

THE EFFECT OF SURFACE TREATMENT ON DELAMINATION FOR A NYLON INTERLEAVING MATERIAL

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ABSTRACT

One method of controlling delamination and increasing the inter-lamina toughness in composite laminates is the use of thermoplastic interleaving films, primarily to absorb energy. In this study the effect of controlling the surface energy of a nylon interleaving film on the interlaminar fracture toughness was investigated. It was found that as the surface energy of the nylon increased so did the Mode I delamination resistance. Surface energy was measured via dynamic contact angle measurements and delamination resistance via double cantilever beam specimens. It was concluded that control of the surface energy of the interleaving material is paramount in controlling delamination.

1. INTRODUCTION

A significant problem for traditional laminates is their susceptibility to delamination due to their poor interlaminar fracture toughness. Delamination can occur in composite materials either at the manufacturing level or during in-service applications. This delamination often occurs from relatively low velocity impact loads, or at free edges resulting from notches bolt holes etc. This delamination may cause a reduction in load bearing capacity resulting in failure.

Much research in the area of increasing the damage tolerance of these laminates has focussed on improving the properties of the constituent phases, tougher matrices, controlled fibre-matrix interface properties or interleaving.¹⁻³ Another popular approach is the stitch, knit or weave through-thickness fibres.⁴⁻⁶

Interleaving⁷ is another method for improving the resistance to delamination. This incorporation of a non-reinforced layer between prepreg plies may involve

- resin interleaving⁸⁻¹²
- thin film insertion (often a thermoplastic)^{7,13,14}

The latter method incorporates a thermoplastic film between reinforced lamina to help overcome the delamination. One problem with this method is assuring that sufficient bonding exists between the thermoplastic interleaf and the resin of the prepreg plies in order to assure damage tolerance of interleaved composite structures. Without sufficient bonding between alternating plies and film, delamination will occur.

The adhesive strength between the prepreg and the interleaf is a function of the surface energy of the thermoplastic material. Typically thermoplastics have low surface energies and thus getting a good adhesive

bond is difficult. The surface energy of polymers, and hence their “wetting” characteristics are governed by the physico-chemical nature of a few atomic layers at the outermost surface.^{15,16} This means that if only the surface region can be precisely controlled, the wetting characteristics would be perfectly regulated without changing any bulk properties of the thermoplastic.

For example, Nay et al.¹⁷ investigated the use of radio frequency plasma processing to increase the number of active bonding sites, and thus the surface energy, for a polyimide film.

This study uses nylon, which has surface energies at the higher end of the thermoplastic range and investigates three methods of increasing this energy in order to enhance the adhesive bonding between prepreg and interleaf.

2. EXPERIMENTAL PROCEDURE

Dynamic contact angle (DCA) measurements were carried out using a Cahn DCA-322 Analyser. The apparatus was calibrated at the start of each analysis by running an internal calibration program. The nylon films were immersed into distilled water at a speed of 20 m sec⁻¹ and results were analysed to determine the relevant advancing and receding contact angles.

The effect of surface treatment on the nylon was determined from surface energies calculated from the contact angles of water using a simple equilibrium approach. The surface energies between solid and air ($\gamma_{S/A}$), solid and liquid ($\gamma_{S/L}$), and liquid and air ($\gamma_{L/A}$) can be resolved as forces (Figure 1).

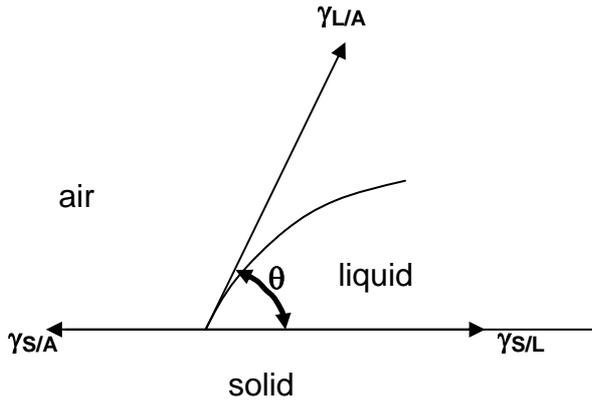


Figure 1 A drop of liquid on a solid surface

This approach gives:

$$\gamma_{S/A} = \gamma_{S/L} + \gamma_{L/A} \cos \theta \quad (1)$$

$\gamma_{L/A}$ is the surface energy of the liquid (water in this case, 72 mN/m^2), and θ is the contact angle. $\gamma_{S/L}$ is generally considered to be small and can be estimated from theory. This equation is generally referred to Young's equation.¹⁸ In combination with the definition of work of adhesion, equation 1 can be re-written

$$W_{S/L} = \gamma_{L/A} (1 + \cos \theta)$$

and was stated by Dupré in 1869.¹⁹ $W_{S/L}$ is the work of adhesion between solid and liquid.

Double cantilever beam (DCB) test specimens were used to determine the Mode I interlaminar fracture toughness, G_{Ic} . The actual design of the specimens were based on the work of Dransfield et al.⁶ in which the load was applied to the specimen through tabs glued to the specimen and were termed TCDB for tabbed double cantilever beam specimens. The tabs in this work were made from standard 25mm steel angle. Figure 2 shows a schematic of the specimen configuration. A piece of 12 μm thick Teflon was placed mid-planer to facilitate delamination at the start of the test. The tabs were glued to the specimen using an appropriate epoxy resin after appropriate surface preparation.

Displacement control mode was used to test the specimens with a crosshead speed of 1 mm/min. Load, displacement and time were recorded on a data logger and crack length was measured using a travelling microscope. The specimen was loaded until the crack grew several centimetres, unloaded and the crack tip marked. This procedure was then repeated several times until the conclusion of the test.

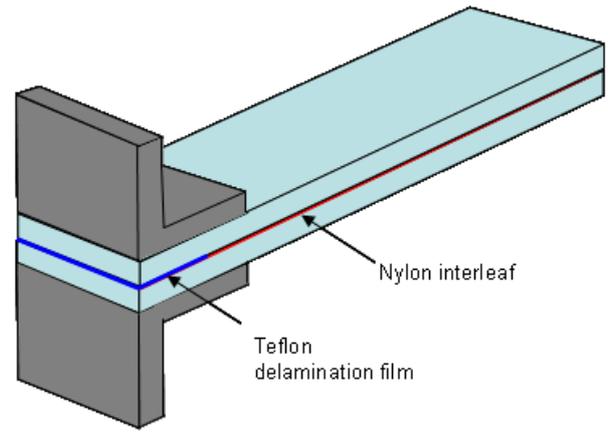


Figure 2 Schematic of TDCB specimen used in this study (not to scale)

The DCB specimens were nominally 150mm long, 25mm wide and 3mm thick.

Carbon fibre/epoxy laminates of $[0]_7$ configuration were made by hand lay-up using 100 μm thick nylon film as an interleaving material. The prepreg used was designated ACG MTM 56 and had a fibre volume fraction of 0.53. Four laminae were hand-rolled, placed under vacuum to remove any air, then the next three were then placed in position and the vacuum treatment repeated. The nylon interleaf material was placed in position and the same procedure as the first 7 laminae applied to the next 7 laminae. The samples were then autoclaved to 0.62 MPa at 120°C for 10 minutes and allowed to cool under pressure as per the manufacturer's instructions.

The surface condition of the nylon interleaf was varied from "as supplied" to soaked in water for 30 minutes before being carefully dried, to washed in toluene and dried, and finally plasma treated. Dynamic contact angles of water on the nylon were measured after each surface treatment

3. RESULTS

Fourier Transform InfraRed (FTIR) spectroscopy showed that the nylon was nylon 6-6 [poly(hexamethylene adipamide)].

The surface energies were calculated using Equation 1 with the assumption that ($\gamma_{S/L}$) was small and could be ignored. Thus the surface energies given in Table 1 are approximations. Even so, comparison with published data¹⁷ of 62 mJm^{-2} for nylon, 54 mJm^{-2} for water washed, and $\sim 70 \text{ mJm}^{-2}$ for plasma treated is good with the values obtained in this work.

Table 1 Dynamic contact angle results for untreated and treated nylon 6,6.

Sample	Contact Angle θ	Surface Energy mJ/m^2
As received nylon 6,6	28.6	63.2
Water treated	44	52
Toluene Treated	20.0	67.7
Plasma	20.2	67.6

The water treated nylon gave a lower surface energy than the untreated material. Nylon is hygroscopic and there would be a diffusion gradient of water into the nylon with the water being hydrogen bonded to the nylon. This sample would maintain a surface that was partially hydrated and thus produce lower contact angles. As the corresponding reduction in surface energy is not large, there is a suggestion that the as-received sample may have picked up moisture, low molecular weight fractions of the polymer, or additives from manufacture.

The toluene treated samples showed a significantly lower contact angle than the water treated samples that resulted in a higher surface energy. Toluene, as a cleaning solvent, is expected to remove low energy contaminants from the surface and was chosen because of its solubility parameter.

Hildebrand developed the following relationship to help describe solubility in polymers²¹

$$H = \delta_s - \delta_p \quad (2)$$

Where δ_s and δ_p are the volume fractions of solvent and polymer, respectively, whereas δ_s and δ_p represent the cohesive energy density (CED) for solvent and polymer, respectively. The magnitude of δ is a measure of the strength of the intermolecular forces keeping the molecules together in the liquid state, and it is known commonly as the solubility parameter.

As a first approximation, significant solubility can be expected if $\delta_s - \delta_p$ is less than 3.5-4, however solubility is not expected if the difference is much larger.²² For this study the appropriate solubility parameters are given in Table 2.

Table 2 Values of the solubility parameter, δ , for the materials used in this study²³

Solvent/polymer	$[\delta (\text{J/cm}^3)^{1/2}]$
Toluene	18.2
Water	47.9
Nylon 6.6	27.8

Using the above criteria and the parameters from Table 2, it would be expected that nylon will not dissolve in water but would be soluble in toluene. How much dissolution of the nylon in toluene occurs would be a

function of temperature and time. These variables were not assessed in this work.

The relatively low contact angle (20°) suggests that, although toluene is an aromatic hydrocarbon (and relatively insoluble in water), both contaminants and toluene have been effectively removed from the treated surface.

The plasma treatment did not provide any increase in surface energy. The plasma is expected to efficiently remove low molecular weight material from the surface and leave it clean of contamination. It may also etch the surface to some extent resulting in some roughening. This morphological change to the surface is known to influence the contact angle of liquids, and hence the surface energy. It appears, however, that the toluene was just as efficient at cleaning the surface as the plasma and is much more cost effective.

Figure 3 shows the Mode I fracture toughness as a function of surface treatment. The figure also provides a value for the critical energy release rate for a laminate without any interleaf from the work of Jain et al.²⁰ That work used the same prepreg and manufacturing conditions as the present work. As can be seen, the presence of the nylon interleaf reduced the critical energy release rate. Of the three surface conditions, the nylon treated with toluene provided the best result, with a critical energy release rate increase of 155% over the as received material. Note that the plasma chamber available did not allow sufficiently large nylon interleaves to be plasma treated for the interlaminar toughness testing. The water treated samples resulted in a decrease of 55% over the as received nylon.

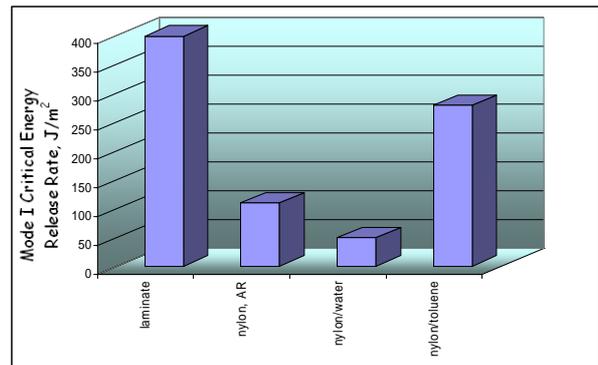


Figure 3 Mode I Critical energy release rate as a function of surface treatment.

Of more practical importance is the observation that the nylon interleaf, regardless of surface condition, provided a significantly inferior interlaminar toughness than that available with the straight laminate without any interleaf material.

The failure mode was adhesive between the nylon and the epoxy prepreg. One sample treated with toluene was tested without a pre-crack. The interlaminar crack path would sometimes switch sides from one side of

the interleaf to the other. No cracks were observed to form between the pre-preg lamina. This resulted in an increase in interlaminar toughness up to the moment when switching occurred causing a reduction until the swap occurred again. This can be seen in Figure 4, which shows a representative graph of critical energy release rate versus crack length for one of the samples. This effect was observed to a lesser extent in the as-received nylon interleaf samples. It was not observed for the water treated nylon samples. This may suggest that bonding was variable along the interlaminar plane or the weak bonding itself is contributing. Hamid et al.²⁴ found with their laminate that for poor bonding between the adhesive and the composite adherends, interfacial crack propagation was observed for very thin bonds with alternating crack jumping from one interface to another across the bond line.

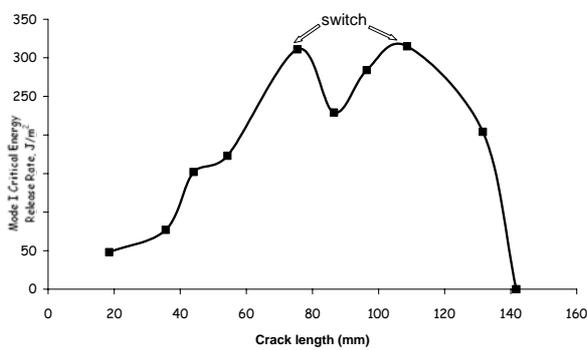


Figure 4 Mode I Critical energy release rate as a function of crack length.

Why the critical energy release rate increases with crack length up to about 70 mm? And a deep of the energy is also observed for crack around 85 mm? This side swapping was also observed, to a lesser extent, for the as received nylon interleaf. It was not observed for the water treated interleaf.

If the interlaminar fracture toughness, G , is assessed in terms of the surface energy of the nylon interleaf () (Figure 5) it can be seen that there is a trend of increasing surface energy resulting in a higher interlaminar toughness.

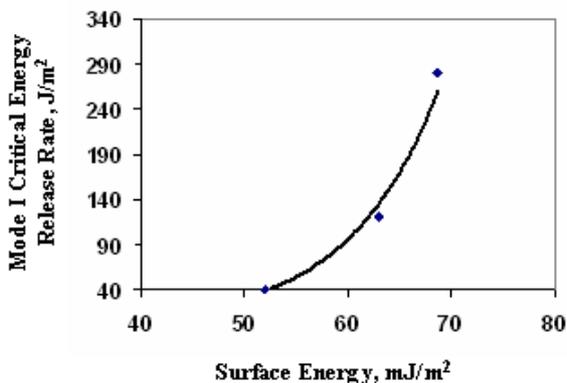


Figure 5 Mode I Critical energy release rate as a function of surface energy of the nylon interleaf

A reasonable fit to the data:

$$G = 0.1009e^{0.1143} \quad (3)$$

is observed for the relationship and is shown by the solid line in Figure 5.

As stated earlier, the much more expensive plasma etching did not provide a significant difference to the surface energy compared to the toluene and one may expect no significant improvement to the interlaminar toughness. A more detailed study of the treated nylon surface is needed though to determine the exact nature of the surfaces.

Comparison with data for stitched laminates from Jain et al.²⁰ (Figure 6) shows that interlaminar toughness of the order of 4 kJm^{-2} is possible. Clearly, stitching of laminates presents its own problems such as localised in-plane fibre damage reducing flexural strength²⁵ and loss of compressive strength²⁶. The stitching also creates a materials discontinuity which can lead to stress concentrations, decreasing mechanical properties.^{27, 28}

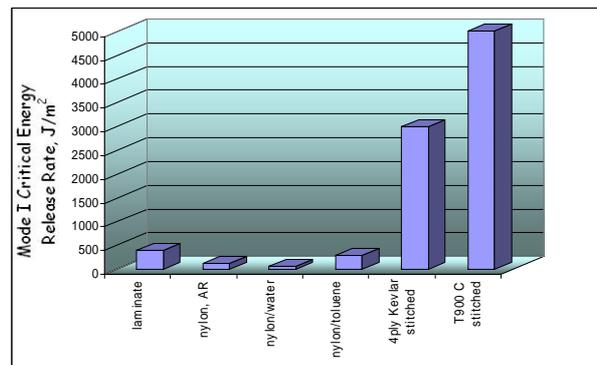


Figure 6 Mode I Critical energy release rate for the surface treatments in this study and for the stitched laminates of Jain et al.

Use of equation 3 suggests that this level of interlaminar toughness should be achievable if the surface energy of the nylon could be increased to approximately $90\text{-}95 \text{ mJm}^{-2}$.

Surface energy in polymers may be controlled by a number of factors. Polymer crystallinity has found to have an effect on the surface energy.²⁹ What effect the crystallinity has depends on the polymer and the liquid used to measure contact angle. For example Zisman³⁰ found that the surface energy decreased with increasing crystallinity whilst Schonhorn and Ryan³¹ found a decrease. In both cases it was the concentration of the endgroups at the surface being increased by the increase in crystallinity that resulted in the observed behaviour. This highlights the importance of endgroups on the surface energy as well.

Pittman and Ludwig²⁹ found similar results to Zisman. They also found that surface energy depended on the fluoralkyl chain length and side chain crystallisation in the fluoroalkyl acrylate system they studied. Molecular

weight will also have an effect.³² It was found for the system studied that the surface chain end concentration was higher than the corresponding bulk value due to its lower surface free energy, and that surface orientation of chain ends was dependent on molecular weight. This again points to the major effect of what is happening at the end of chains

Copolymerisation and blending have also been seen to be effective in increasing or decreasing the surface energy. In her thesis, Meduri³³ reports that the surface energy of nylon was increased from approximately 53mJ/m² to 88.2 mJ/m² for nylon 6,6 /polyaniline blends. The surface energy values of the polyaniline films reported in the literature fall in the range of 42.6 mJ/m² to 150 mJ/m².³⁴

4. CONCLUSION

The interlaminar toughness will be a function of the adhesive strength between the interleaf and the laminate. Adhesive strength is a function of bonding site density between the thermoplastic film and the resin. Because interleaf materials have few or no active bonding sites, adequate bonding necessitates the creation of new bonding sites on the film surface.

The current work has shown that the surface energy of nylon, and thus the adhesion to other materials, can be altered by simple chemical techniques. Toluene and plasma etching provided increases in interlaminar fracture toughness over the as received nylon, but all toughness values were below that of a laminate without interleaving. Indeed there was very little difference between the toluene and plasma treated nylon, with respect to surface energy suggesting the more expensive plasma treated is not warranted.

From the data presented it appears that if a surface energy of 90-100mJ/m² can be made on the nylon then interlaminar fracture toughness of the order of those obtained with stitched laminates may be achievable.

A polymer blend of nylon and polyaniline seems to be a possible candidate, but the mechanical properties of these blends needs to be looked out to determine their suitability. Another issue with this material is its conductivity which may be able to be used for particular applications, but may cause problems with carbon fibres.

Clever materials science relating to controlling the end groups and crystallinity in the interleaf material is needed. Further treatments are needed to be developed and the surface chemistry and structure of the polymer studied in more detail using surface analytical techniques.

References

1. J.K. Kim, C. Baillie, J. Poh, Y.-W. and Mai: *Compos. Sci. Technol.*, 1992, vol. 43, pp 283-97.
2. J.K. Kim, D Mackay and Y.-W. Mai: *Composites*, 1993, vol. 24, pp 485-94.
3. Y.-W. Mai, B. Cotterell and R. Lord: *In Progress in Science and Engineering of Composite Materials*, Vol. 1, ed. T. Hyashi, K. Kawato and S. Umekawa. Japan Society of Composite Materials, 1982, pp 271-78.
4. M.B. Dow, and D.L Smith: *21st Int. SAMPE Tech. Conf*, 1989, pp. 595-605.
5. D. Liu: *J. Reirzf. Plastics Compos.*, 1990, vol. 9, pp 59-69.
6. K.A., Dransfield, Through-thickness reinforcement of carbon fibre composites by stitching. Ph.D. thesis. University of Sydney, 1995.
7. E. Armstrong-Carroll and T. M. Donnellan, *Proc. Mater. Eng. Congr.*, 1992. Atlanta, Am. Soc. Civil Eng, 1992, pp.74-79.
8. E. Armstrong-Carroll and T. M. Donnellan, *Proc. 7th Tech. Conf. Composite Mater.*, Am. Soc. Composites, 1992, pp.1022-29.
9. R. B. Krieger, Jr., *SAMPE Nat. Symp.*, 29, 1989 pp. 1570-77.
10. P. A. Lagace, J. C. Brewer, and D. B. Weems, *Third Japan-U.S. Conf. Composite Mater.*, Tokyo, June 1986.
11. J. E. Masters, J. L. Courter, and R. E. Evans, *SAMPE International Symposium*, Jerome L. Bauer, Ed., 1, 1986, pp. 844-49.
12. G. L. Dolan and J. E. Masters, *SAMPE Int. Tech. Conf.*, 20, 1988, pp. 34-39.
13. Frazier, J L. Clemons, A. *National SAMPE Symposium and Exhibition (Proceedings)*. Publ by SAMPE, Covina, CA, USA., 35, pp. 1620-1627
14. J.E. Masters, *SAMPE Int. Symp.*, V34, 1989, pp. 1792
15. M. Schrader and G. Loeb, in *Modern approach to wettability: theory and applications*. New York: Plenum Press; 1992.
16. A.W. Adamson and A.P. Gast in *Physical Chemistry of Surfaces*, 6th ed. New York: Wiley; 1997
17. J.C. Nay, W.G. Pitt, and E. Armstrong-Carroll, *J. Applied Polymer Science*, 56, 1995, pp. 461-469.
18. T. Young, *Philos. Trans. R. Soc.*, 95, 1805, p. 65.
19. A. Dupré, *Theorie Mecanique de la Chaleur*, Paris, 1869, p. 368
20. L.K. Jain, K.A. Dransfield, Y.-W. Mai., *Comp. Sci. & Tech.*, 1998, 58, pp. 829-37.
21. P. Tsai, P. Roth, J Reece W. Chen, *Textile Research Journal*, 75, 2005. pp. 819-825.
22. J. Hildebrand and R. Scott, *The solubility of Nonelectrolytes*, 3rd Ed., Reinhold, New York, 1950.
23. H. Burrell, *Solubility Parameters for Film Formers*, Off. Dig. Fed. Soc. Paint Tecnnol., 27, 1955, pp. 726-758.

24. R. Hamid, L. Ye, Y.W. Mai, J. Compos. Mater., 30, 1996, p.1248-1265
25. W. Chung, B. Jang, T. Chang, L. Hwang, R. Wilcox, R. C., Mater. Sci. & Eng., All2, 1989, pp.157-73.
26. Y. Ogo, The effect of stitching on in-plane and interlaminar properties of carbon/epoxy fabric laminates. MSc. thesis, University of Delaware, Newark, May 1987.
27. C. Lee, D. Liu, J. Eng. Mater. & Tech., 112, 1990, pp.125-30.
28. G. Farley, L. Dickinson, J. Reinforced Plastics and Composites, 11, 1992, pp. 633-42.
29. A. Pittman, B. Ludwig, J. Polymer Sci. Part A-1, 7, 1969, pp. 3053-3066.
30. W. A. Zisman, in Advances in Chemistry, No. 43, American Chemical Society, Washington, D. C., 1964, p.1.
31. H. Schonhorn and F. W. Ryan, J. Polymer. Sci. A-2, 6, 1968, pp. 231-37.
32. K. Tanaka, D. Kawaguchi, Y. Yokoe, T. Kajiyama, A. Takahara, S. Tasaki, Polymer, 44, 2003, pp. 4171-4177.
33. P. Meduri in Characterization Of Uncoated And Sputter Coated Nanofibers, Master of Science Thesis, The Graduate Faculty of The University of Akron, December, 2005, p.5.
34. A. Al-Ghamdi, Z. Al-Saigh, J. of Chromatography A, 969, 2002, pp. 229-35.