation of hackles in an interphase. The conditions for a crack in an interphase to remain in this inter-ply zone has been studied by[12] for elastic isotropic adhesive between two substrates. In mode I (macroscopic), the pre-stress plays a major role and destabilize the crack that will deviate from the interfacial zone (even in presence of toughening particles [13]). Crack fiber bridging (for interfaces between O° plies) may be involved as mentioned by most of the authors and visible on increasing R-curves. Crack Fiber bridging is related to the local intraply delamination. [14] observed this phenomenon. The plastic zone is assumed to extend in the ply region (very locally because plies are stiff). This plastic zone being at constant stress level (perfectly plastic behavior), the weakest link triggers the delamination which may occur in the ply. Thus crack fiber bridging is related to the matrix toughness via plasticity as shown in the second regime in [9].

[5, 13] shows an increase in KIc and KIIc for PA particles additions at composite inter-ply zones. These particles work as crack bridging when the crack remains in the inter-ply zone, as noted in the second paper. [13] also discussed the differences observed between static and fatigue loadings. Concerning Mode I, [5] proposes a model leading to a good correlation with experimental results in the case of a crack remaining at the interface. In [2], PA particles are much larger and the authors play on many different parameters to study the influence on mode II toughness. A process zone modification is demonstrated. [15, 16] also shows this action using high resolution X ray computed tomography. [5] has developed a model for mode I based on particles pinning the crack. The particle partial debonding and drawing can also be described using a simple model of a spherical particle in a cracked domain as in [17, 18]. This model doesn’t describe the evolution of the debonding of the particle. Contrary to mode I, the toughening
mechanism for mode II is deployed ahead of the crack tip. First, plasticity develops in the inter-
ply zone more or less depending on the epoxy blend properties enforcing the PA deformation.
For a sufficient loading, the formation of a hackle network can be observed. This network has been
modeled by [11] using a pure mode I crack propagation criterion or by [19] for the global GIIc
estimation. These hackles do not extend on the entire width of the specimen but on dimensions
related to the size of the fibers or the thickness of the interface as shown by [2]. Some of these
cracks especially develop close to the PA particles because of stress concentration. The crack
reaching the particles are deviated as in [20, 21] or [22] for thick interphases. A particle/matrix
debonding then occurs which allows the particle to develop plasticity by drawing if the debonding
is not total. Finally, the debonding or the failure of the particles leads to the macroscopic crack
front increase.

Note that more recent references exist on the characterization of this kind of materials as some
are already used in the aeronautical industry. However, they do not focus on the understanding
of the role of the microstructure.

3. Experimental results
To evaluate the impact of the morphology on the mechanical behavior of the laminate, the
meso-model developed by [6] has been chosen.

3.1. Ply characterization
Classical tests associated to the characterization of the ply have been conducted. Regarding
tension tests on [0/90]s coupons, the force/strain curves are the same but not the stress/strain
curves. The addition of particles modifies the thickness of the laminate leading to different
definitions of stresses for the same volume of fiber. Regarding tension tests on [±45] laminates
to characterize the shear behavior, the damage evolution law as well as the plasticity evolution
law are not changed as shown on Figure 1 and 2.

![Figure 1. Shear damage evolution vs. shear elastic strain.](image1)

![Figure 2. Shear hardening evolution vs. cumulated effective plasticity strain.](image2)

For [0/90]s coupons, the evolution of the crack density versus the applied strain is plotted
on Figure 3. The crack density is defined as the ratio of the mean crack spacing and the 90
plies thickness. The addition of particles leads to an early transverse crack creation. Their
evolution speed remain comparable while the saturation seems to be delayed by the presence of
particles. Considering that delamination at the transverse crack tips is delayed by particles, the transverse crack density can be higher.

![Figure 3. Transverse crack density vs. applied strain.](image)

### 3.2. Inter-ply characterization

DCB tests have been performed on purely unidirectional coupons. The measured energy release rates are greater of about 50\% for the toughened composites. Note that bridging is observed for the toughened coupons, this may explain part of the meso-scopic improved properties. Regarding mode II delamination, 3ENF tests have been performed. The results are presented in Table 1. Two configurations are treated related to crack propagation from an existing crack (and the associated process zone) or not. For the same kind of materials, the results are significantly different, showing the impact of the curing cycle.

| Type | Mean, non pre-cracked | Mean, pre-cracked |
|------|----------------------|-------------------|
| 1    | 1303                 | 728               |
| 2    | 1535                 | 999               |
| 3    | 1061                 | 879               |
| 4    | 533                  | 459               |

### 4. Numerical model

The experimental results shown before are not intuitive. The use of analytical or numerical model is therefor of great interest. At the scale of the fiber, [23] uses the elasto-plastic model from [24] to describe the mechanical behavior of the matrix. This model, implemented in Abaqus, as been preferred to the model from [25] in a first time. The model is calibrated using data from the literature. The behavior is supposed to be elastic brittle in tension. In compression, the behavior is identified regarding shear. A compact tension test is performed to identify the post-peak behavior of the material to obtain the good macroscopic energy release rate. For the sake of simplicity, first simulations have been conducted with pure matrix inter-plies. An inter-ply zone is considered (thickness about 10 microns), it is composed of pure epoxy matrix between two stiff plies. The fiber/matrix debonding is modeled using cohesive elements. The applied boundary conditions on the upper and lower plies are extracted from a maroscopic beam.
analysis to get a relevant representation of the local loading. First a DCB test is performed as shown on Figure 4. The initial crack deviates from the inter-ply region to rich the fiber/matrix region.

Figure 4. Crack propagation in inter-ply region for a DCB test.

In mode II, a CLS test has been simulated. On Figure 5, hackles can be observed. Their inclination is about 60° while the maximum traction direction is at 45°. This leads to a large crack spacing. The associate process zone is not compatible with fracture mechanics. In fact, it is impossible, from the local kinematics to define an equivalent crack front. The localization orientation is not well predicted, it is directly linked to the model and not tunable. Another model such as [25] has to be used. Also note that this last model should be able to describe the plasticity development at the crack tip that occurs at this scale. One pure matrix coupons, the plastic zone ahead of the crack tip is about 10 to 20 microns. Inside the inter-ply region, such a zone can’t develop totally, the model must take this into account.

Figure 5. Crack propagation in inter-ply region for a CLS test.

The next step is to be able to introduce particles in the inter-ply region. For that, a 3D model is necessary. The PA particle has been modeled using [24] and an interface between the particle and the epoxy matrix described by a cohesive zone model. An explicit algorithm is used to overcome convergence difficulties while the kinetic energy is controlled to remain negligible. Note that the application of relevant boundary conditions is not straight-forward as the model is of very limited size.

5. Conclusion
This paper presents several ingredients towards the understanding of the link between toughened composite morphologies and mesoscopic mechanical properties. Different morphologies have been tested (mainly 3). The in-plane shear properties remain unchanged while the transverse cracking evolutions are impacted by the toughening. Transverse cracks appear earlier for toughened composite and their saturation is higher. Regarding delamination, critical energy release rates are generally improved due to fiber bridging for the tested configurations between 0° plies. Regarding simulations, a first model from the literature has been used to describe the mechanical behavior of the matrix. The localization properties of this model leads to slightly
mis-oriented crack networks and to the difficulty to identify mesoscopic associated quantities. A first 3D model of an inter-ply reinforced by a particle has been developed. The application of relevant boundary conditions remains an issue.

Acknowledgement
This work has been found by the ANR PROMORPH project which is greatly acknowledged.

References
[1] Kinloch A, Yuen M and Jenkins S 1994 Journal of materials science 29 3781–3790
[2] Groleau M, Shi Y, Yee A, Bertram J, Sue H and Yang P 1996 Composites science and technology 56 1223–1240
[3] Ritchie R O 2011 Nature materials 10 817–822
[4] Cardwell B and Yee A 1998 Journal of materials science 33 5473–5484
[5] Ladeveze P and LeDantec E 1992 Composites Science and Technology 43 257–267
[6] Allix O, Leveque D and Perret L 1998 Composites Science and Technology 58 671–678
[7] Varley and Hodgkin 1996 polymer papers 38 1005–1009
[8] Bradley W L 1991 Key Engineering Materials 37 161–198
[9] Kinloch A 1985 Epoxy Resins and Composites I (Springer) pp 45–67
[10] Fleck N 1991 Proceedings of the Royal Society of London. Series A: Mathematical and Physical Sciences 432 55–76
[11] Fleck N, Hutchinson J and Zhigang S 1991 International Journal of Solids and Structures 27 1683–1703
[12] Hojo M, Matsuda S, Tanaka M, Ochiai S and Murakami A 2006 Composites Science and Technology 66 665–675
[13] Johnson W S and Mangalgiri P 1986 Investigation of fiber bridging in double cantilever beam specimens. Tech. rep. DTIC Document
[14] Wright P, Fu X, Sinclair I and Spearing S 2008 Journal of Composite Materials 42 1993–2002
[15] Moffat A, Wright P, Hellen L, Baumbach T, Johnson G, Spearing S and Sinclair I 2010 Scripta Materialia 62 97–100
[16] Gang B and Chung-Yuen H 1990 International journal of solids and structures 26 631–642
[17] Sigl L S, Mataga P, Dalgleish B, McMeeking R and Evans A 1988 Acta Metallurgica 36 945–953
[18] Lee S M 1997 Journal of materials science 32 1287–1295
[19] Ming-Yuan H and Hutchinson J W 1989 International Journal of Solids and Structures 25 1053–1067
[20] Leguillon D, Lacroix C and Martin E 2000 Journal of the Mechanics and Physics of Solids 48 2137–2161
[21] Lacroix C, Leguillon D and Martin E 2002 Composites science and technology 62 519–523
[23] Mora D F, Gonzalez C, Lopes C, Naya F and Llorca J 2014 *ECCM 16 -16th European Conference on Composite Materials* (Séville, Spain)

[24] Lee J and Fenves G L 1998 *Journal of engineering mechanics* 124 892–900

[25] Boyce M C, Parks D M and Argon A S 1988 *Mechanics of Materials* 7 15–33