ELEVATED TEMPERATURE TREATMENT OF ARAMID FIBERS TO IMPROVE ADHESION

Shigeru Ishihara[1] and **Lawrence T. Drzal**[2]

[1]*Teijin Limited, Fibers Technology Department, Minami-Yoshida-cho Matsuyama, EHIME 791 –8042 Japan*
[2]*Composite Materials and Structures Center, Depts of Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan 48824-1226*
517-353-5466; Email: drzal@egr.msu.edu

SUMMARY: The objective of this research is to develop a fundamental understanding of adhesion of aramid fibers to an epoxy matrix. In general, aramid fibers are para phenylene terephthalamide, rod-like polymers having a high degree of orientation and high crystallinity. Although these para type aramid fibers have high strength and high modulus, their surface is relatively inert. For composite applications it is necessary to improve the adhesion between fibers and matrices to improve the composite properties. For aramid fibers in tire rubber applications, an epoxy containing coating is placed on the aramid fiber bundle and given a high temperature treatment prior to incorporation into tire rubber. Investigation of this high temperature treatment has led to the conclusion that a minimum temperature of 240^{o}C produces a significant number of chemical bonds between the matrix epoxy groups and the amide groups on the aramid fiber surface which produces a substantial increase in fiber-matrix adhesion. This elevated temperature treatment does not reduce the tensile properties of the aramid fiber.

KEYWORDS: fiber-matrix adhesion, aramid, epoxy, surface treatment, Technora,

INTRODUCTION

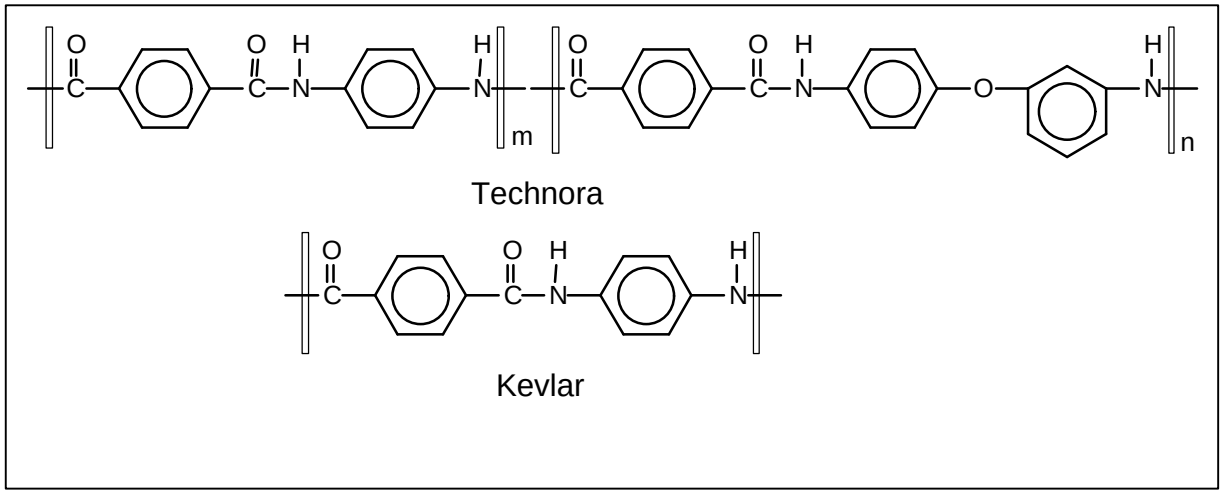
In general, among aromatic polyamide fibers, the para-type aramid fibers (Kevlar™, Twaron™ and Technora™) have high strength and high modulus and are used not only for reinforcements of high performance composites but also for reinforcement of rubber, plastics and concrete. These para type aramid fibers are rod-like polymers having high crystallinity but differ slightly in their structure. Kevlar™ and Twaron™ are poly-paraphenylene terephthalamide (PPTA) while Technora™ is a co-polymer, poly-(paraphenylene/ 3,4' -oxydiphenylene terephthalamide). (Figure 1) The surface of this class of fibers is not active chemically at low temperatures and the adhesion between fibers and matrices is less than optimum [1].

In general, to improve adhesion and interfacial strength, silane coupling treatments are used for glass fibers and oxidization treatments for carbon fibers but these methods are not

effective with aramid fibers. Surface treatments to improve adhesion are roughly divided into two types [2]. One is a physical treatment and the other is chemical treatment.

Among various physical treatments, plasma treatment is commonly used for aramid fibers. For example, Ar, N_2 or CO_2 gas plasma treatment of Kevlar™ results in a 10 to 20% improvement of interfacial strength to bisphenol-A epoxy but on the other hand, Technora™ shows a 10 to 20% decrease. When O_2 plasma is used followed by grafting with ethylene,

Fig. 1 Chemical Structures of Para-type Aramid Fibers



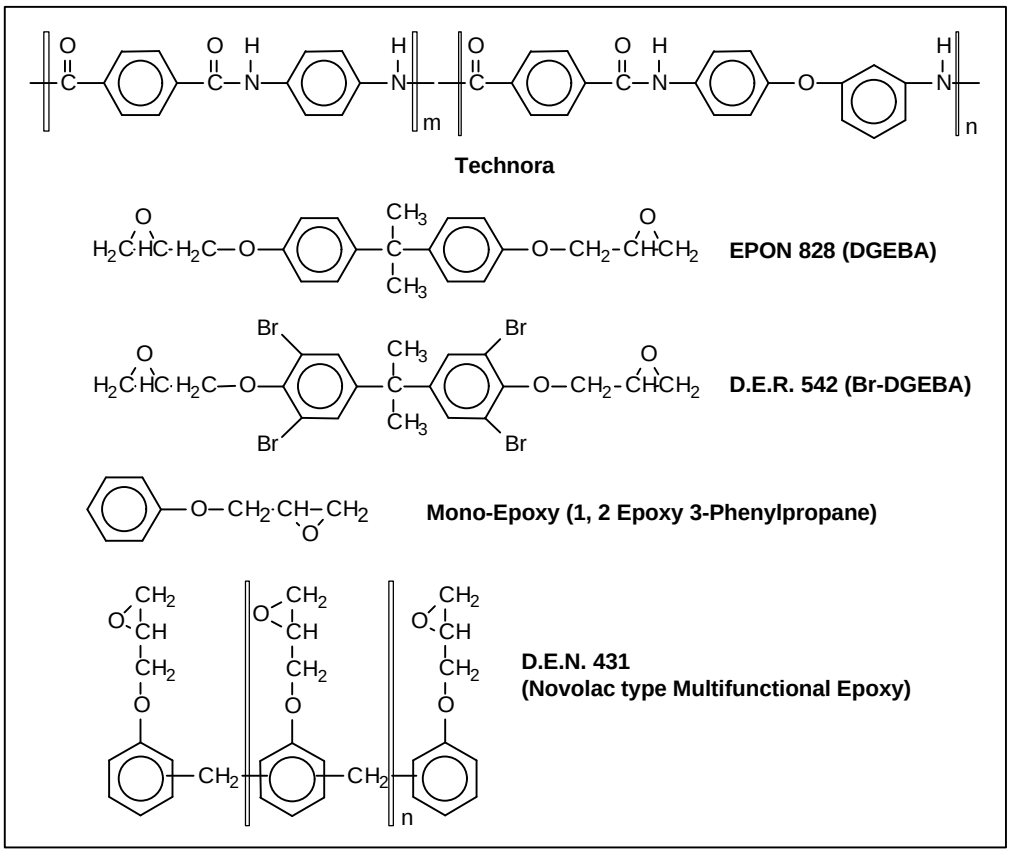
Kevlar™ shows an improvement of adhesion to high density polyethylene. Takayanagi et al.[3] reported that PPTA can be treated with DMSO and sodium hydride and subsequently, by octadecilation or carbomethylation, to introduce an alkyl group or a carboxyl group, or by grafting, to introduce a poly acrylonitrile group to amide bond. Wu et al. [4] reported that amide groups could be added to the benzene ring by bromination and ammonolysis, or by nitration and reduction. Furthermore, chlorosulfonation and subsequent reaction of SO_2Cl group has been used to treat Kevlar 149™ to improve the adhesion to epoxy. Improvement of adhesion between Twaron™ and natural rubber resulted from treatment by fluorine gas.

Commercially, a typical chemical treatment for improvement of adhesion to rubber is the RFL (resorcinol formaldehyde latex) treatment. This treatment was developed for improvement of adhesion between nylon or polyester fibers and rubbers at first and applied to aramid fibers later. RF resin, which is made from resorcinol and formaldehyde, reacts with an epoxy coated fiber to strengthen the adhesion between latex and rubber. For aramid fibers in tire rubber applications, an epoxy containing coating is placed on the aramid fiber bundle and given a high temperature treatment prior to incorporation into tire rubber. It appears that a minimum high temperature exposure is required for this coating to be effective suggesting that chemical bonding may take place during this treatment

This investigation was undertaken to determine the role of chemical bonding between the aramid fiber surface and epoxy by conducting treatments at high temperature (~240^{o}C) on the aramid fiber, Technora™. Both monofilament and multifilament Technora fiber were used in this research. Fiber samples were immersed in liquid epoxy DGEBA, brominated DGEBA or other epoxy functional resin of longer chain length and/or higher functionality and treated at increasing tempertaures up to 240^{o}C. (Figure 2) Temperatures in excess of 240^{o}C were not used since homopolymerization of the epoxy was likely at higher temperatures. Excess non chemisorbed material was removed from the surface by soxhlet extraction. Surface analysis of the fibers after exposure to multifunctional and monofunctional epoxy as well as

brominated epoxy was completed using Xray Photoelectron Spectroscopy (XPS). Adhesion was measured by determination of the interfacial shear strength (ISS) through the use of the single fiber fragmentation test (SFFT) using a DGEBA epoxy cured with m-phenylene diamine as the matrix.

Fig. 2: Chemical Structure of Various Epoxy Resins Used to Pretreat the Technora Aramid Fiber



RESULTS AND DISCUSSION

High temperature exposure to chemicals such as epoxy could cause defects to form on the fiber surface resulting in a loss in tensile strength. Tensile strength and modulus measurements were made on the aramid fibers after exposure to mono and multifunctional epoxy at 240^{o}C. The aramid fiber tensile strength was unaffected by the elevated temperature treatment to 240^{o}C as the data in Table 1 shows.

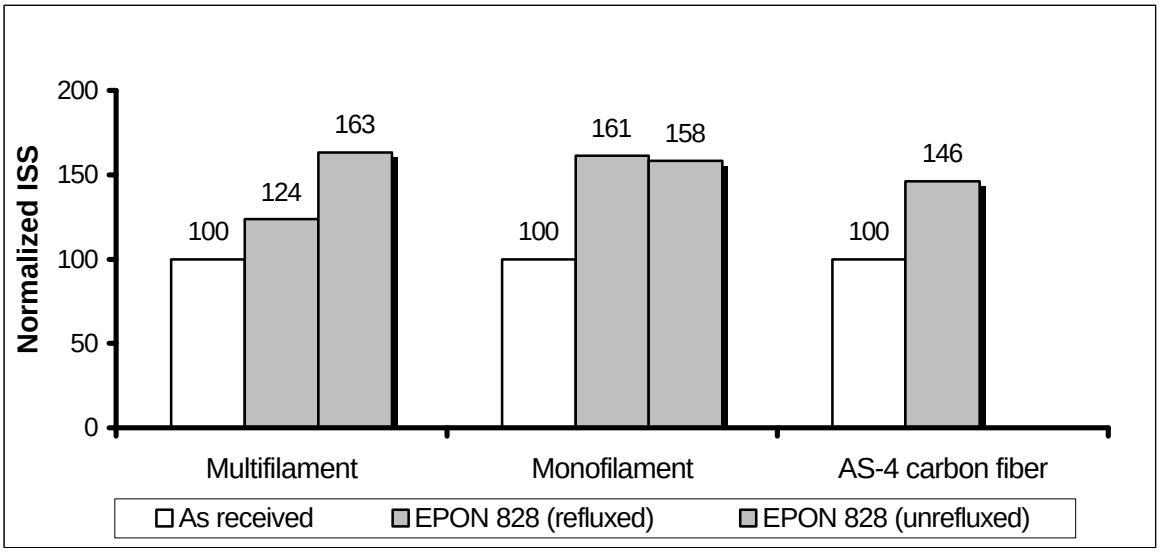
However, after the Technora fiber is exposed to the elevated temperature epoxy treatment, a significant increase in the fiber-matrix interfacial shear strength (ISS) of up to ~60% between the aramid fiber and an amine cured epoxy matrix was measured through use of the single fiber fragmentation test. (Figure 3) Both for the multifilament and monofilament aramid fibers. A similar increase was detected for an AS4 carbon fiber as well. Previously published work has shown that the increase in adhesion to carbon fibers is due to chemical bonding of epoxy to the carboxylic acid and amine groups present on the fiber surface [5].

Table 1: Effect of Elevated Epoxy Temperature Treatment on Tensile Strength of Technora Fiber

Fiber	*Treatment*	*Tensile Strength (GPa)*	*Retention of Tensile Strength (%)*
Multifilament	Mono-epoxy	3.95	101
	Epon 828	3.90	100
	As-Received	3.90	100
Monofilament	Mono-epoxy	2.84	101
	Epon 828	2.81	100
	As-Received	2.81	100

A possible cause for this improvement in adhesion to the aramid fiber is also the chemical bonding of the epoxy group to the aramid fibers surface.

Fig. 3: Effect of Elevated Temperature Treatment on Interfacial Shear Strength of Technora Fiber to Amine cured Epoxy Matrix



The aramid fiber surface has an entirely different chemistry than carbon fibers but reactions between polymer chain amine end groups and mid-chain surface amide groups with epoxy are possible. (Figure 4) In order to determine if chemical bonding between the epoxy group and the aramid fiber surface was responsible for this increase in adhesion, the fibers were treated in both monofunctional and difunctional epoxy. All samples were refluxed in acetone after the 240^{o}C treatment to remove any excess epoxy. XPS analysis was conducted on the treated fiber surfaces. Samples were then cast in a stoichiometric mixture of Epon 828 with meta-phenylene diamine and the ISS was measured with the single fiber fragmentation test.

Fig. 4: Possible Chemical Reactions Between Epoxy Resin and Aramid Fiber Surface

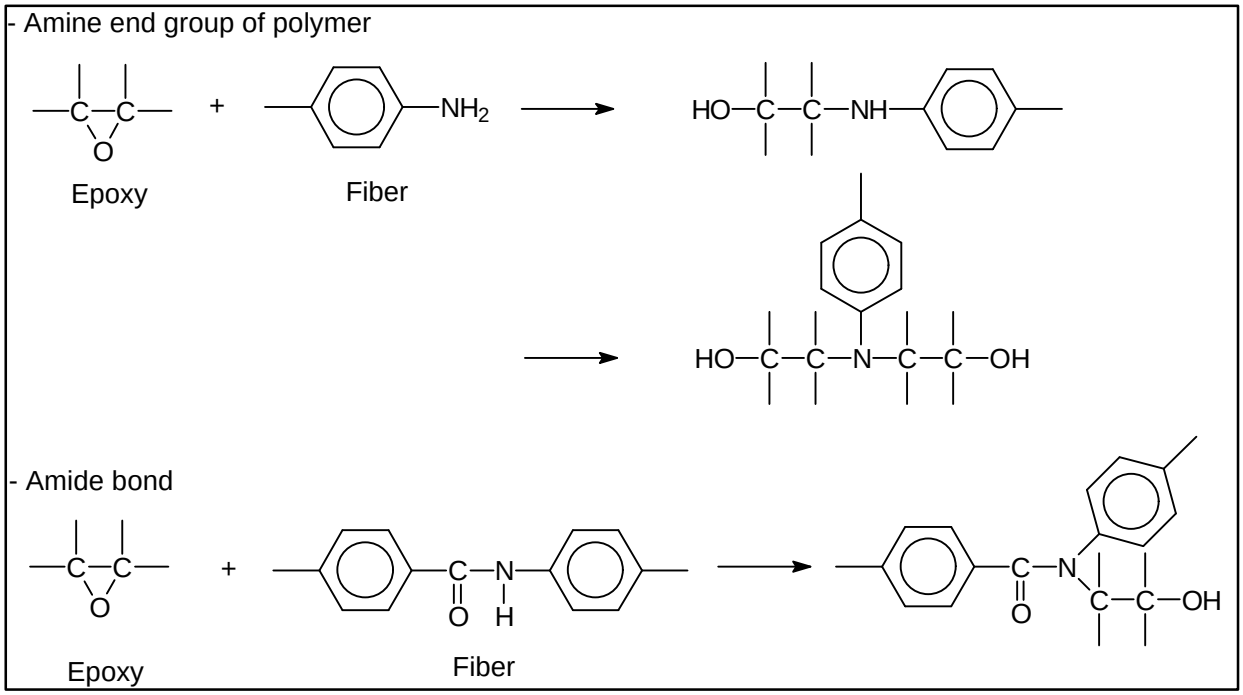
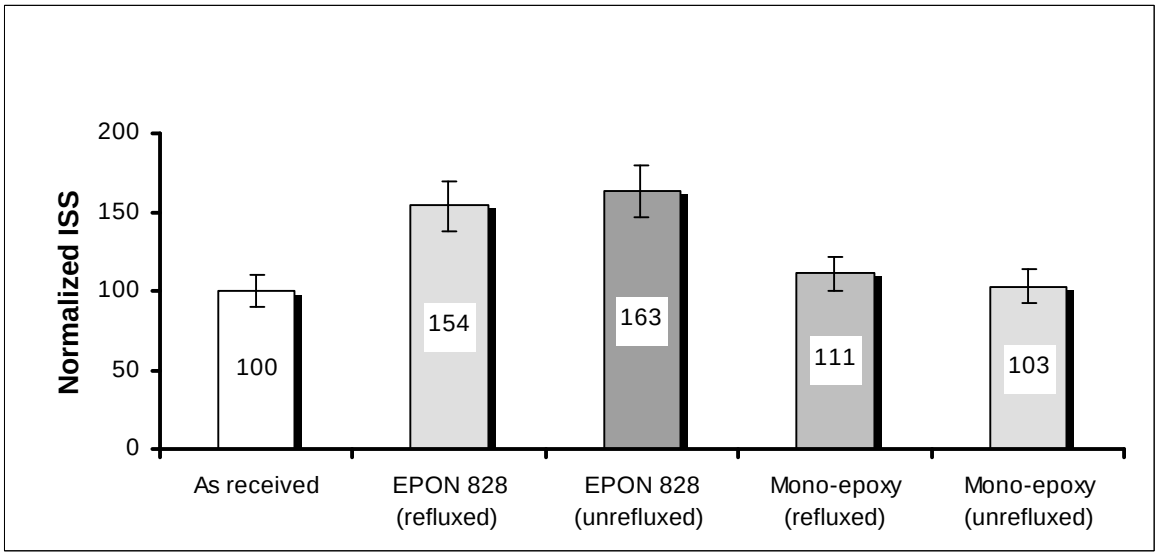
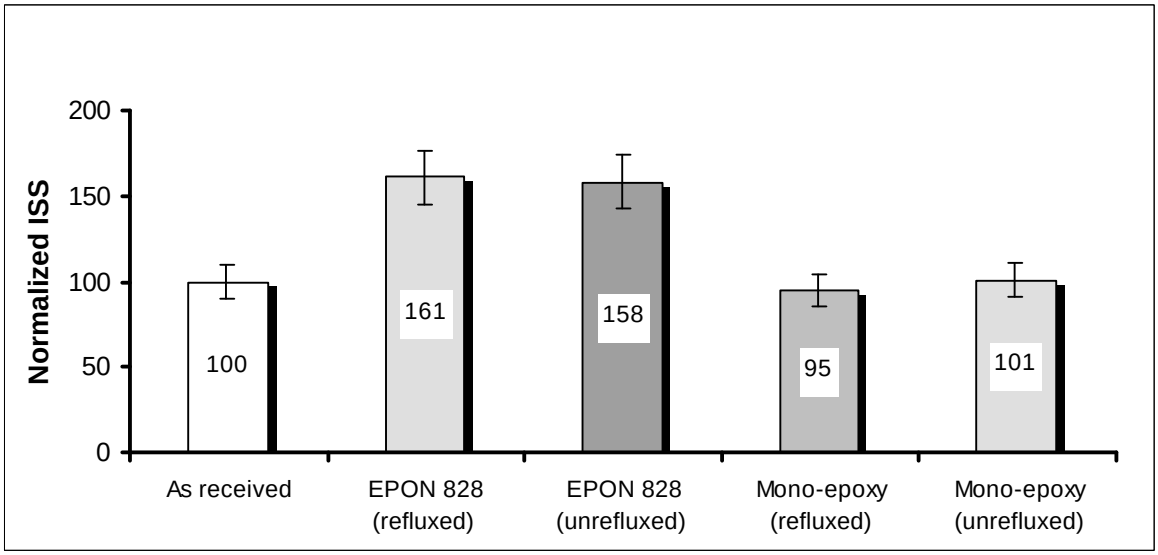


Fig. 5: Interfacial Shear Strength of Technora Fiber after Treatment with Difunctional and Monofunctional Epoxy Resin.



The ISS results (Figure 5) indicated that Technora™ fiber-epoxy adhesion had increased 60% after the 240°C exposure to difunctional epoxy when compared to the as-received baseline fiber. In addition, there was no detectable change in adhesion for the Technora fibers treated in the monofunctional epoxy compared to the 'as- received'. Refluxing of the fiber with acetone did not reduce the ISS indicating that the epoxy was chemisorbed to the aramid fiber surface. This same result was obtained for both the multifilament and the monofilament fibers (Figure 6). Overall these results appear to support the conclusion that epoxy groups are chemisorbed to the fiber surface and can not be removed by solvent reflux. Apparently only one epoxy group from each of the difunctional epoxies reacts with the aramid fiber surface allowing the other reactive epoxy group to react into the amine-epoxy matrix subsequently when the fiber is fabricated into coupons.

Fig. 6: Interfacial Shear Strength of Technora Monofilament after Treatment with Difunctional and Monofunctional Epoxy Resin.



It has been reported that the molecular weight of polymers that are grafted to the fiber surface play a role in increasing adhesion. In particular, the efficacy of grafted chains would increase with molecular weight. The effect of epoxy oligomer chain length was investigated by repeating the high temperature treatment with various difunctional epoxies (Figure 2) having either longer chain length of possessing a multifunctionality grater than two. DER 661 (Mw 1050) DER 667 (Mw 3600)and DEN 431 (4 epoxy rings/molecule) were used to treat the Technora fiber surface by immersion in these epoxy resins at elevated temperature and under the same conditions as used previously.

Fig. 7: Effect of Increasing Molecular Weight and Functionality of Interfacial Shear Strength of Technora Fiber to Epoxy Resin.

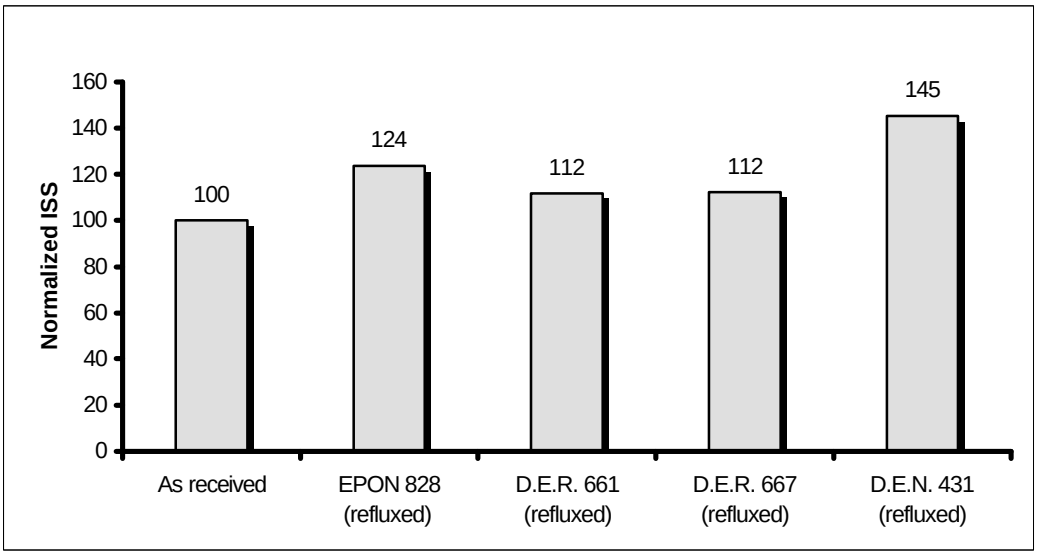
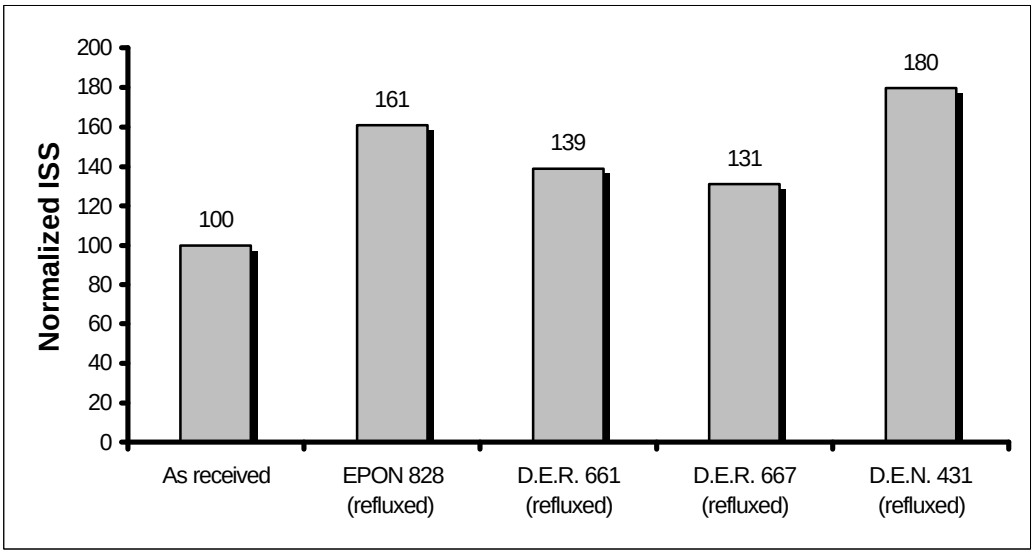
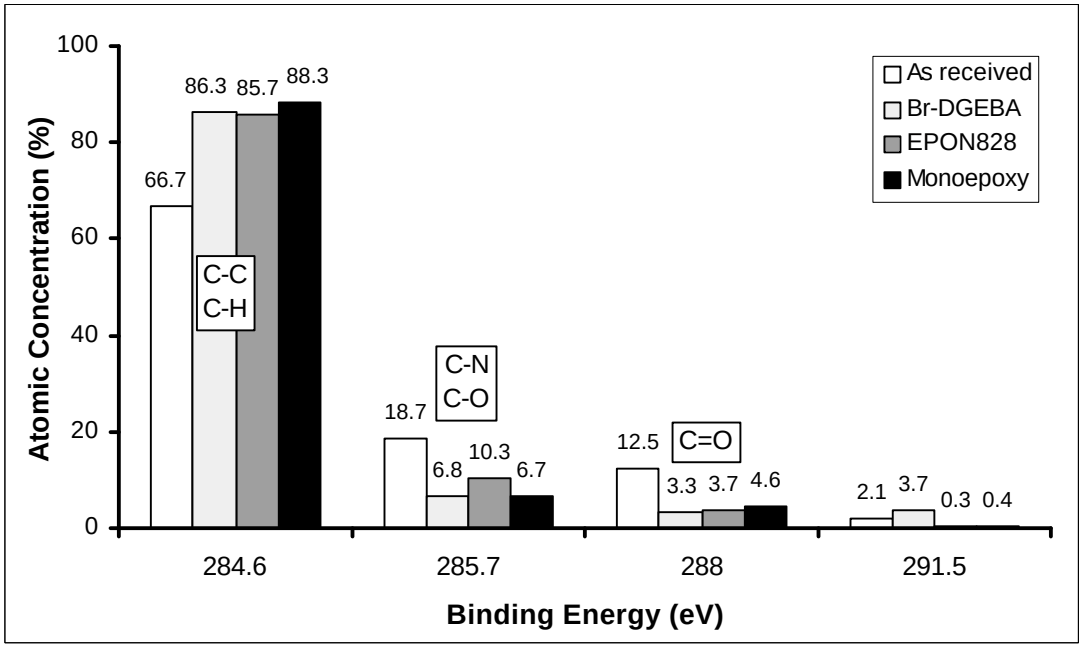


Fig. 8: Effect of Increasing Molecular Weight and Functionality on Interfacial Shear Strength of Monofilament Technora Fiber to Epoxy Resin.



Single fiber fragmentation coupons were fabricated and the adhesion was measured between the treated aramid fiber surfaces and an amine cured epoxy in an identical manner to that described previously. Increasing the epoxy oligomer length from DER 661 (Mw 1050) to DER 667 (Mw 3600) did not produce an increase in adhesion over the Epon 828 (Mw~380) treated fibers (Figure 7). Indeed, for both the monofilament and multifilament fibers, the adhesion was actually less for the longer oligomers than for the shorter difunctional Epon 828 epoxy (Figure 8). However, when the multifunctional epoxy (DEN431) was chemisorbed to the aramid fiber surface, adhesion was increased to a level greater than for the difunctional epoxy (Epon 828). (Figures 7 & 8). It can be speculated that the higher molecular weight difunctional epoxies were less effective at increasing adhesion perhaps due to their ability to loop around and react with a second sites on the aramid fiber surface., making them much less effective than the shorter length difunctional epoxy.

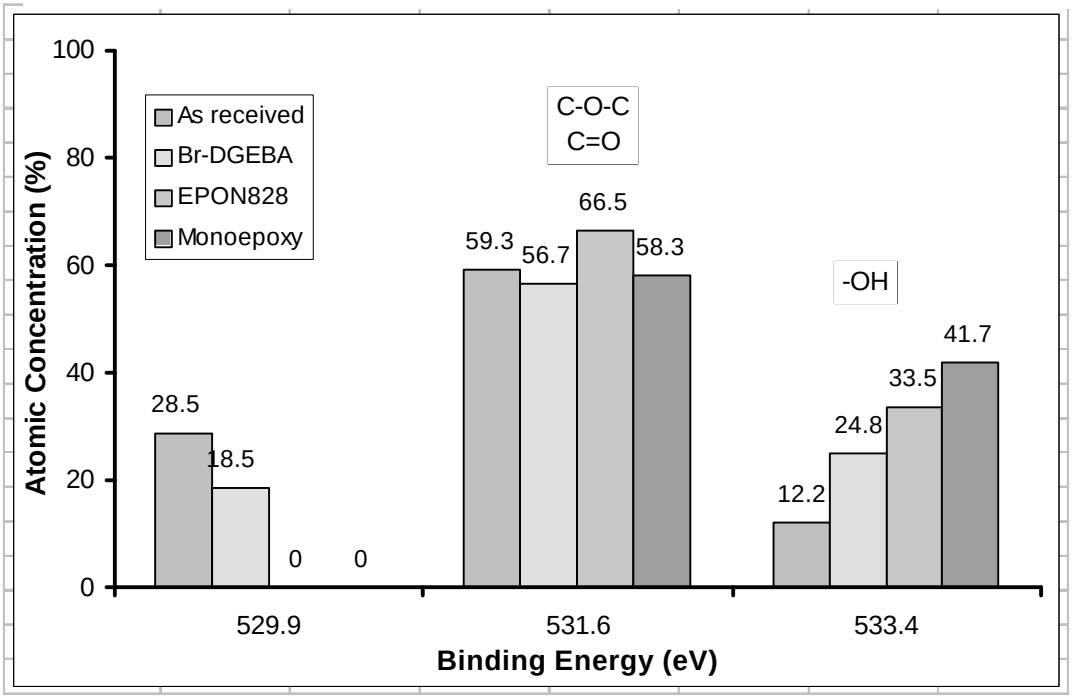
Fig. 9: Carbon 1s XPS Spectra of Technora Monofilament Fiber Before and After Elevated Temperature Epoxy Treatments.



Surface analysis of the Technora fiber surface after the elevated temperature epoxy treatments by XPS showed that chemisorption of epoxy did take place on the Technora fiber surface. Indeed, it appears that the amount of chemisorbed epoxy remained approximately the same for all of the epoxy resins that were used in the Technora fiber pretreatments. An increase in carbon associated with the epoxy groups is detected for both di- and monofunctional epoxy as shown in Figure 9. Deconvolution of the C1s peak area in Figure 9 shows an increase in the C-H concentration on the fiber surface as expected for epoxy which was chemisorbed to the fiber surface. Further confirmation is obtained by deconvoluting the O1s peak area (Figure 10). A definite detectable increase in hydroxyl groups is detected which is attributable to the hydroxyl created when the epoxy reacts with the surface amine or amide group. Chemical grafting to aramid fiber surfaces has been reported previously [6] but not for the epoxy reaction. Previous citations have not detected reaction between epoxy and aramid because composite processing temperatures have been below 125^{o}C [7].

In reviewing the positive results of the elevated temperature epoxy treatments on adhesion, a question arises as to the maximum improvement that can be expected. Based on the surface concentration of epoxy groups, calculations were made of the fiber surface area that was covered by the chemisorbed epoxy molecules both in a surface parallel or surface perpendicular conformation. XPS results lead to the determination of approximately 2-4 epoxy molecules per aramid segment for the Epon 828 difunctional epoxy as a result of this 240^{o}C treatment. The higher molecular weight oligomers have a lower density of attachment to the aramid surface because of their greater size.

Fig. 10: Oxygen 1s XPS Spectra of Technora Monofilament Fiber Before and After Elevated Temperature Epoxy Treatments.



This is slightly less than the theoretical close packed density of 4 epoxy molecules per aramid segment and helps explain why the higher molecular weight oligomers are not as effective in increasing adhesion.

CONCLUSIONS

As a result of this study, the following conclusions can be made:

- Elevated temperature treatment (240^{o}C) of aramid (Technora) fibers with difunctional epoxy oligomers increases adhesion to amine cured epoxy matrices by up to 60%.
- Aramid fiber structure or tensile strength is not adversely affected by the elevated temperature epoxy treatment to temperatures of 240^{o}C.
- XPS analysis of the treated aramid fiber surfaces has established that chemisorption of epoxy molecules to the aramid fiber surface takes place as a result of the elevated temperature epoxy treatment.
- Treatment of aramid fibers with monofunctional epoxy does not improve the adhesion in a similar manner to the use of difunctional epoxy oligomers. This is further

verification that the presence of a second reactive epoxy group is necessary for chemical interaction with the crosslinking agent on the epoxy matrix.
• Treatment with multifunctional epoxy enhances the adhesion more than difunctional epoxy due to more epoxy rings being available to react with the matrix.

ACKNOWLEDGEMENTS

The authors are grateful to Teijin Limited for financial support and the availability of the Technora multifilament and monofilament fibers used in this study.

REFERENCES

1. Morgan, R. J. and Pruneda, C. O., "The Relationship Between the Physical Structure and the Microscopic Deformation and Failure Processes of Poly (p-phenylene Terephthalamide) Fibers", *J. Polym Sci.Part B,* 21 1757-1775 (1983).
2. Kalantar, J. and Drzal, L. T., "The Bonding Mechanism Of Aramid Fibers To Epoxy Matrices: Part 1: A Review of the Literature" *J. Matr. Sci*., 24 (1990).
3. Takayanagi, M, Ueta, S, Lei, W-Y and Koga, K, "A New Chemical Method of Surface-Treatment of Kevlar Fiber for Composites With Epoxy Resin ", *Polym. J.*, 19, no. 5, pp. 467-474, (1987).
4. Wu, Y. and Tesoro, G. C., "Chemical Modification of Kevlar Fiber Surfaces and of Model Diamides", *J. Applied Polymer Science*, 31, 1041-1059 (1986).
5. Drzal, L. T., Sugiura, N. and Hook, D., "The Polymer Interphase in Composites: Intrinsic Limitations to Adhesion", *Composite Interfaces***,** 4, 337-354 (1997).
6. Chou, R. C. T., Tsai, J. Y. C. and Penn, L. S., "The Effects of Pendent Chains on Adhesion Between Kevlar 29 Fiber and Epoxy Resin", *SAMPE J*. 35, pp. 214-225, (1990).
7. Kalantar, J. and Drzal, L. T., "The Bonding Mechanism of Aramid Fibers to Epoxy Matrices: Part 2: An Experimental Investigation", *J. Matr. Sci*. 25, pp. 4194-4202 (1990).