

ΕΥΝΕΔΡΙΑ ΤΗΣ 13ΗΣ ΝΟΕΜΒΡΙΟΥ 1986

ΠΡΟΕΔΡΙΑ ΚΩΝΣΤΑΝΤΙΝΟΥ ΤΡΥΠΑΝΗ

---

ΦΥΣΙΚΟΧΗΜΕΙΑ.— **Morphological Developments in Bismaleimide Matrix Composites during Processing**, by *James C. Seferis\**,  
διὰ τοῦ Ἀκαδημαϊκοῦ κ. Περικλῆ Θεοχάρη.

A B S T R A C T

A series of silicone modified bismaleimide resins have been examined as matrices for high performance continuous fiber reinforced composites. Detailed studies of the interrelation between processing structure and properties of both the neat resin and corresponding carbon fiber reinforced composite have identified that the silicone additive provides important morphological modification to the bismaleimide matrix for toughness improvements while at the same time retaining the elevated temperature performance. Micrographs of fracture surfaces of cured samples demonstrate remarkable similarities to fracture surfaces of rubber-modified epoxy matrices. Specifically, a fracture surface covered with non-communicating microcavities of 1.5  $\mu\text{m}$  in diameter was observed. However, unlike in rubber modified epoxies where the observed morphology is assumed to be created during fracture of the specimen, this study demonstrates that the microcavities are created during the cure process and also exist in the bulk of the material before fracture. In a simulated cure of the sample in the polarizing microscope and in SEM micrograph of samples at different stages of the cure, it is established that the silicone modifier in conjunction with the processing conditions employed is responsible for the specific morphological developments. Accordingly, a model capable of describing the observed morphology was developed based on physical changes that the silicone additive experiences during the curing process.

---

\* ΔΗΜ. ΣΕΦΕΡΗΣ, «Χαρακτηριστικοί μεταβολαί συνθέτων ὑλικῶν με Δι-Μα-λεϊμιδικήν μήτραν κατά τήν παρασκευήν των».

## INTRODUCTION

Polyimide resin matrices offer an increase in use temperature of structural composites over the traditionally used epoxy based matrices. However, the exceptionally high thermo-oxidative stability of wholly aromatic polyimides is countered by their difficult processability which involves a mixture of monomers in a low boiling point alcohol. The solvent impregnation route has the familiar problem in creating crack and void free composites. An alternate to solution impregnation has been the creation of a polyaddition route of short pre-imidized segments which then with other additives offer a melt-impregnation route similar to epoxy matrices. Such a resin system based on bismaleimide chemistry was investigated in this work as a model high temperature system adding to an overall developing methodology for interrelating processing structure and properties of polymer based composites [1, 2, 3].

## EXPERIMENTAL

*Materials and Processing*

The model bismaleimide examined in this work as well as the individual constituents was made available from Rhone-Poulenc, Inc. The system was based on the patented Kerimid R family whose components are shown in Fig. 1. The model formulation Kerimid FE 70003 which has been examined in other studies as well [4] formed the base system with the following composition (by weight %): Diphenylmethane BMI (35%); tolylene BMI (25%); Triallylisocyanurate T.A.I.C. (15%); Diphenylsilanediol DPS (25%) with Imidazole (0.06%) as the catalyst. The basic cure reactions are also schematically illustrated in Fig. 1. A basic cure cycle for laminating prepregs of carbon fibers has been developed in our previous studies based on thermal and rheological analysis [2, 3]. Specifically, however, the cure is as follows: Three plateaus of temperature: 50 minutes at 150° C (B-staging and DPS polymerization); 2 hours at 200° C (BMI cure); 1 hour at 250° C (postcure). Windows of vacuum and pressure are applied according to the viscosity curve for the neat resin.

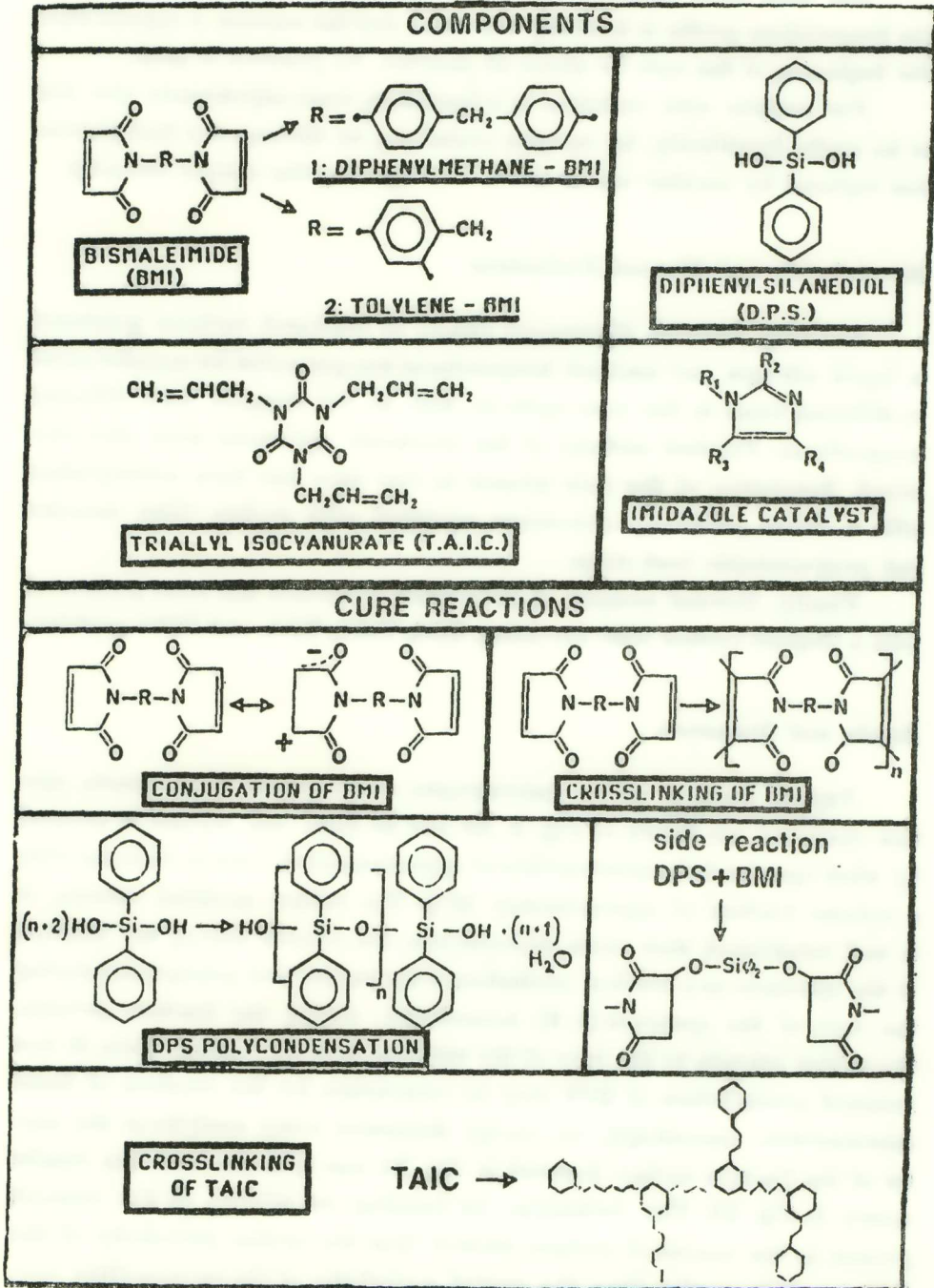


Fig. 1. Chemical components of Kerimid FE 70003 and their main cure reactions

For neat resin samples, the following cure procedure was adapted: the temperature profile is basically the same, but the vacuum is applied from the beginning of the cure for about 40 minutes. No pressure is used.

For samples with variation in composition, some adjustments also had to be made. Specifically, for samples containing no silicone, the first plateau was replaced by another one at 100°C for degassing the sample correctly.

### *Morphological and Thermal Evaluations*

Scanning Electron Microscopy (SEM) of fractured surfaces generated in liquid nitrogen and ambient temperatures was generated for samples cured to different times in the cure cycle as well as for samples with different compositions. Polished surfaces of the fractured specimens were also examined. Simulation of the cure process in real time has been accomplished with a Nikon polarizing microscope equipped with on-line video recorder and programmable heat stage.

Finally, thermal analysis of all systems examined has been performed with a Dupont System 9900 operating, DSC, TMA, TGA, and DMA modules.

### *Results and Discussion*

Typical fracture surface micrographs of the model bismaleimide system examined are shown in Fig. 2. As can be seen, the surface is covered by what appears to be microcavities of approximately 1.5  $\mu\text{m}$  in diameter with a volume fraction of approximately 20%. For rubber modified epoxies, it is well established that these microcavities are created during the fracture of the specimen as a result of cavitation of the rubber that precipitated during the cure of the specimen [5, 6]. Accordingly, during the fracture process, the rubber retracts to the base of the microcavities. By analogy then, it was assumed precipitation of DPS may be responsible for the creation of these microcavities. Accordingly, an energy dispersive x-ray analysis at the center of the fracture surface depicted in Fig. 2A was obtained and the results shown in Fig. 2B. This technique, by focusing on silicone as the element present in the examined surface, showed that the spatial periodicity of the DPS is much smaller than the spatial periodicity of the microcavities covering the fracture surface. To prove, however, that indeed DPS is respon-

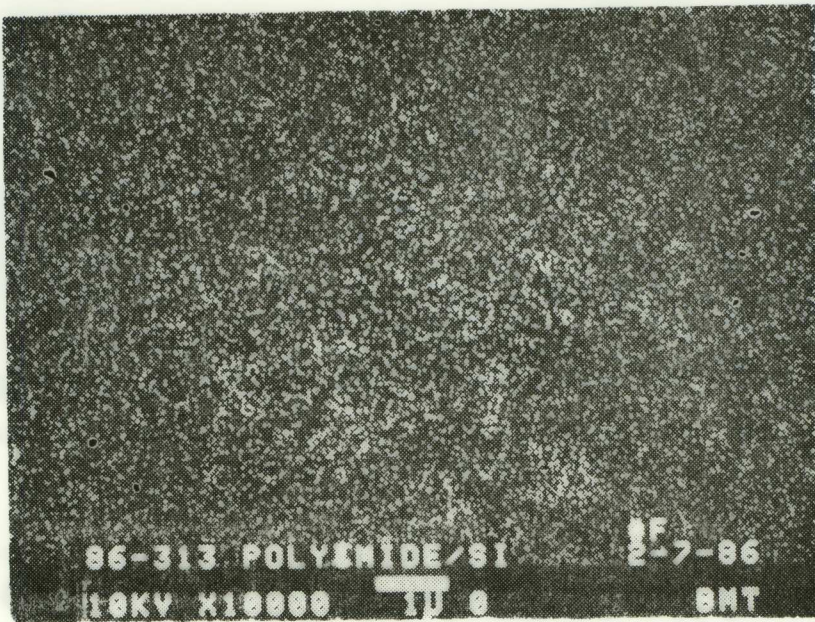
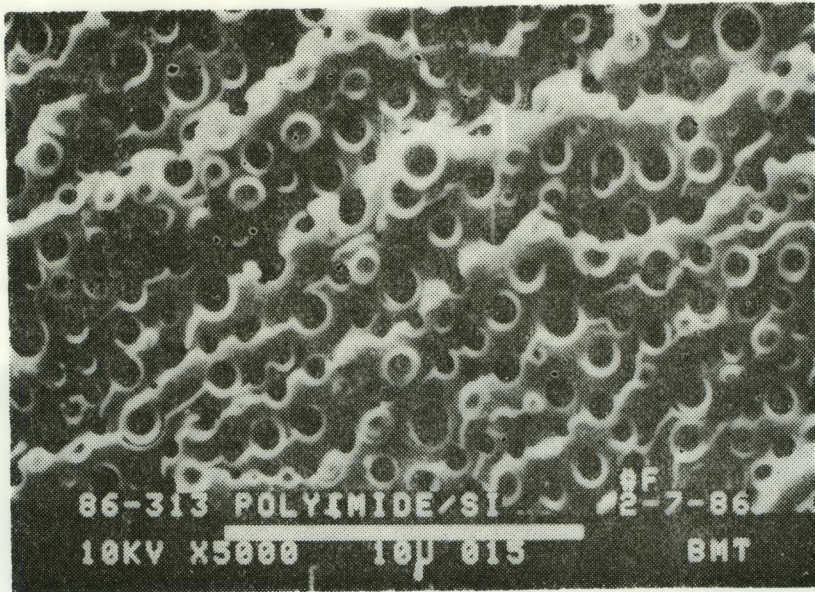


Fig. 2. Energy Dispersive X-Ray Analysis of the Kerimid 70003 Bismaleimide Model Formulation Showing Microcavity Morphology: (a) SEM micrography of a fracture surface (b) Map of the silicone present on the same area (doubled magnification)

sible for the creation of the observed microcavities, a formulation without DPS was prepared and the fractured surface of the cured sample examined by SEM. As can be seen in Fig. 3, there were no microcavities observed for the sample containing no DPS in its makeup composition. In order to investigate further at which point during the cure the microcavities appear, samples from the basic FE 70003 formulation were obtained from different points in the cure cycle and their fracture surface examined in the SEM. The results shown in Fig. 4, along with corresponding cure cycle employed,

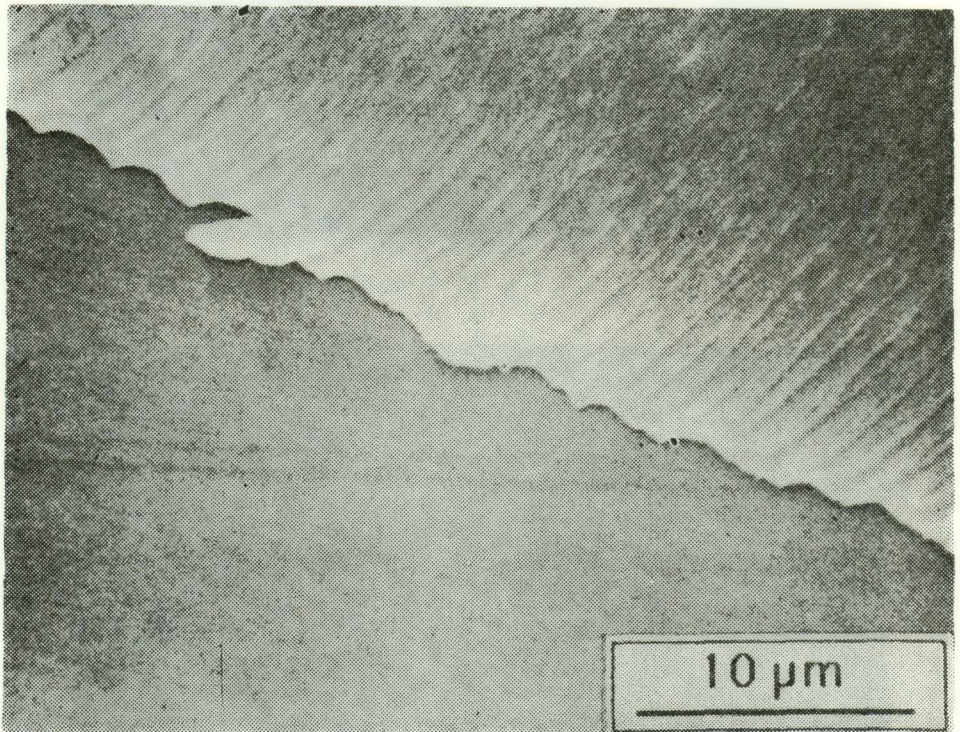


Fig. 3. Fracture surface of the formulation without diphenylsilanediol: No microcavity.  
The sample is totally transparent

demonstrate that the microcavities indeed appear during the early part of the cure. This was also confirmed in real time cure experiments with the hot stage polarizing microscope, establishing the formation of the microcavities in the bulk during cure. In order to establish the influence of each component in the basic composition, TGA experiments as a function of

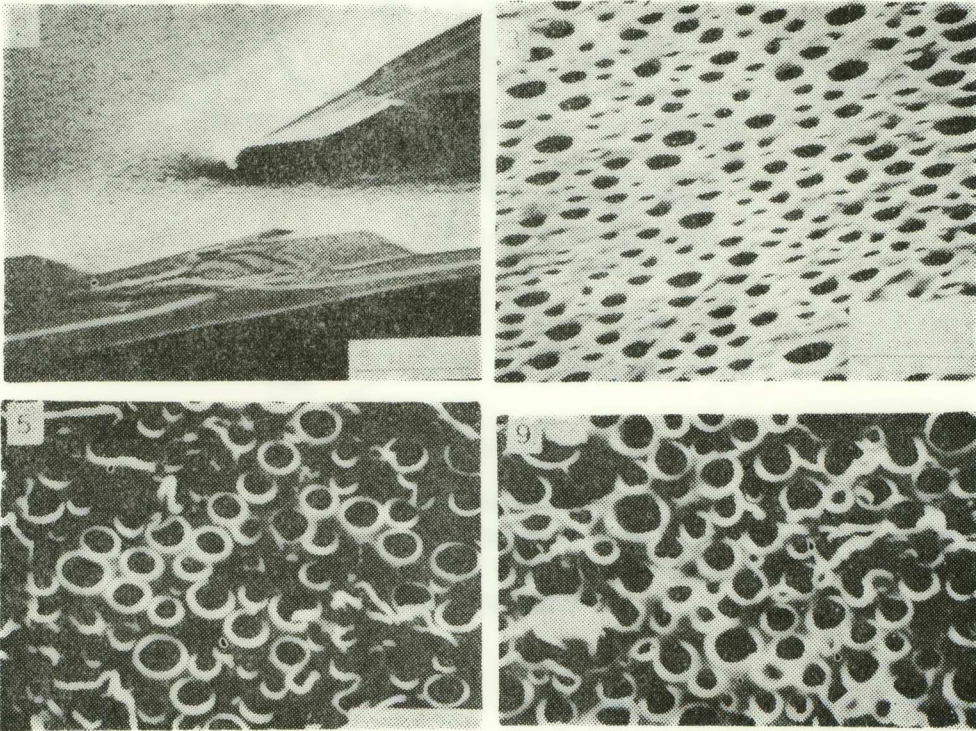
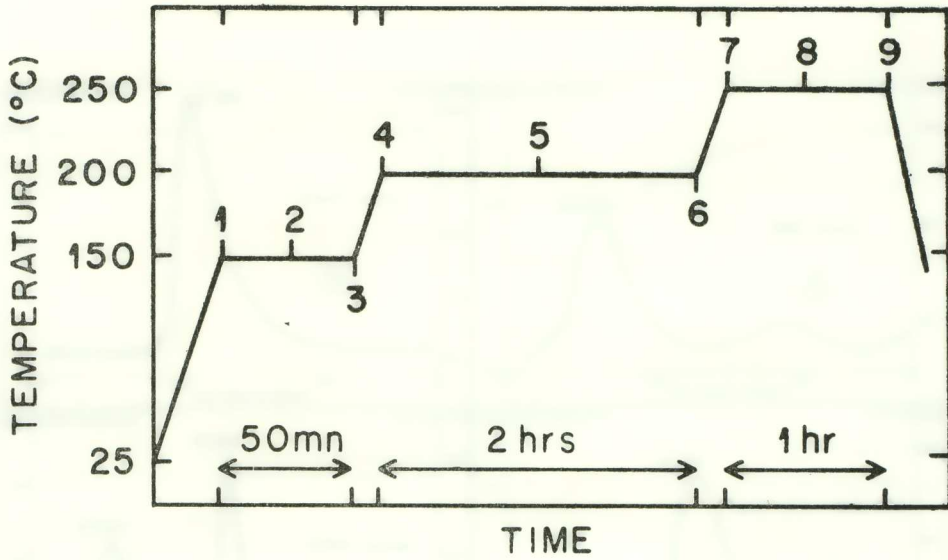


Fig. 4. SEM of fractured surfaces from bismaleimide samples taken at different steps during the cure cycle shown above. Note the formation of microcavities in steps 3, 5, and 9.

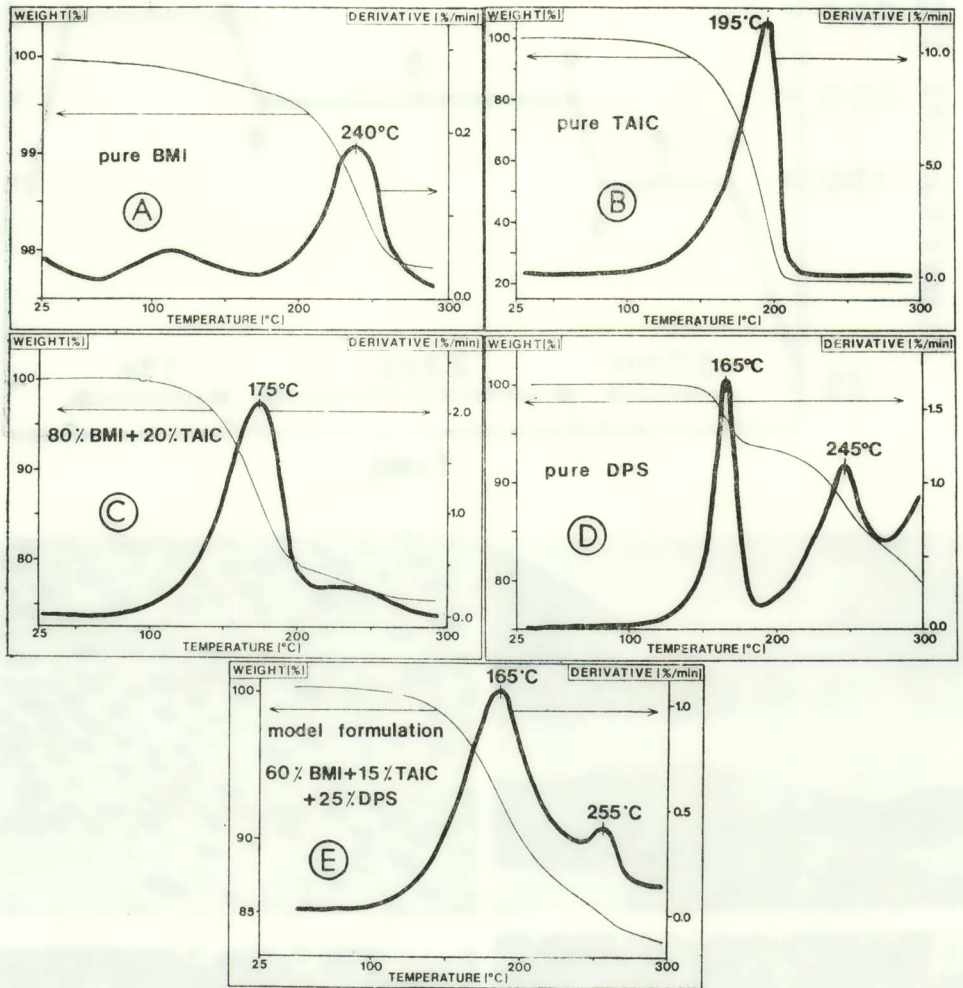


Fig. 5. TGA results on the major components (and their combinations) of the model BMI system when submitted to a ramp of temperature of 5° C/min. (a) pure BMI; (b) pure TAIC; (c) 80% BMI+20% TAIC; (d) pure DPS; (e) final formulation; 60% BMI, 15% TAIC, 25% DPS



temperature were performed at a rate of 5° C/min. As seen in Fig. 5 summarizing the TGA results, in addition to DPS, TAIC also contributes to loss of weight during cure. However, since no microcavities were observed on samples with TAIC present but with no DPS, it may be safely assumed that volatile evolution is not solely responsible for the creation of microcavities.

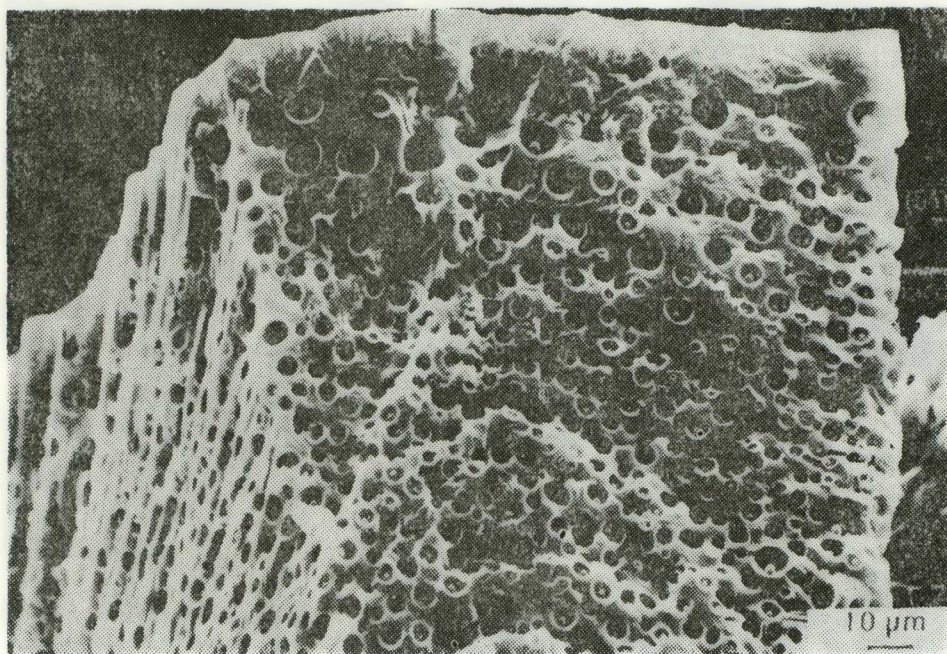


Fig. 6. Fracture surface of the Kerimid 70003 bismaleimide formulation exposed to hexafluoropropanol for 10 minutes. Swelling of DPS in the microcavities is observed.

The simple thermoanalytical observation that the DPS shrinks as a function of temperature coupled with the evaluation of volatiles during the cure may be responsible for the microcavity formation. To further demonstrate that the microcavities indeed were coated with a DPS shell, a fractured surface was immersed in hexafluoropropanol which is well established as a swelling solvent for DPS. As can be seen in Fig. 6, swollen DPS appears in the center of the microcavity morphology. The mechanism explored is not incompatible with an epoxy system giving rise to a similar microcavity morphology described by Peters and Logan [7]. Finally, SEM of

fractured surfaces shown in Fig. 7 for carbon fiber reinforced Kerimid 70003 samples also exhibited the microcavity morphology. This indicates that the presence of the reinforcing fibers does not affect the basic processes involved in creation of the microcavities for the matrix polymer.

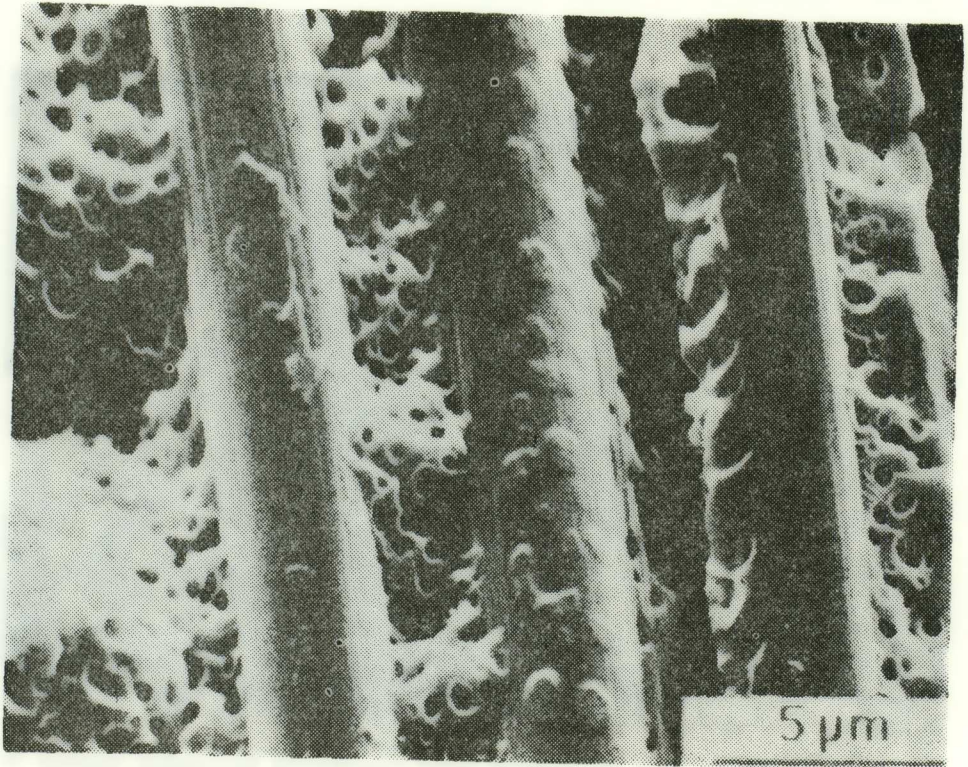


Fig. 7. Fracture surface of the Kerimid 70003 bismaleimide model formulation reinforced with continuous carbon fibers showing microcavity morphology.

#### CONCLUSION

A silicone modified bismaleimide resin has been examined in this work as a model high temperature thermosetting matrix for structural composites. It was established that the silicone additive can induce morphologies in the cured samples similar to those observed for rubber modified toughened epoxies. It was demonstrated that the observed non-communicating microcavities are created, not during the fracture process of the sample, but rather during processing as a result of a combination of shrinkage of the silicone

additive and volatile products emission during cure. Collectively, the results of this investigation have provided an important step toward understanding the importance of kinetics of morphology development during processing in order to effectively control the final properties of high temperature based composite systems.

#### ACKNOWLEDGMENT

The author expresses his appreciation to his assistant, Dr. Jean-François Viot of Rhone-Poulenc who spent a year in the Polymeric Composites Laboratory working on this research. The author would also like to express his appreciation to Dr. M. Carrega of Rhone-Poulenc for helpful discussions and expert coordination of this project. The invaluable input of the late Dr. M. Rakoutz and his colleagues, Drs. Balme and Barthelemy of Rhone-Poulenc, in chemical formulation issues is also acknowledged. Financial assistance for this project was provided by Rhone-Poulenc, Inc., through the Polymeric Composites Laboratory.

#### REFERENCES

1. J. C. Seferis, «Polyetheretherketone (PEEK): Processing-Structure and Properties Studies for a Matrix in High Performance Composites», *Polymer Composites*, **7**, 158, 1986.
2. P. Lopez, «Characterization and Processing of Polyimide Matrix Composites», M.S. Thesis, Dept. of Chem. Eng., Univ. of Washington, Seattle, WA (1986); P. R. Lopez and J. C. Seferis, in preparation.
3. J. - F. Viot and J. C. Seferis, submitted *Polymer Composites* (1986).
4. D. A. Scola, M. Bak, and D. J. Parker, *SAMPE*, pp. 47-54 (1986).
5. L. T. Manzione, J. K. Gillham and C. A. McPherson, *J. Appl. Polym. Sci.*, **26**, 889, 1981.
6. L. T. Manzione, J. K. Gillham, and C. A. McPherson, *J. Appl. Polym. Sci.*, **26**, 907, 1981.
7. R. A. Peters and T. J. Logan, *Adhesive Age*, pp. 17-21, April (1975).

## ΠΕΡΙΛΗΨΙΣ

**Χαρακτηριστικά μεταβολαί συνθέτων ύλικων με Δι-Μαλεϊμιδικήν μήτραν κατά την παρασκευήν των.**

Αί πολυιμιδικαί μήτραι εκ ρητινῶν εἶναι κατάλληλοι διὰ χρήσεις συνθέτων ύλικων ύψηλῶν θερμοκρασιῶν, υπερέχουσαι τῶν κλασσικῶν μητρῶν με βάσιν τὰς ἐποξειδικὰς ρητίνας. Λεπτομερεῖς μελέται διὰ τήν συσχέτισιν μεταξύ τοῦ τρόπου διαδικασίας παρασκευῆς καὶ τῶν ιδιοτήτων τόσον τῆς καθαρᾶς ρητίνης, ὅσον καὶ τῶν ἀντιστοιχῶν συνθέτων ύλικῶν ἐνισχυμένων με ἴνας ἀνθρακος ἀπέδειξαν ὅτι προσθήκη σιλικόνης συντελεῖ εἰς ἐντόνους μορφολογικάς τροποποιήσεις τῆς δι-μαλεϊδικῆς μήτρας, συντελοῦσας εἰς τήν βελτίωσιν τῆς στερεότητος, ἐνῶ συγχρόνως τὸ σύνθετον ύλικὸν διατηρεῖ τὰς ιδιότητάς του εἰς ύψηλὰς θερμοκρασίας.

Μικρογραφίαι τῶν ἐπιφανειῶν θραύσεως τῶν πολυμερισμένων δοκιμῶν δεικνύουν σημαντικὰς ὁμοιότητας με τὰς ἐπιφανείας θραύσεως ἐποξειδικῶν μητρῶν τροποποιημένων με ἔλαστικὸν κόμμι.

Εἰδικῶς ἔχουν παρατηρηθῆ ἐπιφάνειαι θραύσεως καλυπτόμεναι ἀπὸ μικροκοιλότητος μὴ ἐπικοινωνούσας μεταξύ των, διαμέτρου 1,5 μm. Ἐν πάσῃ περιπτώσει, ἀντιθέτως πρὸς τὰς ἐποξειδικὰς ρητίνας τὰς τροποποιημένας με ἔλαστικὸν κόμμι, ὅπου αἱ παρατηρούμεναι μορφολογίαι θεωροῦνται ὡς δημιουργούμεναι κατὰ τήν θραῦσιν τῶν δοκιμῶν, ἀποδεικνύεται εἰς αὐτὴν τήν μελέτην, ὅτι αἱ μικροκοιλότητες δημιουργοῦνται κατὰ τήν διάρκειαν τῆς διαδικασίας πολυμερισμοῦ καὶ ἐπίσης ὑπάρχουν εἰς τὸν ὄγκον τοῦ ύλικοῦ πρὸ τῆς θραύσεως.

Εἰς ἐξομοιουμένην διαδικασίαν πολυμερισμοῦ τῶν δοκιμῶν ἐντὸς πολωτικοῦ μικροσκοπίου ἢ καὶ ἠλεκτρομικροσκοπίου σαρώσεως, δοκίμια εἰς διαφόρους βαθμίδας πολυμερισμοῦ μελετώμενα, ἀποδεικνύουν ὅτι ὁ τροποποιητῆς τῆς σιλικόνης, ἐν συνδυασμῷ με τὰς συνθήκας παρασκευῆς τῶν συνθέτων ύλικῶν, εἶναι ὑπεύθυνος διὰ τήν εἰδικὴν μορφολογικὴν ἀνάπτυξιν τῶν συνθέτων αὐτῶν ύλικῶν.

Ἐκ τῶν ἀνωτέρω ἀνεπτύχθη ἀφομοίωμα κατάλληλον διὰ τήν περιγραφὴν τῆς παρατηρουμένης μορφολογίας τῶν συνθέτων ύλικῶν, βασιζόμενον ἐπὶ τῶν φυσικῶν μεταβολῶν αἱ ὁποῖαι λαμβάνουν χώραν εἰς τήν προστιθεμένην σιλικόνην κατὰ τήν διάρκειαν τῆς κατεργασίας.