

# AD-A279 200



## DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

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2. REPORT DATE April 2, 1994		3. REPORT TYPE AND DATES COVERED 1/1/93 - 4/1/94	
4. TITLE AND SUBTITLE Use of Titanate Coupling Agents in Kevlar®/Phenolic Composites		5. FUNDING NUMBERS PE-N0014-91 PR-1274	
6. AUTHOR(S) Nalini Menon, Frank D. Blum, and Lokesh R. Dharani		8. PERFORMING ORGANIZATION REPORT NUMBER UMR-FDB-37	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Missouri-Rolla Department of Chemistry Rolla, MO 65401 ATTN: Frank D. Blum		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research - Code 5000 Chemistry Division 800 Quincy Street Arlington, VA 22217 ATTN: Kenneth J. Wynne		11. SUPPLEMENTARY NOTES For publication in Journal of Applied Polymer Science	
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unlimited - Approved for unlimited public release		12b. DISTRIBUTION CODE	
13. Surface modification of Kevlar® fibers with titanate coupling agents for improved adhesion of the fiber and resin in Kevlar®/phenolic composites has been attempted to explore the possibility of enhancement in adhesion and bulk properties of composites for friction materials. Titanate coupling agents were used and flexural properties of the Kevlar®-fiber reinforced composites determined. A study of different amounts of the coupling agents at the fiber-matrix interface suggested that 2% by weight of fiber was the optimum amount, in terms of improvement in flexural properties. The composite samples with the coupling agents, showed an increase in flexural strength, over the untreated samples with the maximum increase being ~18% over the control. Water absorption studies were conducted on Kevlar®/phenolic composites treated with organotitanates to determine the effectiveness of these coupling agents in improving resistance to moisture attack. The treated Kevlar®/phenolic composite samples exhibited greater resistance to moisture-ingress over the untreated samples. The control samples showed a decrease of 17% in flexural strength. The largest decrease in strength was 14% for the treated samples containing coupling agent tetrakis(2-ethylhexyl)titanate (TYZOR TOT). Recovery in strength on reconditioning, was also greater for treated samples over control. A recovery in strength of ca. 94% was seen for some treated samples.			
14. SUBJECT TERMS coupling agents, composites, Kevlar, interfaces, mechanical properties		15. NUMBER OF PAGES 27	
17. SECURITY CLASSIFICATION OF REPORT Unclassified		16. PRICE CODE	
18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		20. LIMITATION OF ABSTRACT	
19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified			

**DTIC  
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OFFICE OF NAVAL RESEARCH

Grant N00014-91-J-1274

R&T Code 413m005---04

Technical Report # UMR-FDB-37

Use of Titanate Coupling Agents  
in Kevlar®/Phenolic Composites

by

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94-14269



Prepared for Publication in

*Journal of Applied Polymer Science*

April 2, 1994

Accession For	
NTIS	CRA&I <input checked="" type="checkbox"/>
DTIC	TAB <input checked="" type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification .....	
By .....	
Distribution /	
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### Synopsis

Surface modification of Kevlar® fibers with titanate coupling agents for improved adhesion of the fiber and resin in Kevlar®/phenolic composites has been attempted to explore the possibility of enhancement in adhesion and bulk properties of composites for friction materials. Titanate coupling agents were used and flexural properties of the Kevlar®-fiber reinforced composites determined. A study of different amounts of the coupling agents at the fiber-matrix interface suggested that 2% by weight of fiber was the optimum amount, in terms of improvement in flexural properties. The composite samples with the coupling agents, showed an increase in flexural strength, over the untreated samples with the maximum increase being ~18% over the control. Water absorption studies were conducted on Kevlar®/phenolic composites treated with organotitanates to determine the effectiveness of these coupling agents in improving resistance to moisture attack. The treated Kevlar®/phenolic composite samples exhibited greater resistance to moisture-ingress over the untreated samples. The control samples showed a decrease of 17% in flexural strength. The largest decrease in strength was 14% for the treated samples containing coupling agent tetrakis(2-ethylhexyl)titanate (TYZOR TOT). Recovery in strength on reconditioning, was also greater for treated samples over control. A recovery in strength of *ca.* 94% was seen for some treated samples.

## INTRODUCTION

In discontinuous fiber-reinforced composites, the fiber-matrix interface plays an important role in determining the mechanical properties. At the interface, load transfer from the matrix to the fiber takes place. This load transfer mechanism is dependent to a great extent on the fiber-to-matrix adhesion. Polyaramid fibers, such as Kevlar<sup>®</sup>, can have strengths, toughness, and densities that make them very attractive for use in composites. However, the interface between polyaramids and resin matrices usually do not attain the level of adhesion reached by other fiber-resin systems.

Recently a review of bonding mechanisms at the interface in aramid-epoxy composites has been published. [1] The most important mechanisms affecting interfacial adhesion were believed to be mechanical stresses, chemical interactions, and physico-chemical weak boundary layers. Chemical interactions involve covalent bonding and fiber-matrix wetting. Modification of the fiber surface to improve adhesion has become increasingly important in the recent years. [2, 3] The use of coupling agents to improve the interaction between the matrix and the reinforcing fiber, thereby enhancing the load carrying capabilities of the composite, is also of importance. Amongst the several existing theories that account for the adhesion promoting ability of coupling agents, the most widely accepted theory is that of chemical bonding. [4,5] According to this theory, coupling agents act as molecular bridges between the fiber and the organic matrix. The resulting covalent bonds contribute to improved adhesion and thus, the bulk properties of the composite.

In order to utilize fiber reinforced composites to their fullest potential, the performance characteristics of the materials during their entire service life must be known. This includes the changes in the mechanical, physical, thermal, and chemical properties of the material caused by exposure to moisture and elevated temperatures. Comparative studies on different theories on water absorption have been conducted. [6] Some of the factors that are important with respect to the water resistance of composites to water are time of contact, nature and magnitude of working stress, geometrical organization of the fiber, chemical treatment and the chemical nature of the fibers and the polymer matrix. Absorption of water followed by rapid heating has shown to severely degrade the performance of advanced composites such as graphite and boron reinforced

epoxies. [7] Depression of the glass transition temperature of the matrix to below service temperatures by the absorbed water, is believed to be the primary degradation mechanism in these composites. [8]

The current work is focused on the role of titanate coupling agents in improving the mechanical properties of Kevlar<sup>®</sup>/phenolic composites. The titanates studied are surface-active and also may contribute to convenient material handling. These have been labelled "pseudo coupling agents" [9] because they may not provide water-resistant bonds and, therefore, no true adhesion to the substrate under wet conditions. This hypothesis was examined, by treating Kevlar<sup>®</sup> pulp with different organotitanates and also a organozirconate, and studying the effect of the coupling agents on flexural properties of the Kevlar<sup>®</sup>/phenolic system. A few studies of titanate coupling agents and their use in composites have been reported. [10-12] These have demonstrated modest gains in strength with changes in the interface. The method of treatment of the fiber with the coupling agents, has been verified by simple estimation techniques using FT-IR and also by ESCA and SEM. The composite materials treated with coupling agents were tested for mechanical properties such as flexural strength and modulus. The effectiveness of the titanates, in providing resistance to deterioration in mechanical properties of the Kevlar<sup>®</sup>/phenolic composites on exposure to moisture, has also been investigated. The vulnerability of composites to moisture-attack and temperature; rather than for any anticipated significant improvement in mechanical properties was the motivation for the testing of the moisture sensitivity.

## EXPERIMENTAL

### Materials and Sample Preparation

Kevlar®-29 pulp (duPont Corp., Wilmington, DE) was used in this study. These short, 400 denier fibers were received with the sizing removed and used directly as supplied. The resin used is a cashew modified free-flowing phenol-formaldehyde resin (NC-126, Cardolite Corp., Newark, NJ), shown in figure 1, which contains 5% added curing agent, hexamethylenetetramine (HEXA). Five different coupling agents were employed in the study. They are: tetra-*n*-butyltitanate (TYZOR TBT); tetra-*i*-propyltitanate (TYZOR TPT); *i*-propoxy(triethanolaminate)titanium (TYZOR TE); tetrakis(2-ethylhexyl)titanate (TYZOR TOT); and a mixture of alkanolamine chelates of zirconium (TYZOR 212 Crosslinker). The idealized structures of the coupling agents are shown in figure 2. Solvents such as isopropanol, 1-butanol, 2-propanol, 2-ethylhexanol were added, as appropriate, to the coupling agent under study. The physical properties of the coupling agents are shown in Table I.

Weighed samples of Kevlar® pulp (5% by weight of the composite) were treated with 2%, 5% and 8% (w/w) of coupling agent in solution. A few were also treated with less. The fibers were kept immersed in the coupling agent solution for 24 hours, during which they were shaken. The treated fibers were washed with solvent to remove excess untreated coupling agent and then dried for 24 hours at room temperature. The dried fibers were stored in a desiccator, away from sunlight, until they were ready to be used. The same treatment was used for all the coupling agents.

The treated Kevlar® was mixed with the appropriate amount of the resin (95% by weight of the composite) and dry blended in a commercial lab-scale blender. Thorough dispersion and good wetting of fiber by resin was ensured by employing long blending times. The mixture, obtained after blending, was then compression molded in a hydraulic hot press using a steel mold which had a 150 mm x 150 mm x 3 mm cavity. This was done at a temperature of 160 °C and a pressure of 3.33 MPa for a curing period of 15 minutes. The heating and applied pressure were discontinued at the end of the curing period. The specimen was allowed to cool down to room

temperature and the sample post-cured in an air-oven at 160 °C for two hours. This process seemed to be optimum with respect to the cure temperature, volume of the batch, absence of any voids or warpage in the sample, and reproducibility of results. Samples of composite with untreated fibers were prepared in a similar fashion for comparison.

### Testing

The water absorption studies on Kevlar®/phenolic composites were based on ASTM test methods. [13] Sample plates of Kevlar®/phenolic composites with the fibers treated with 2% (w/w) coupling agents were fabricated as described earlier in this paper. Specimens 76 mm long by 25 mm wide and 3 mm thick were cut and the edges carefully smoothed using a standard 100-grit sandpaper. The two hour boil test was adopted. [13] The test specimens were conditioned by drying in an oven for two hours at 110 °C. The conditioned specimens were weighed before immersion in distilled water for the test. At the end of the boiling water test, the specimens were cooled to room temperature in distilled water for fifteen minutes, wiped dry, and weighed immediately. The percentage increase in weight during immersion was calculated from:

$$\text{Percent increase in weight} = \frac{[\text{Wet weight} - \text{Conditioned weight}] * 100}{[\text{Conditioned weight}]} \quad (1)$$

For specimens whose recovery in flexural strength was to be measured after being subjected to the water absorption, reconditioning was done by drying the samples at 110 °C for two hours. Samples of composites with untreated Kevlar® were subjected to identical water absorption tests.

The hot pressed composite plates were cut into specimens 76 mm long and 25 mm wide using a band saw. All the samples were molded to 3 mm thickness. The edges of the specimens were finished with standard 100-grit sandpaper, with utmost care to prevent excessive abrasion of the material. These were then tested for flexural properties by performing a three point bend test, based on the ASTM standard D790-86. [14] The flexural strength (MPa),  $S$ , was determined from the maximum load  $P$  (Newtons) before break and calculated from: [14]

$$S = 3PL/(2bd^2) \quad (2)$$

where  $L$  is the support span (mm), and  $b$ , and  $d$  the width (mm) and the thickness (mm) of the specimen.

The tangent modulus of the elasticity, the ratio within the elastic limit of stress to corresponding strain, is determined from the slope of the tangent of the initial straight-line portion of the load-deflection curve as [14]:

$$E_B = L^3 m / 4bd^3 \quad (3)$$

where  $E_B$  is the modulus of elasticity in bending (MPa), and  $m$  is the slope (N/mm) of the tangent to the initial straight-line portion of the load-deflection curve. The testing was done on a Material Testing System (MTS - 810 system). A loading rate of 1.27 mm/min was used for the test. At least, five specimens from each sample plate were tested.

Electron Spectroscopy for Chemical Analysis (ESCA) runs were carried out on treated and untreated Kevlar<sup>®</sup> fiber samples, using a Perkin-Elmer Physical Electronics instrument. Kevlar<sup>®</sup> fibers were treated with an 8% solution of the coupling agent, TYZOR TPT in isopropanol. ESCA runs were used to verify the presence of the coupling agent, in the bound state on the treated fiber. Scanning Electron Microscopy (SEM) of the treated and the untreated fibers were obtained using a JEOL 35 CF instrument. SEMs of the untreated Kevlar<sup>®</sup> pulp and Kevlar<sup>®</sup> pulp treated with 5% solution of the coupling agent, TYZOR TBT were acquired. The structures of the coupling agents used were verified by infra-red spectroscopy (FT-IR) and nuclear magnetic resonance (NMR). The amount of the coupling agent bound to the surface of the fiber was done based on a method suggested by Blum, et al. [15]. Solutions of various concentrations of the coupling agent, TYZOR TBT, in 1-butanol were prepared for this purpose. Data from the above studies suggested that about 91% of the coupling agent remained on the fiber as a result of the treatment.



## RESULTS AND DISCUSSION

### Untreated Fiber Systems

In order to determine baseline behavior for the coupling agent containing systems the effect of loading levels of fiber was studied. Different levels of fiber-loading, starting from 5% to 15% (by weight of the composite) were attempted. For each level of fiber-loading, six to eight specimens were tested from a single panel and at least, two panels were used in each case. This was done to determine the repeatability of the measurements. Figure 3 gives the experimental results for the flexural properties of the neat resin (unfilled) samples and samples of aramid-filled phenolic composites. The error bars shown are for  $\pm 1$  standard deviation. The flexural strength values for the neat resin NC-126, falls within the reported literature range for phenolic resins of 83-103 MPa. [16] A comparison of the flexural properties of neat resin to those of the composites reinforced with 5% (w/w) of Kevlar<sup>®</sup>, yielded a reduction in strength of about 22%. This is as expected, due to the presence of a weak interface, the formation of microcracks at the interface or in the matrix, and increased stress-concentration effects in the composite due to the introduction of the fiber. [17] A rough calculation [17] of the critical fiber volume fraction,  $V_{crit}$  yields about 2.6%. This is within the range of the minimum found here, but these fibers are typically shorter than that corresponding to the critical fiber aspect ratio (*ca.* 160). An increase in the level of loading of untreated fiber from 5% (w/w) to 15% (w/w) in the composite, shows an increase in the flexural strength values. The increase in going from 5% to 15% is probably due to the fact that an increase in fiber volume fraction means much more load carrying capacity. Beyond a fiber loading of 15%, there is a lack of good dispersion of the fiber (as was visible to the naked eye) and fiber wetting appeared poor, although there are other methods of achieving better dispersion at these levels. The flexural modulus increases slightly with increasing fiber content.

A similar study, based on the effect of variation of fiber content in Kevlar<sup>®</sup>/phenolic composites, has been reported [18,19]. In that study, introduction of fiber into the neat phenolic resin has been reported to decrease the flexural strength of the latter, similar to our observations here. Also, on increasing the fiber-loading from 5% through 10% to 15% (w/w), the authors have

found steady improvement in the flexural strength values of the composite. However, the previous values for the flexural strength of the composite in [18,19] seem to be slightly lower (10-20%) than those in figure 3 for an equivalent amount of fiber. Factors such as: the mixing time, fiber size, shape, and orientation after mixing; wetting of the fiber by the resin; and the properties of the fiber and the resin such as polarity, thermal and mechanical stability [20] influence the effectiveness of a particular mixing/dispersion process. Variations in any, possibly all, of the above factors could result in the discrepancy between these two sets of values.

On the basis of these preliminary studies, it was decided that 5% (by weight of composite) would be an appropriate level of fiber in the Kevlar®/phenolic system. Factors such as handleability, good dispersion of fibers in the matrix and maintenance of extremely low levels of moisture-content in the composite (aramids are highly hygroscopic) contributed to the selection of this loading level. This level of fiber-loading is also similar to the typical quantity of fiber commonly used in the friction materials industry today.

#### **Organotitanate-Treated Fiber Systems**

The primary chemical structure of the coupling agents was verified using FT-IR and, proton and carbon NMR. Some of the samples were shown to be mixtures of closely related compounds. In order to verify the presence of coupling agent on the fiber, ESCA was used. The ESCA spectra of samples treated with TYZOR TBT and untreated fiber samples are shown in figure 4a and 4b. For the treated sample, the additional peaks at 450, 454, 575, and 880 eV correspond to the titanium. A detailed study of the carbon 1s region for possible reaction product differences, such as that done for treatment with oxalychloride, [21] was not necessary because the titanium resonance was sufficient for the confirmation of the presence of the TYZOR TBT on Kevlar®.

Scanning electron micrographs of the untreated Kevlar® pulp and Kevlar® pulp treated with 5% solution of TYZOR TBT are shown in figure 5. The treatment procedure seemed to increase the surface roughness, leaving a more uneven contour and fewer broad smooth fibers. This is partially observed by comparing the SEM's at x1000 magnification in figure 5a and 5b. The SEM's at higher magnification, figure 5c and 5d, display several patches of torn filaments and

internal splits in the treated fiber. These contrast the smoother and more rod-like appearance of the untreated fiber. The chemical treatment has modified the fiber, causing its surface to fibrillate as seen in the micrographs. The role of the solvent in this process has not been studied. A similar effect on roughness was observed for Kevlar<sup>®</sup> treated with methacryoyl chloride [22].

The experimental values of the flexural strengths for 2%, 5% and 8% (wt. coupling agent/wt. fiber) and flexural moduli for 2% levels of each coupling agent on 5% Kevlar<sup>®</sup> pulp/95% (w/w) resin are shown in Tables II and III. From the experimental values for the flexural strength, the 2% level of coupling agent showed the maximum increase, over the untreated composite. Limited studies at lower amounts of coupling agent (ca. 1%) showed poorer properties. Also, the moduli of these composites did not seem to change much due to the treatment with the coupling agents, in fact there was a slight decrease with the coupling agent addition. Figure 6 shows the variation of flexural properties of composites treated with 2% (wt. coupling agent/wt. fiber) of the different coupling agents. An increase in the amount of coupling agent at the fiber-matrix interface has not resulted in an increase of strength, as seen for the 5% and the 8% levels of titanates and zirconate. In order to confirm the findings for these levels of treatment, the experiments were repeated under conditions as identical as possible. These two batches were found to be reproducible to within 15%.

A possible explanation for the above gradation in flexural strength values can be based on the mechanism of cross-linking action of the organotitanates between fiber and polymer matrix and also on the chemical reactivities of the coupling agent molecules with respect to the polymer-fiber interface. Considering the chemical reaction of the fiber/matrix interface with coupling agent (as assumed by the chemical bonding theory of coupling agents), the filler properties, polymer matrix properties, titanate properties, mechanism of coupling, and the method of application of the coupling agent will be highly critical. For the same fiber, matrix and method of application, only variables such as properties of the titanate and the mechanism of coupling control the role of the coupling agent at the interface. Consequently, the alkoxy or chelate nature of the coupling agent and the binding groups on the molecule are most significant. [23-26]

### Water Absorption Studies

In Kevlar®/phenolic composite systems, the influence of moisture is significant because the filament is hygroscopic. Studies have indicated that Kevlar® fibers are degraded by moisture at room temperature and that the degradation is enhanced at higher temperatures. [27] The phenolic matrix on the other hand, only absorbs about 0.1-0.2 % over a 24 hour absorption period. [16] The attack of moisture on the phenolic matrix and Kevlar® fiber during a 24 hour immersion test or a 2 hour boiling water test would be significant with respect to the degradation in mechanical properties. The effects of temperature and moisture on the flexural properties of composites, is perhaps greater than for any other mechanical properties. This is because the bending test is much more sensitive to moisture attack than tensile tests. [28] For example, in most molded sheet applications, failure due to bending seems more critical than other modes.

Coupling agents should protect the interface from hydrolytic deterioration. Hence, the coupling agents should provide water resistant bonds at the interface. In the case of titanate coupling agents, the tendency to polymerize and form -Ti-O-Ti-O- linkages can lead to enhanced resistance to moisture in systems in which they have been applied. The alkoxide titanates are highly sensitive to moisture and tend to hydrolyze very quickly. The chelates, on the other hand, are claimed to be hydrolytically stable and have greater affinity for filler protons, rather than for water molecules. [29]

The objective of the water absorption studies was to evaluate the effectiveness of the different titanate coupling agents against moisture-attack. Flexural properties of the samples were measured after they were subjected to water absorption tests. Figure 7 shows a plot of the variation in flexural strength of treated and control samples for the different stages of the 2-hour boil test.

For a composite material exposed to an environment in which the temperature and moisture levels vary with time in a prescribed manner, parameters such as the temperature, total mass of moisture and moisture- and temperature-induced (hygrothermal) stresses inside the material, and the dimensional changes of the material as a function of time are of importance. The temperature and moisture distributions inside the composite can be readily calculated when moisture penetrates

into the material by "Fickian" diffusion. The diffusion in the untreated Kevlar®/phenolic composites has been determined to be Fickian. [30] The nature of the diffusion process in the treated composites has not been studied. However, it is known that moisture absorption, in many polymers, lowers the glass transition temperature; the absorbed water acts as a plasticizer, lowering the stiffness, hardness and other mechanical properties of the material. [31]

It is clear from figure 7 that the strength of control or treated samples, decreases on exposure to water. The percentage water gain, calculated for each of the samples using equation (1), was found to be *ca.* 0.7 % for all the samples. The test conditions (2 hour boil test) for the samples were kept as identical as possible. The treated samples show a smaller reduction in strength when compared to the control. For the samples treated with coupling agents, TYZOR TPT, 212, TBT, and TE, the decrease in flexural strength is  $\leq 10\%$ ; while the control samples show a decrease of 17%. It should be noted that the dry samples were tested as fabricated. Slight changes in strength from the values shown here, can be expected if these samples were conditioned (postcured at 110 °C and 2 hours) before flexural testing.

Apart from measuring the wet strength of the untreated and the treated composite samples, an effort was made to study the recovery in flexural strength after reconditioning. This was done in order to simulate one complete dry-wet-dry cycle that the material might undergo in actual service conditions. Reconditioning of the composite samples subjected to water absorption tests involved the drying of the specimens in an oven at 110 °C for two hours. Figure 7 also gives the flexural strengths of the reconditioned composite samples. Generally, the flexural strengths of the samples have not fully recovered with the reconditioning process. This could be due to many reasons including: (i) moisture being trapped in the microvoids of the samples, possibly bonded to the interface by some means and therefore, not completely removed during reconditioning; (ii) the reconditioning being insufficient for the complete removal of the moisture from the samples; and, (iii) incomplete reversibility of chemical reactions on that time-scale. However, the treated samples appear to have recovered in strength to a greater extent when compared to the control. Thus, while the exact mechanism of the coupling agent's ability to improve resistance to moisture-ingress is still

unknown, this study has shown that the coupling agents do affect the interface between the fiber and the resin and also provide some moisture resistance to the fiber/matrix interface.

## CONCLUSIONS

The addition of Kevlar® fibers to phenolic resin causes the formation of weak interfaces and results in increased stress-concentration effects, which result in the deterioration of flexural properties. For higher levels of fiber loading, such as 8-15 % by weight, an improvement in the flexural properties was observed as expected, due to the superior load handling capability of the fibers. However, higher levels of fiber-loading also leads to poor dispersion of fibers in the matrix and possible formation of microvoids.

The effect of the organotitanates (alkoxide and chelate) and zirconate (chelate) coupling agents on the flexural properties of Kevlar®/phenolic composites was also studied. It was suggested that *ca.* 2% of coupling agent (by weight of fiber) was the optimum amount, in terms of improvement in flexural properties. The composite samples with the coupling agents showed an increase in flexural strength over the control samples, the maximum increase being *ca.* 18% over the control, which is only a modest increase.

The Kevlar®/phenolic composite samples treated with titanates exhibited greater resistance to moisture-ingress over the untreated composites. The control samples showed a decrease of 17% in flexural strength due to moisture absorption; while the maximum decrease in strength for treated samples was 14% for samples treated with TYZOR TOT. Recovery in strength on reconditioning, was also greater for treated samples over control. Maximum percent recovery in strength of *ca.* 94% was for samples treated with TYZOR 212.

## ACKNOWLEDGEMENTS

We acknowledge the financial and materials support provided by the duPont Corporation, Cardolite Corporation, and the Office of Naval Research for this project. Our thanks are also due to Dr. D. Hoiness of DuPont, Dr. N. Subramaniam of Chemir/Polytech, and Mr. Gopal Padmanabhan of University of Missouri-Rolla whose suggestions and advice were extremely helpful.

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**TABLE I.**  
**Physical Properties of Organic Titanates**

Coupling agent	TYZOR TPT	TYZOR TBT	TYZOR TOT	TYZOR TE	TYZOR 212
Chemical Type	Tetra alkyl titanate	Tetra alkyl titanate	Tetra alkyl titanate	Titanate chelate	Zirconate chelate
Formula Wt.	284	340	565	462	-
Effect of water	Extremely rapid hydrolysis	Very rapid hydrolysis	Rapid hydrolysis	Very slow hydrolysis	Very slow hydrolysis
Typical solvent	2-propanol	1-butanol	2-ethyl- 1-hexanol	2-propanol	1-propanol

Table II.  
Flexural Strengths of Kevlar®-Phenolic Composites  
Treated with Differing Amounts of Coupling Agents

<u>Coupling agent</u>	<u>Flexural Strength (MPa)</u>		
	2% <sup>a</sup>	5% <sup>a</sup>	8% <sup>a</sup>
TYZOR TPT	78.9 ± 2.7	67.0 ± 7.1	88.2 ± 6.1
TYZOR 212	79.1 ± 7.4	61.9 ± 1.5	73.8 ± 4.2
TYZOR TBT	81.3 ± 3.9	60.4 ± 3.9	70.5 ± 3.2
TYZOR TE	83.9 ± 3.6	70.3 ± 4.2	78.6 ± 0.8
TYZOR TOT	86.8 ± 1.8	73.7 ± 4.8	68.5 ± 3.9

<sup>a</sup> amount of coupling agent by weight of fiber.

**Table III.**  
**Flexural Moduli and Moduli of Kevlar®-Phenolic Composites**  
**Treated 2% (W/W) Coupling Agents**

<u>Coupling agent</u>	<u>Flexural Modulus (GPa)</u>
Control	7.9 ± 0.3
TYZOR TPT	6.5 ± 0.1
TYZOR 212	5.8 ± 0.3
TYZOR TBT	7.1 ± 0.2
TYZOR TE	7.0 ± 0.2
TYZOR TOT	7.2 ± 0.2

## Figure Captions

- Figure 1. Idealized structure of NC-126, a cashew-modified phenolic resin.
- Figure 2. Idealized chemical structures of the coupling agents used.
- Figure 3. Variation in flexural strength (■) and modulus (●) of neat resin and Kevlar<sup>®</sup>/phenolic composites with 5%, 8%, 10%, and 15% Kevlar<sup>®</sup> fiber content.
- Figure 4. ESCA spectra of (A) untreated and (B) TYZOR TPT treated Kevlar<sup>®</sup> fibers.
- Figure 5. SEM's of (A and C) untreated and (B and D) TYZOR TPT treated Kevlar<sup>®</sup> fibers at magnifications of x1000 (A and B) and x3000 (C and D). The bar size is 10 μm.
- Figure 6. Flexural strength (■, MPa) and moduli (●, GPa) for Kevlar<sup>®</sup>/phenolic composites treated with 2% (w/w) of titanate and zirconate coupling agents. Note: Control samples are untreated; and TPT, TBT, and TOT are titanate alkoxides, while TE is a titanate chelate; 212 is a zirconate chelate.
- Figure 7. Plot showing the variation in flexural strength (MPa) values for Kevlar<sup>®</sup>/phenolic composites subjected to moisture. (■) Dry, as fabricated; (●) Wet, after the 2 hour boil test; and (▲) Reconditioned, dried at 110 °C and for 2 hours, after 2 hour boil test. The control samples are untreated.

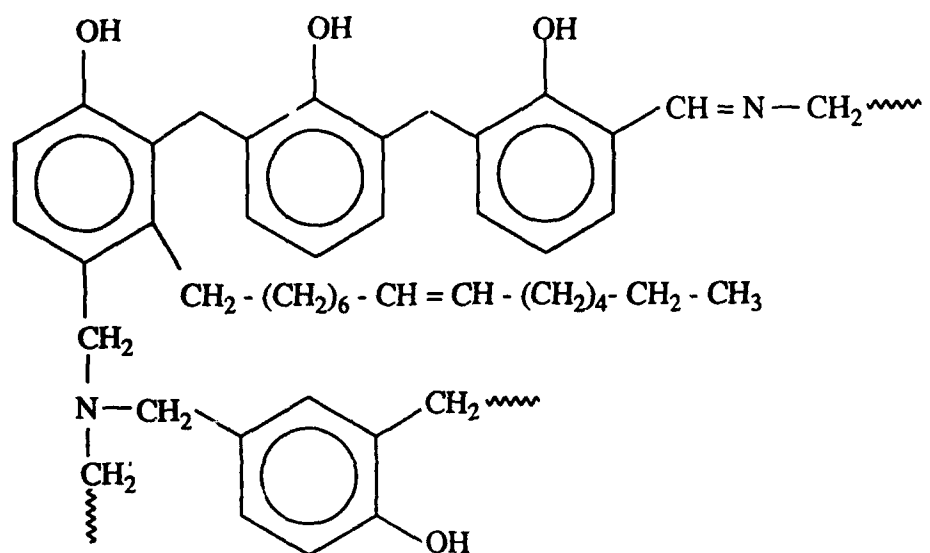


Figure 1. Idealized structure of NC-126, a cashew-modified phenolic resin.

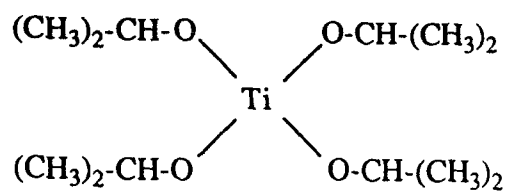
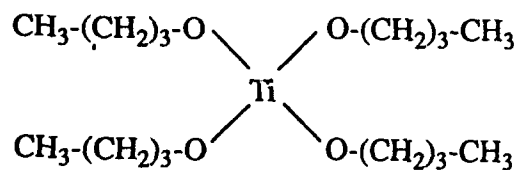
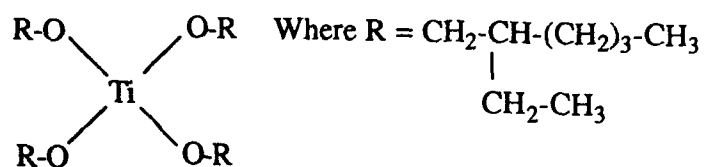
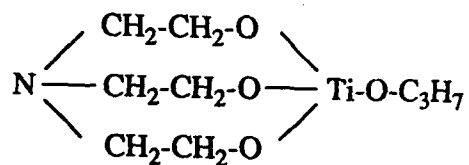
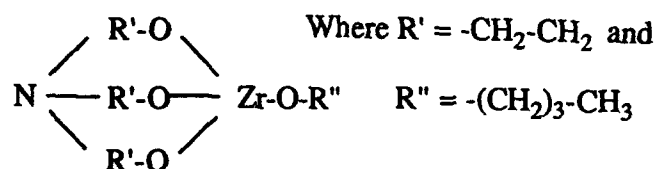
**TYZOR TPT****TYZOR TBT****TYZOR TOT****TYZOR TE****TYZOR 212**

Figure 2. Idealized chemical structures of the coupling agents used.

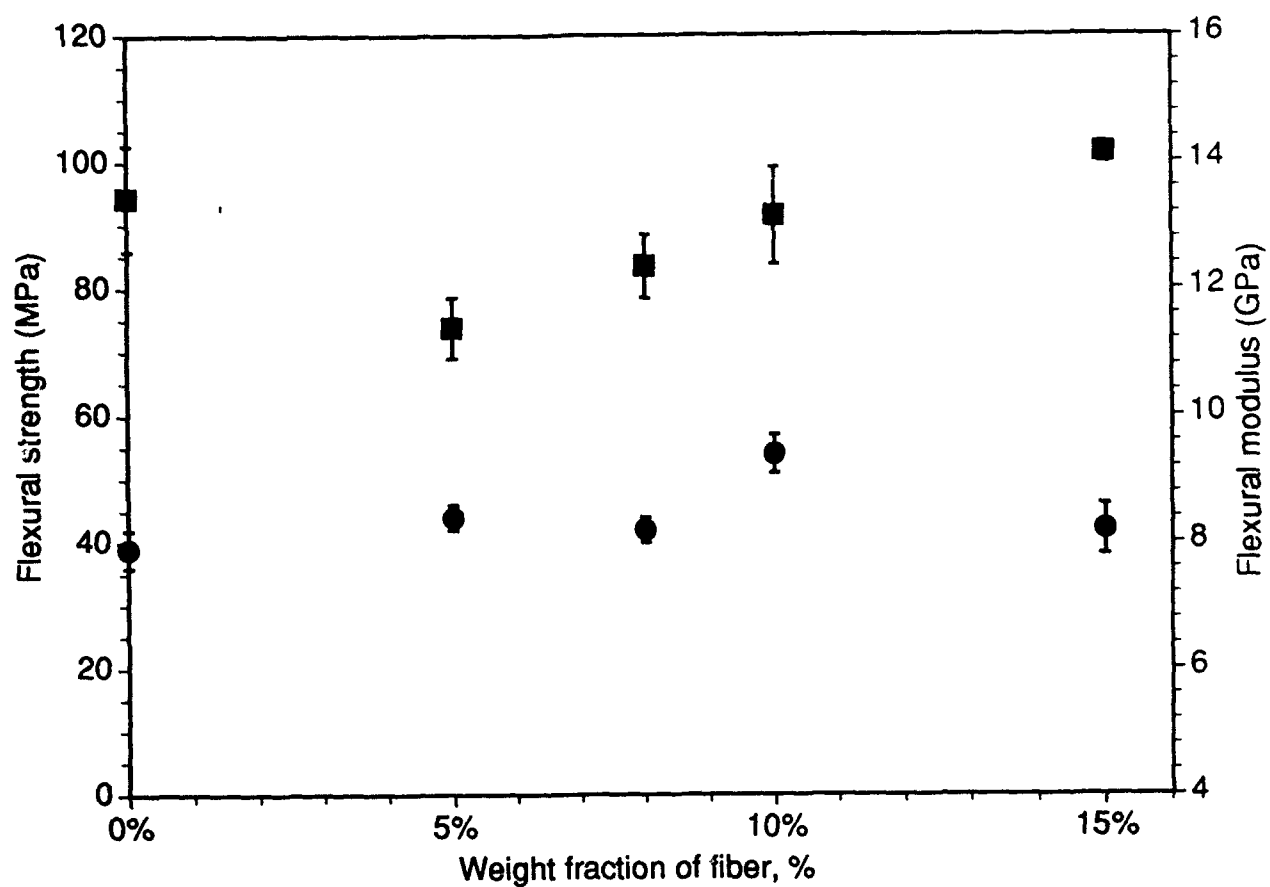


Figure 3. Variation in flexural strength (■) and modulus (●) of neat resin and Kevlar®/phenolic composites with 5%, 8%, 10%, and 15% Kevlar® fiber content.



Figure 4. ESCA spectra of (A) untreated and (B) TYZOR TPT treated Kevlar® fibers.

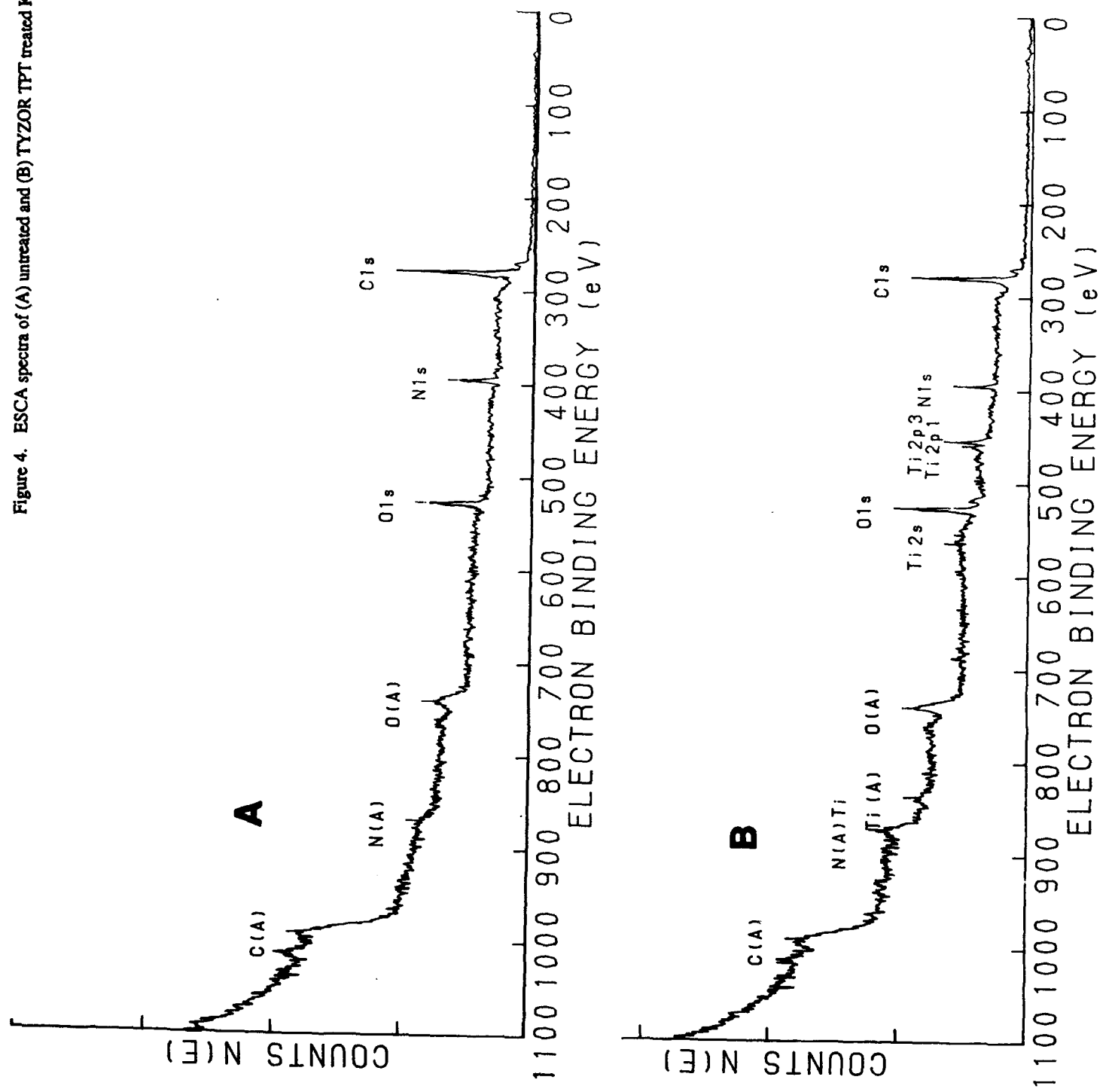
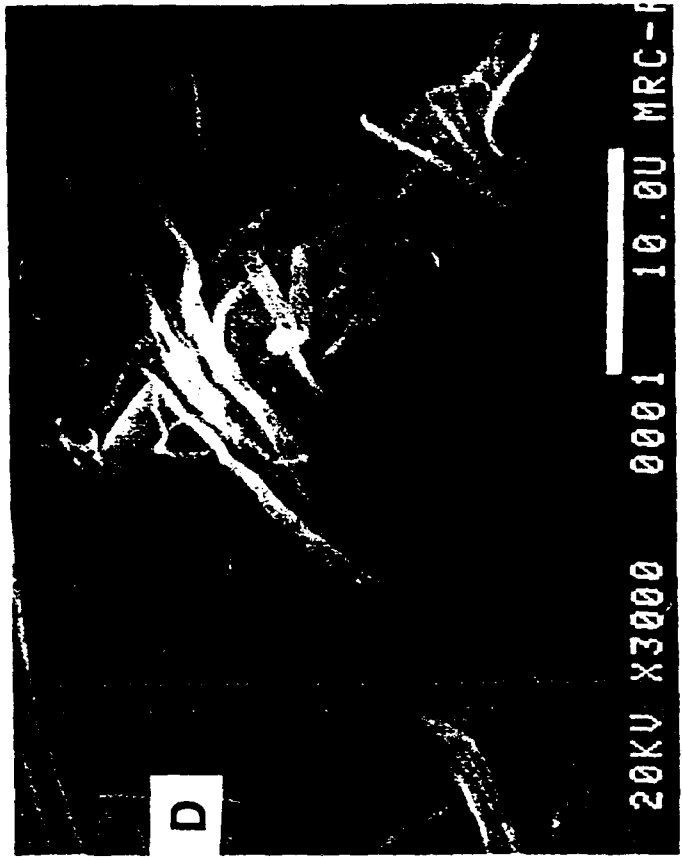
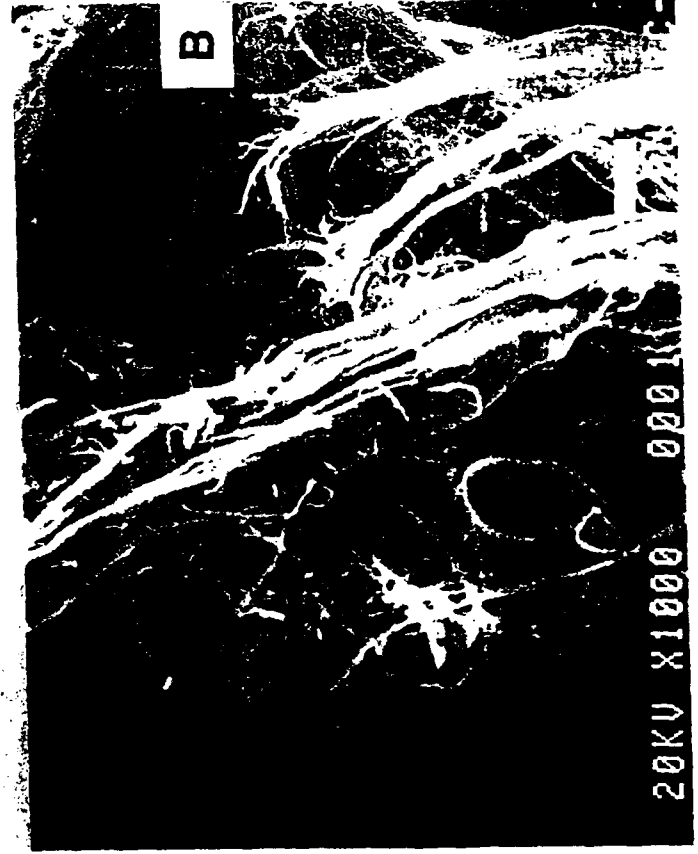


Figure 5. SEM's of (A and C) untreated and (B and D) TYZOR TPT treated Kevlar® fibers at



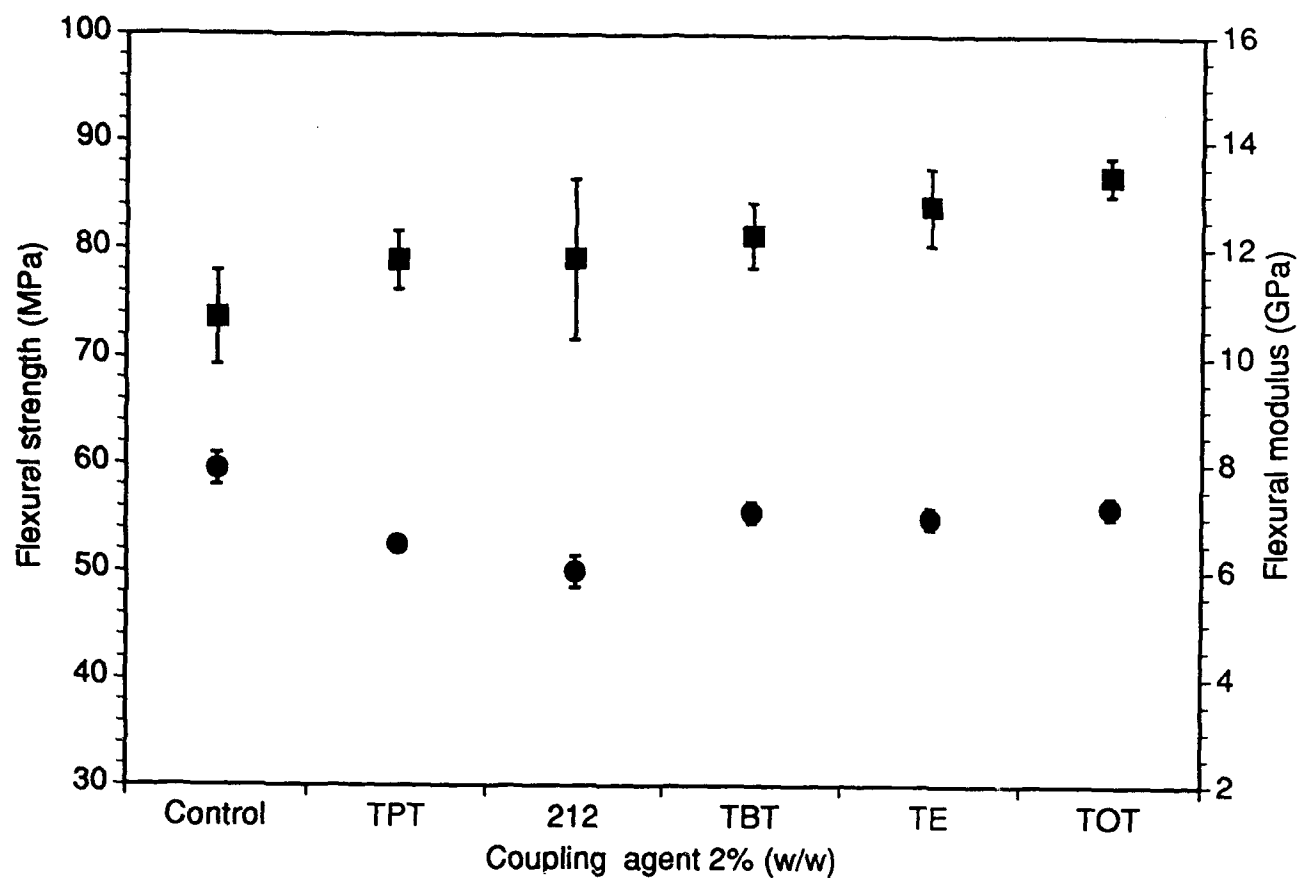


Figure 6. Flexural strength (■, MPa) and moduli (●, GPa) for Kevlar®/phenolic composites treated with 2% (w/w) of titanate and zirconate coupling agents. Note: Control samples are untreated; and TPT, TBT, and TOT are titanate alkoxides, while TE is a titanate chelate; 212 is a zirconate chelate.

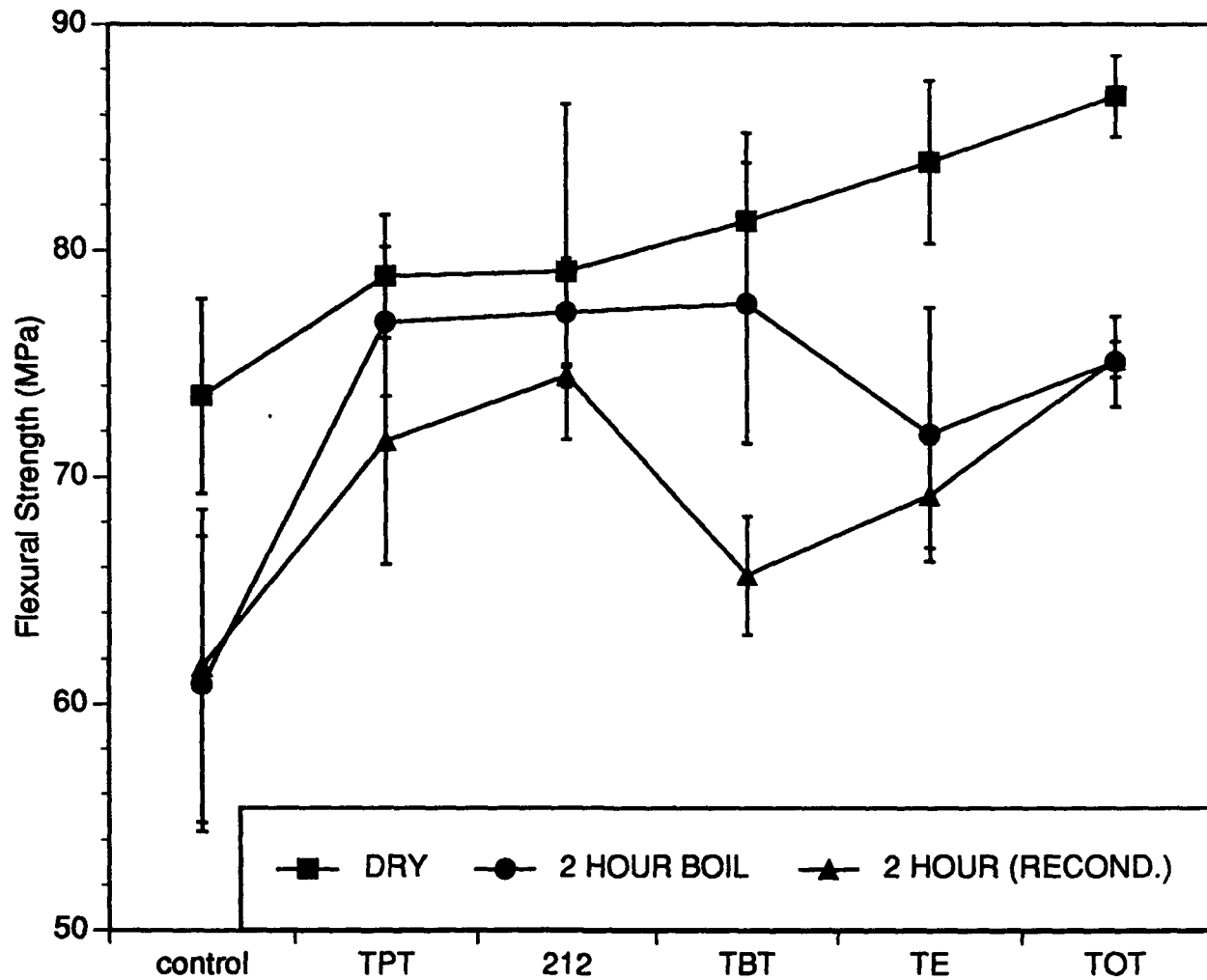


Figure 7. Plot showing the variation in flexural strength (MPa) values for Kevlar®/phenolic composites subjected to moisture. (■) Dry, as fabricated; (●) Wet, after the 2 hour boil test; and (▲) Reconditioned, dried at 110 °C and for 2 hours, after 2 hour boil test. The control samples are untreated.