JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **11** (2000) 407–419

Physical and mechanical characteristics of a chlorine-substituted poly(para-xylylene) coating on orthodontic chain modules

ROSS P. McKAMEY[1], JOHN Q. WHITLEY[2], ROBERT P. KUSY[1,2,3,4]*,
[1]*Department of Biomedical Engineering, University of North Carolina, Chapel Hill, NC 27599-7575*
[2]*Department of Dental Research Center, University of North Carolina, Chapel Hill, NC 27599-7455*
[3]*Department of Orthodontics, University of North Carolina, Chapel Hill, NC 27599-7450*
[4]*Department of Curriculum in Applied and Materials Sciences, University of North Carolina, Chapel Hill, NC 27599-3290*
E-mail: rkusy@bme.unc.edu

A 10 μm film of a chlorine-substituted poly(para-xylylene) was evaluated as a protective coating for commercial chain modules. Segments of modules were either non-coated or coated using five modes: 0%, 100%, and 200% elongation during coating and shipping; and 100% and 200% elongation only during coating. Prior to hydration, coating coverage was examined via light and electron microscopy. When hydrated, the presence or absence of the coating did not appreciably change the total weight gain (1.5%). However, when the modules were post-coating elongated to either 100% or 200%, neither the non-coated nor the coated modules sorbed water. Hydration did not significantly change the mechanical properties of the modules. As expected, most of the mechanical properties of the coated modules were greater than the properties for the uncoated modules. With regard to the coated modules only the properties of those modules having 0% elongation during coating and shipping were, in general, significantly different from the other coated modules. Post-coating elongation reduced the stiffness of the coated modules more than 79%. In regard to stress relaxation, the non-coated and coated modules recovered approximately 74% and 62% of the peak loading, respectively. Using the load-time data from these curves, Maxwell-Weichert models accurately predicted the decay profiles of both the non-coated and coated modules. Because the water sorption and the mechanical properties of these coated modules were favorable, they should be further characterized for staining.

1. Introduction

Orthodontists have traditionally placed esthetic improvement as an outcome that ranks only second to expedited treatment [1]. Orthodontic treatment was originally intended to correct malalignments of the teeth and mouth. To accomplish these goals, high strength metallic alloys were employed to provide the forces required. This treatment modality acquired the nickname, ''metal mouth'', which enhanced the patient's awareness of treatment and made the patient more self-conscious. This increased feeling of embarrassment led to the patient's demand for improved esthetics during treatment. As Hershey accurately observed, ''Because orthodontic therapy normally extends for many months, the appearance of the appliance itself is often a significant factor considered by individuals contemplating orthodontic treatment (particularly older adolescents and adults)'' [1].

The demand by the consumer market for esthetic treatment has produced great changes in orthodontic techniques and appliances. These changes have included direct bonding of brackets to teeth, lingual application of products, esthetic ceramic or plastic brackets, and the increased use of rubber and elastomeric appliances [2–4]. Chain modules have become a common elastomeric appliance used in orthodontic treatments [2–4]. However, these materials commonly assimilate odors and colors during treatment due to degradation of the elastomer in the presence of water, bacteria, and enzymes [5–8]. A potential solution to this problem involved coating the chain modules with a thin layer of a tough polymer.

---

*Author to whom correspondence should be addressed, University of North Carolina, Bldg. 210H, Rm. 313, CB 7455, Chapel Hill, NC 27599.

A polymer coating of a chlorine-substituted poly(1,4-xylylene) [9, 10] (Cl-PPX) was previously investigated for its thin film characteristics to solve sorption and containment problems encountered with an esthetic archwire. When normalized for the mass of the matrix copolymer of an S2-glass/acrylic composite, the water sorption decreased from 5 wt % for non-coated composites [11] to 3.6 wt % for coated composites [12]. Such a polymer coating was transparent, hydrolytically (water) stable, and extremely resistant to chemical attack at room temperature [13]. Poly(para-xylylene)s also have met USP standards for classification IV biocompatability (implantation) [14–16].

In this paper the criteria of coating coverage was investigated to determine the ability of the coating to remain intact on the chain modules during and after normal and extensive elongation. The effect of the coating on water sorption by the modules and the influence of water sorption on the mechanical properties of the non-coated and coated chain modules were studied. Using stress relaxation, the decay of the load response of the chain modules to a given elongation was evaluated. Maxwell-Weichert two-element models were applied to the stress-relaxation results to predict, *in vitro*, the loss of loads with time.

2. Materials and methods

2.1. Materials

Fifteen rolls of GAC's Super Chain (No. 34-013-78, 2 mm, clear, medium weight; Commack, NY) were obtained. Due to the external factors that can influence the physical and mechanical properties of elastomeric chains, this study focused on a single production batch. One thousand samples, each having five complete links, were cut from the rolls. From these samples ten module segments were selected at random, and the mechanical and stress-relaxation properties were measured (cf. Section 2.2.3 and 2.2.4 below) to serve as controls (As received; Table I, **A**). The remaining module segments were placed in polyethylene bags and stored in the dark at − 5 °C prior to coating (0% NC @ − 5 °C; Table I, **B**). When the modules were mounted for coating, module segments were randomly removed from storage to complete all tests and were then stored in the dark at 23 °C (0% NC @ 23 °C; Table I, **C**).

Special frameworks were designed and constructed (Fig. 1) that held the chain modules during shipping and coating in a relaxed mode (0% S&C), at 100% elongation (100% S&C), or at 200% elongation (200% S&C) (Table I; **D**, **E**, & **F**, respectively). Additional holders were constructed to allow modules to be shipped in a relaxed mode, then to be elongated preceding coating to either 100% (100% C) or 200% (200% C) of their initial length, and finally allowed to recover for return shipping (Table I; **G** & **H**). This coating framework maintained spacing between the modules so that they would not overlap or contact adjacent modules during shipping or coating. One hundred and sixty modules of each coating mode were mounted on the framework in a class 100 clean room to alleviate dust contamination of the modules. The framework was bagged and shipped.

The modules were plasma coated (Specialty Coatings Systems, Indianapolis, IN) with a chlorine-substituted

TABLE I Number of samples tested for each module condition and test modality

		Coating mode and label							
Test number	Test name and post-coating elongation	As received **A**	0% NC @ − 5 °C **B**	0% NC @ 23 °C **C**	0% S&C **D**	100% S&C **E**	200% S&C **F**	100% C **G**	200% C **H**
1.	***Coating coverage:*** 50 samples								
1.a	0%			5	5	5	5	5	5
1.b	100%			5	5				
1.c	200%			5	5				
2.	***Water sorption:*** 50 samples								
2.a	0%			5	5	5	5	5	5
2.b	100%			5	5				
2.c	200%			5	5				
3.	***Hydrolytic stability:*** 132 samples								
3.a	0% (dry)[a]	5	5	7	7	7	7	7	5
3.b	100% (dry)			5	5				
3.c	200% (dry)			5	5				
3.d	0% (wet)[b]			7	7	6	6	5	7
3.e	100% (wet)			5	5				
3.f	200% (wet)			7	7				
4.	***Stress relaxation:*** 110 samples								
4.a	0% (dry)	5	5	5	5	5	5	5	5
4.b	100% (dry)			5	5				
4.c	200% (dry)			5	5				
4.d	0% (wet)			5	5	5	5	5	5
4.e	100% (wet)			5	5				
4.f	200% (wet)			5	5				

[a] Dry condition is defined as storage at either 23 °C (Tests 3.a and 4.a) or 37 °C (Tests 3.b, 3.c, 4.b, and 4.c) and prevailing humidity.

[b] Wet condition is defined as storage in 37 °C distilled water for at least five weeks (Tests 3.d, 3.e, 3.f, 4.d, 4.e, and 4.f).

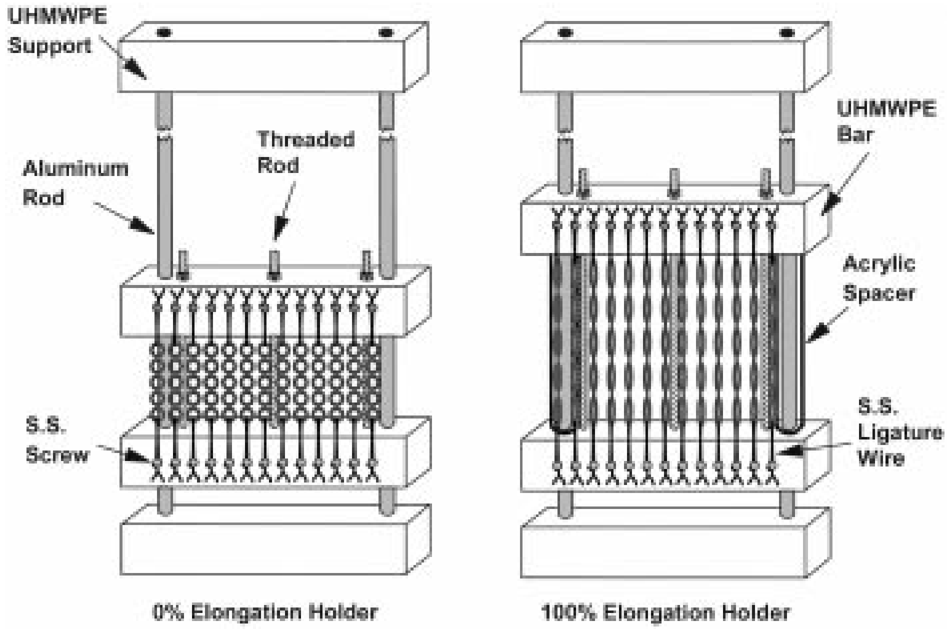

Figure 1 Examples of the special frameworks that were used during transport and coating of the chain modules at 0% elongation (left) and at 100% elongation (right). Note that UHMWPE is ultra-high molecular weight poly(ethylene) and that S.S. is stainless steel.

poly(1,4-xylylene) (Fig. 2). This method vaporized and pyrolyzed the solid dimer to produce a stable monomeric diradical that was simultaneously deposited and polymerized on the module surface [13]. This process produced a continuous, smooth, and even thickness (10 μm) coating on all exposed surfaces.

Upon receiving the framework after coating, the contents were inspected to insure that no damage had occurred during shipping. None of the modules that were elongated during coating (**E**, **F**, **G**, & **H**) had recovered to their original lengths. Even after removal from the framework and being stored at 23 °C for three months, these modules only partially recovered their original length. For this reason these modules were only used in the hydration study with no additional post-coating elongation (Table I, Test 2.a). Only the non-coated (Table I; **C**) and 0% S&C (Table I; **D**) modules were studied with post-coating elongation (Tests 1.b, 1.c, 2.b, 2.c, 3.b, 3.c, 3.e, 3.f, 4.b, 4.c, 4.e, and 4.f).

2.2. Methods

2.2.1. Coating coverage (Tests 1.a–1.c)

Fifty modules were included in this test: five modules from each of the coating modes (**C**, **D**, **E**, **F**, **G**, & **H**) at their resting length (0% post-coating elongation; Table I,

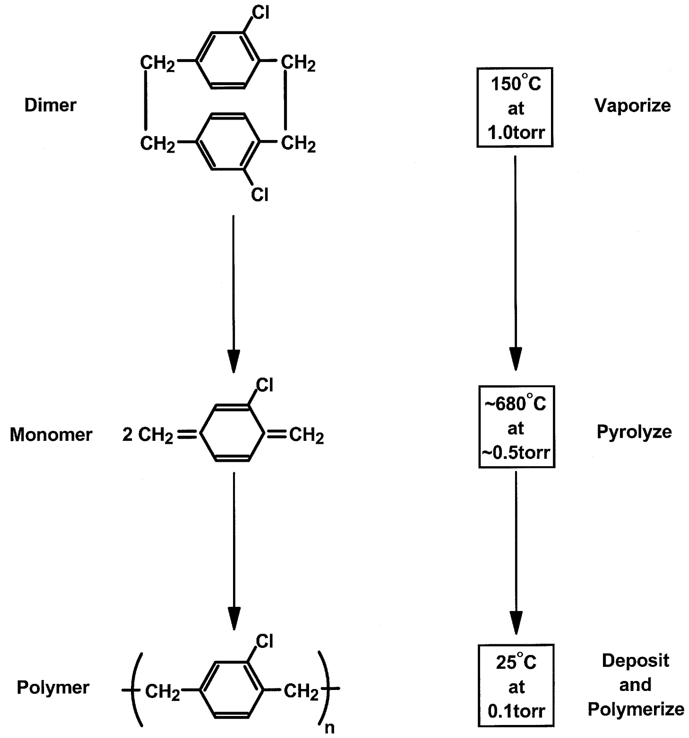

Figure 2 Chemical formula of the chlorine-substituted poly(1,4-xylylene) molecule that is also known as poly(chloro-*p*-xylylene) or Cl-PPX and the sequence of chemical events that lead to the plasma coating.

Test 1.a); and, five modules of both **C** and **D** that were post-coating elongated to 100% and 200% of their original lengths (Table I; Test 1.b and 1.c, respectively). Using dark field illumination, all modules were pre-examined by light microscopy for defects (e.g. pinholes) or breaks (e.g. rips) in the Cl-PPX coating. After this preliminary examination, selected modules had gold-palladium deposited on their surfaces and were examined using a JEOL scanning electron microscope (SEM, Model JSM-6300; Oberkochen, Germany) at 15 keV by secondary electron imaging. The **C** and **D** modules were observed at post-coating elongations of 0%, 100%, and 200% of their original lengths. The **E**, **F**, **G**, and **H** modules were observed at their resting length. Any observed defects or breaks in the Cl-PPX coating indicated a test failure.

2.2.2. Water sorption (Tests 2.a–2.c)

After sealing the ends of the modules with a silicone adhesive (Silicone II, General Electric Company, Waterford, NY), five modules of each coating mode (**C**, **D**, **E**, **F**, **G**, & **H**) were weighed before being immersed in 37 °C distilled water at their resting length (Test 2.a). Additionally, five modules each of **C** and **D** were post-coating elongated to 100% (Test 2.b) and 200% (Test 2.c) and placed in the water. All modules were removed, blotted dry, and immediately weighed each day for the first four days and then weekly through five weeks. Thereafter the five modules of each type were blotted dry, desiccated at 23 °C over $CaSO_4$ for at least one week, and then weighed again. After accounting for the weight gain of the silicone, the amount of water sorbed by the modules was determined from the weight gain between the initial weight and the hydrated conditions. The total weight gain, which represents the total amount of water sorbed in the modules, was determined from the change in weight between the adjusted dehydrated and hydrated conditions.

2.2.3. Hydrolytic stability (Tests 3.a–3.f)

In addition to five modules of **A** and **B** tested only in the dry[1] condition, at least five modules each of **C**, **D**, **E**, **F**, **G**, and **H** were tested both in the dry and wet[2] conditions. Also, after being post-coating elongated to 100% and 200% for at least five weeks in both the dry and wet conditions, at least five modules each of **C** and **D** were tested at 37 °C. The mechanical stiffness, strength, range, and toughness as defined by Fig. 3 and ref. [17, 18] were measured using an Instron model TTCM Universal Testing Machine (Canton, MA) at a constant crosshead displacement rate of 1.0 cm/min. All modules were tested at 37 °C in tension from their resting lengths until failure occurred.

2.2.4. Stress relaxation (Tests 4.a–4.f)

Five modules each for all coating modes (**A–H**) were tested after storage at 23 °C in the dry condition at their resting lengths (Test 4.a). Five modules of **C** and **D** were each post-coating elongated 100% and 200% in the dry condition at 37 °C for five weeks prior to testing (Tests 4.b and 4.c). Additionally fifty modules were tested after hydration at 37 °C for at least five weeks (Tests 4.d, 4.e, and 4.f). All modules were tested in the Instron at 37 °C by extending them at a loading rate of 2 cm/min to a displacement of 4 cm and allowing the modules to relax for fifteen minutes. The relaxations of these modules were compared to the as-received (**A**) modules, and a predicted engineering response was generated via a mechanical model.

This Maxwell-Weichert model of a viscoelastic material assumes the parallel connection of two Maxwell elements, each containing a spring and a dashpot in series, as represented by the equation [19, 20],

$$F(t) = x_0(\kappa_1 e^{-t/\tau_1} + \kappa_2 e^{-t/\tau_2}).$$

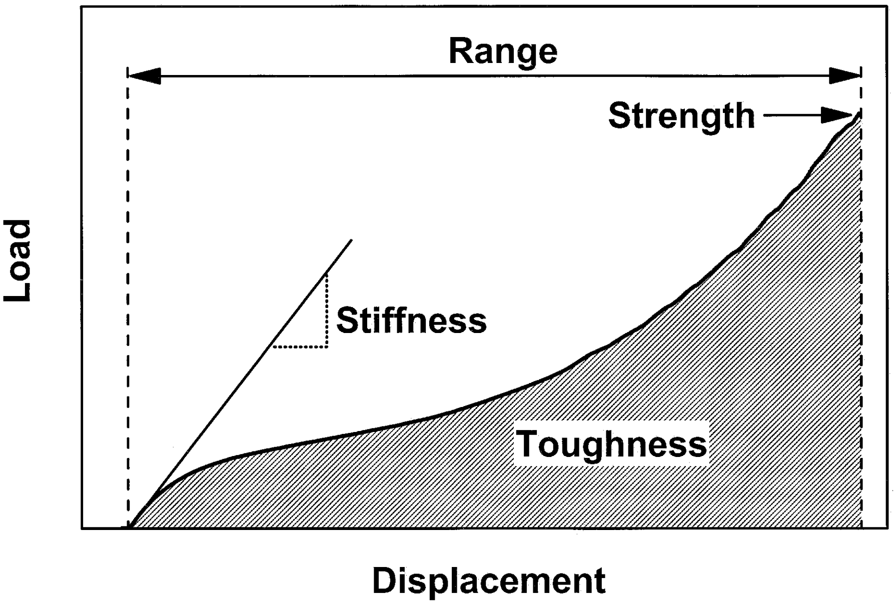

Figure 3 Representative load-displacement curve for five links of a chain module tested in tension with the mechanical properties of interest identified.

Here F is the resulting load at time (t), x_0 is the change in chain length, κ is the stiffness of a spring, and τ is the relaxation time of a Maxwell element.

2.2.5. Statistics

Means and standard deviations were calculated for all water sorption (Test 2), hydrolytic stability (Test 3), and stress-relaxation (Test 4) tests. In addition the statistical significance of the dry and wet conditions, the five coating modes, and post-coating elongation were evaluated in Test 3 using multiple analysis of variance (MANOVA, SYSTAT Version 5, SYSTAT, Inc., Evanston, IL). Tukey-Kramer pairwise comparisons were made to examine further those results that were highly significant. The results of the **C** and **D** modules were compared using a Student's t test to determine the significance of the coating on the mechanical properties. For the Maxwell-Weichert model (Test 4), the values for the κs and τs were determined from load versus time plots using an iterative process. A ''least-squares'' approach was used to minimize the square of the residual errors between theory and experiment. This minimization provided future insight as to the predictability of the stress relaxation *in vitro*.

3. Results

3.1. Coating coverage

The **C** and **D** modules were compared at 100% post-coating elongation using the SEM. Neither showed any obvious features or failures (Fig. 4, top). All of the modules that were coated in an elongated condition (**E**, **F**, **G**, & **H**) showed that bunching of the membrane occurred primarily at the link sections (Fig. 4, middle). Pinholes were seen in two of the **D** modules that were post-coating elongated 100% (Fig. 4, lower left). Rips were observed on all of the **D** modules that were post-coating elongated 200% (Fig. 4, lower right).

3.2. Water sorption

At 0% post-coating elongation the coated modules in Test 2.a (**D**, **E**, **F**, **G**, & **H**) had an average weight gain of 1.04 wt % as compared to 0.33 wt% for the non-coated **C** modules (Table II). The non-coated and coated modules at 0% post-coating elongation had an average total weight gain of 1.53 and 1.54 wt %, respectively. For the modules in Test 2.b and Test 2.c no weight change was measured, regardless of whether a coating was present. For all modules most of the weight change occurred during the first day.

3.3. Hydrolytic stability

Representative load-displacement curves are shown for the modules that were hydrated at 0% post-coating elongation (Fig. 5). For the modules that were tested at 0% post-coating elongation (Tests 3.a and 3.d), the **D** modules had stiffnesses (0.2844 and 0.4151 kg/mm; Table III) that were an order of magnitude greater than all other modules. The mechanical properties of the **C** modules were substantially less than the **D** modules, although the relative difference between strength, range, and toughness were not as great as the stiffness (Table III and Fig. 6). The **G** and **H** modules generally had mechanical properties that were less than the **E** and **F** modules in both the dry and wet conditions. For the modules that were post-coating elongated before being tested (Tests 3.b, 3.c, 3.e, and 3.f), the coated modules generally had higher mechanical properties than the non-coated modules, particularly for stiffness (Table IV and Fig. 7).

3.4. Stress relaxation

Overall, the **C** modules returned approximately 78% of the peak loading imparted to them (Tables V and VI). Post-coating elongation in the dry condition increased the residual/peak value from 73% (**C**, 0% post-coating elongation; cf. Table V) to over 83% (**C**, 200% post-coating elongation; Table VI). When the **C** modules were tested in the wet condition, the residual/peak value increased from 75% (**C**, 0% post-coating elongation; cf. Table V) to approximately 83% (**C**, 100% post-coating elongation; Table VI).

In contrast, with 0% post-coating elongation the **D–H** modules returned approximately 67% of their load in the dry condition (cf. Table V). For **D** modules, post-coating elongation in the dry condition increased the residual/peak value from 63% (**D**, 0% post-coating elongation; Table V) to 77% (**D**, 200% post-coating elongation; Table VI). When the **D–H** modules were hydrated without post-coating elongation, modules **D** and **E** lost approximately 3% of their original residual/peak value; whereas **F**, **G**, and **H** modules were not clearly affected (cf. Table V). After 200% post-coating elongation, the residual/peak value of the **D** modules increased nearly 15% whether in the dry or wet condition (Tables V and VI).

The Maxwell-Weichert model indicated that modules with 0% post-coating elongation had a faster initial stress-relaxation response (τ_1) in the dry than the wet condition (**C–H**; Table VII). A similar outcome was observed with post-coating elongation (**C** & **D**; Table VIII). Stress-relaxation profiles of **A–H** modules in the dry condition (Figs 8 and 9) and **C** & **D** modules in dry and wet conditions (Fig. 10) illustrate the overall behavior of κ_1, τ_1, κ_2, and τ_2.

4. Discussion

4.1. Coating coverage

For the modules not elongated during the coating process (**D**), the coating provided a continuous, smooth coating of the entire module surface (cf. Fig. 4, upper right). When the **D** modules were observed at a post-coating elongation of 100% (Test 1.b), pinhole defects (Fig. 4, lower left) suggested that the coating might best be applied with the module slightly elongated. When the **D** modules were observed at 200% post-coating elongation (Test 1.c), the coating separated from the module in all cases (Fig. 4, lower right). This confirmed the manufacturer's claim that the coating has an elastic limit of less than 200% [13].

All of the modules that were coated in an elongated mode (**E**, **F**, **G**, & **H**) revealed an undulating coating over

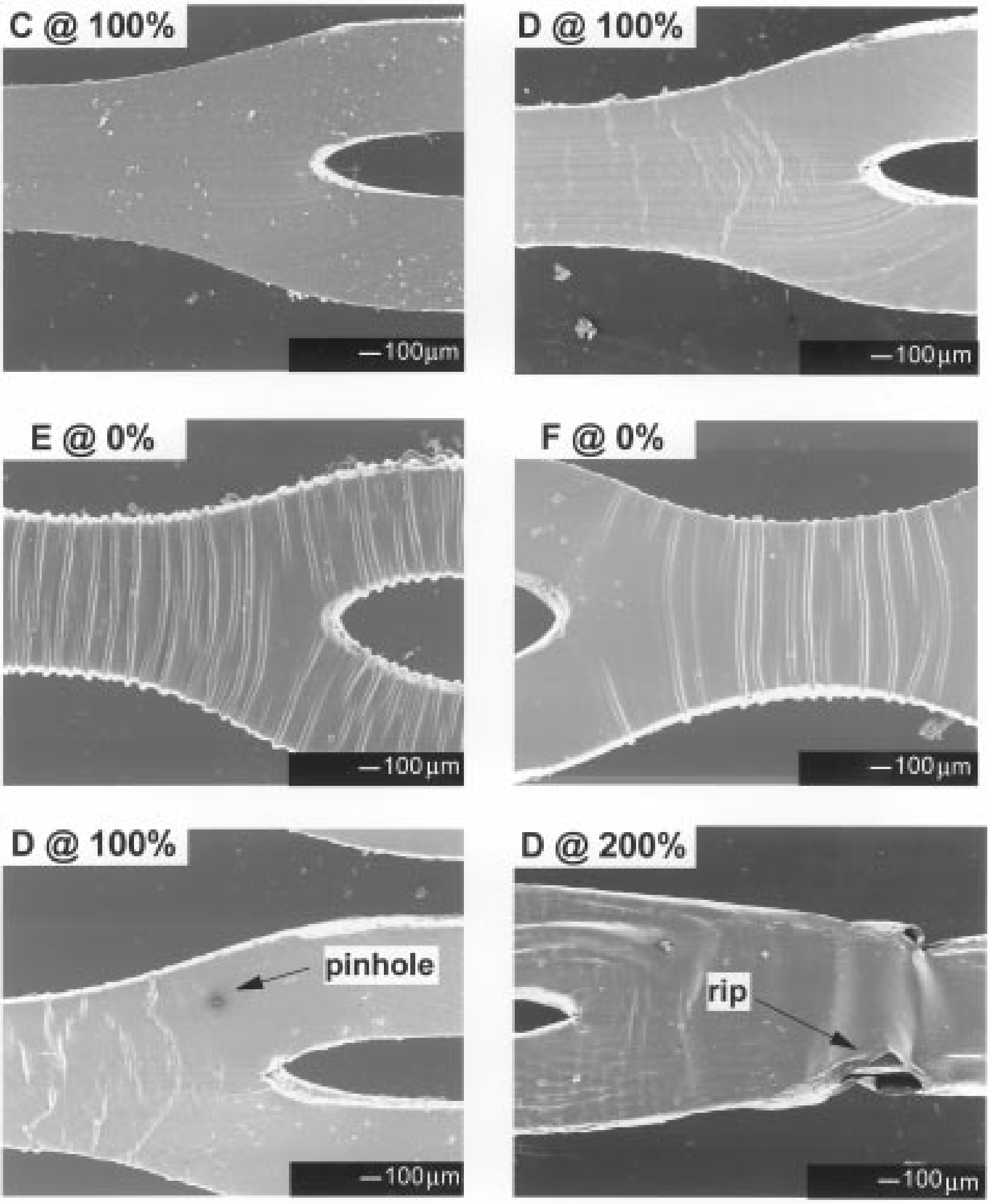

Figure 4 Scanning electron photomicrographs of modules from different coating modes and different post-coating elongations in the dry condition. For coating modes, see Table I.

TABLE II Mean values of the water sorption of modules at 37 °C

Coating mode	Coating label	Post-coating elongation (%)	Weight gain (wt%)	Total weight gain (wt%)
0% NC @ 23 °C	**C**	0	0.33 ± 0.15[a]	1.53 ± 0.20
0% S&C	**D**	0	1.01 ± 0.26	1.50 ± 0.11
100% S&C	**E**	0	1.17 ± 0.25	1.66 ± 0.14
200% S&C	**F**	0	0.99 ± 0.08	1.52 ± 0.09
100% C	**G**	0	1.01 ± 0.16	1.46 ± 0.17
200% C	**H**	0	1.02 ± 0.16	1.54 ± 0.18
0% NC @ 23 °C	**C**	100	0.01 ± 0.00	0.01 ± 0.00
0% NC @ 23 °C	**C**	200	0.00 ± 0.00	0.00 ± 0.00
0% S&C	**D**	100	0.01 ± 0.01	0.02 ± 0.01
0% S&C	**D**	200	0.02 ± 0.01	0.01 ± 0.00

[a] Mean ± standard deviation of five samples per test (see Table I).

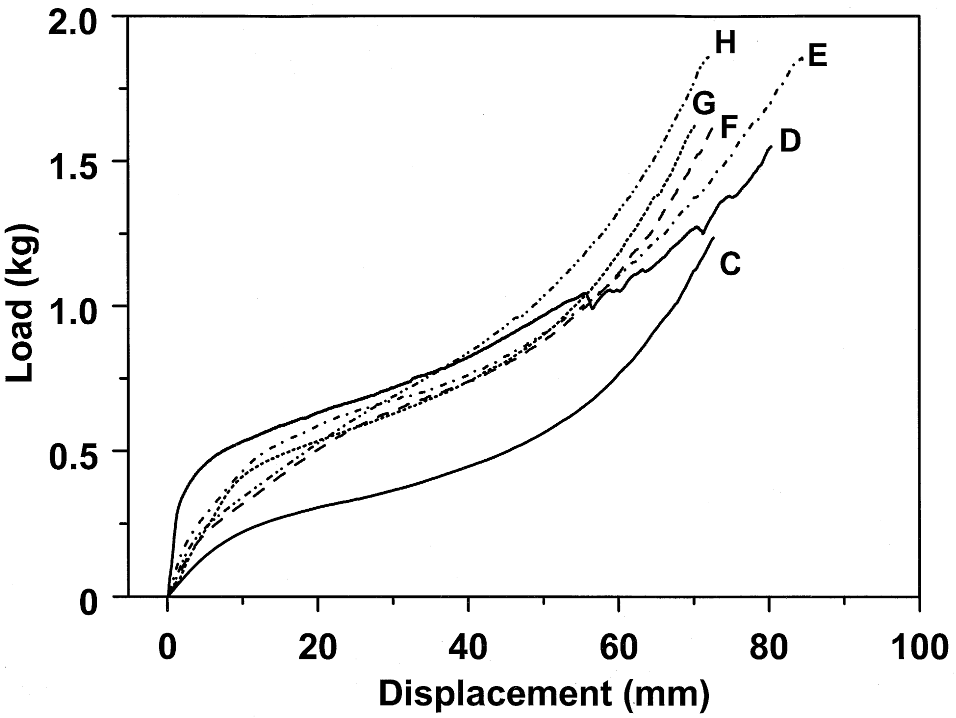

Figure 5 Representative load-displacement curves of the modules with 0% post-coating elongation in the wet condition (**C** = 0% NC @ 23 °C, **D** = 0% S&C, **E** = 100% S&C, **F** = 200% S&C, **G** = 100% C, **H** = 200% C). For definition of the wet condition, see Table I.

the entire surface of each module when observed at their resting length (Test 1.a and Fig. 4, middle frames). These undulations were due to the surface coating ''bunching-up'', since the coating was applied while the modules were elongated. This feature improved the coating integrity, providing the post-coating elongation of the module did not exceed the elastic limit of the coating.

4.2. Water sorption

The total weight gain of the non-coated modules was not different from the total weight gain of the coated modules (cf. Table II, top), although the coated modules actually sorbed over 200 wt % more water during the hydration process. The major cause was that the coated modules were substantially drier before hydration. There was also a 1.20 ± 0.33 wt % and a 0.49 ± 0.15 wt % difference between the initial and desiccated weights for the non-coated and coated modules, respectively, which was attributable to the vacuum used in the coating process. Once coated, further sorption was prevented while stored in the dry condition. The total weight gain of 1.5 wt % represents the maximum sorption for non-coated or coated modules.

The lack of sorption by both non-coated and coated modules that were post-coating elongated to either 100% or 200% (Table II, bottom) suggests the theory of a reduction in free volume between the elastomeric

TABLE III Mean values of the mechanical properties of chain modules tested to failure with 0% post-coating elongation

Coating mode	Coating label	Stiffness (kg/mm)	Strength (kg)	Range (mm)	Toughness (kg-mm)
Dry[a]					
As received	**A**	[b] 0.0542 ± 0.0046[c]	1.85 ± 0.15	76.0 ± 2.5	55.8 ± 5.7
0% NC @ − 5 °C	**B**	0.0332 ± 0.0013	1.47 ± 0.11	72.7 ± 2.1	40.6 ± 2.4
0% NC @ 23 °C	**C**	0.0380 ± 0.0050	1.59 ± 0.18	75.9 ± 3.0	48.6 ± 6.1
0% S&C	**D**	0.2844 ± 0.0423	1.81 ± 0.18	78.7 ± 4.7	72.5 ± 11.3
100% S&C	**E**	0.0545 ± 0.0025	1.85 ± 0.10	73.2 ± 4.9	62.8 ± 7.4
200% S&C	**F**	0.0386 ± 0.0048	2.10 ± 0.22	69.9 ± 4.1	64.9 ± 11.1
100% C	**G**	0.0612 ± 0.0063	1.75 ± 0.20	69.5 ± 2.1	57.6 ± 7.9
200% C	**H**	0.0435 ± 0.0029	1.85 ± 0.09	68.3 ± 2.3	55.4 ± 2.9
Wet[a]					
0% NC @ 23 °C	**C**	0.0292 ± 0.0025	1.34 ± 0.12	73.8 ± 1.9	40.0 ± 4.5
0% S&C	**D**	0.4151 ± 0.0517	1.52 ± 0.07	80.5 ± 1.9	66.1 ± 3.0
100% S&C	**E**	0.0944 ± 0.0091	2.02 ± 0.14	87.0 ± 4.3	83.5 ± 9.6
200% S&C	**F**	0.0492 ± 0.0051	1.77 ± 0.18	74.7 ± 4.9	62.1 ± 12.3
100% C	**G**	0.0562 ± 0.0030	1.61 ± 0.09	69.3 ± 2.3	52.0 ± 3.1
200% C	**H**	0.0504 ± 0.0049	1.75 ± 0.14	71.7 ± 2.9	58.1 ± 6.5

[a] See Table I for the definitions of dry and wet.

[b] Sidebars indicate the statistical significance determined by MANOVA or Student's t-test (**C** to **D** comparisons): double line, $p < 0.001$; single line, $p < 0.01$; and dashed line, $p < 0.05$.

[c] Mean ± standard deviation. For the number of samples per test, see Table I.

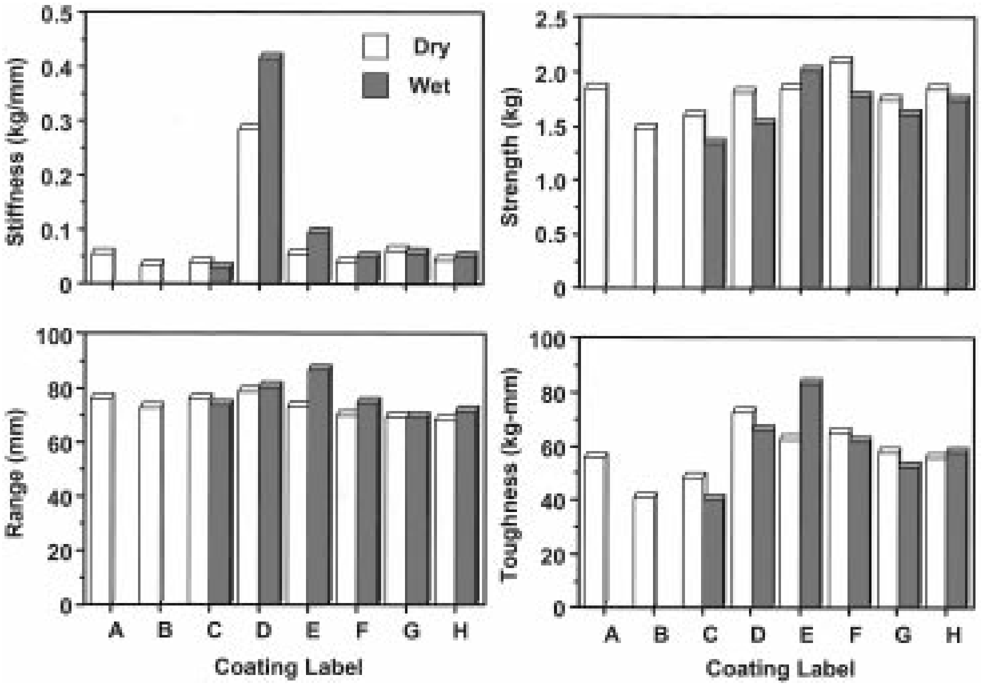

Figure 6 Mechanical properties of the modules tested with 0% post-coating elongation in the dry and wet conditions. For coating modes, see Table I.

TABLE IV Mean values of the mechanical properties of chain modules tested to failure with post-coating elongation

Coating mode	Coating label	Post-coating elongation (%)	Stiffness (kg/mm)	Strength (kg)	Range (mm)	Toughness (kg/mm)
Dry[a]						
0% NC @ 23 °C	**C**	100	0.0249 ± 0.0027[b]	1.72 ± 0.13	70.9 ± 3.0	46.9 ± 6.6
0% NC @ 23 °C	**C**	200	0.0168 ± 0.0022	1.84 ± 0.09	72.2 ± 2.8	47.9 ± 5.4
0% S&C	**D**	100	0.0586 ± 0.0083	1.89 ± 0.16	72.0 ± 1.6	66.9 ± 4.6
0% S&C	**D**	200	0.0345 ± 0.0020	1.87 ± 0.05	69.7 ± 1.3	60.3 ± 2.8
Wet[a]						
0% NC @ 23 °C	**C**	100	0.0192 ± 0.0009	1.50 ± 0.10	69.0 ± 1.7	41.6 ± 2.7
0% NC @ 23 °C	**C**	200	0.0133 ± 0.0014	1.49 ± 0.04	69.1 ± 3.2	38.0 ± 3.0
0% S&C	**D**	100	0.0424 ± 0.0046	1.66 ± 0.09	75.2 ± 2.9	61.6 ± 5.8
0% S&C	**D**	200	0.0221 ± 0.0027	1.64 ± 0.22	66.4 ± 10.1	51.1 ± 10.4

[a] See Table I for the definitions of dry and wet.

[b] Mean ± standard deviation. For the number of samples per test, see Table I.

molecules and a concurrent increase in crystallinity [21]. The post-coating elongation must have ''squeezed-out'' the free volume so that no space existed for the water to enter the molecular structure as the reduction in entropy increased the crystalline state of the elastomer. Since these modules are used in an elongated condition, this outcome implies that such elongated modules should better resist staining by water-transported substances.

4.3. Hydrolytic stability

With 0% Post-Coating Elongation (Tests 3.a and 3.d). The modules had characteristic ''J -curve'' load-displacement curves [21–23] (Fig. 5). The ''jaggedness'' of most **D** modules at the higher loads was attributed to the gradual separation or ripping of the coating film as the displacement exceeded the elastic limit.

A MANOVA and a Student's *t* test indicated that many of the mechanical properties were statistically different when compared as a function of the storage condition (for the non-coated modules) and coating mode (Table III). As expected, the Cl-PPX coating increased most of the mechanical properties of these modules (Table III and Fig. 6). A Tukey-Kramer analysis as a function of the coating mode generally indicated that only the properties of the **D** modules were significantly different from the other (**E–H**) modules (Table III). The order of magnitude difference in stiffness for the **D** modules was evident as the curve for the **D** sample quickly rose above the other curves in the initial portion of the load-displacement curve (cf. Fig. 5). Between different coating modes (modules **C–H**) hydration had no consistent positive or negative effect on the mechanical properties of the modules (Fig. 6). A Tukey-Kramer analysis indicated that, in general, no statistical difference existed between the dry and wet samples of each module.

Comparison With Post-Coating Elongation (Tests 3.b, 3.c, 3.e, and 3.f). The primary effect of the post-coating elongation was the reduction of the stiffness for the **D** modules. For these **D** modules there was a 79% and 89% reduction in the stiffness after post-coating elongation at 100% in the dry and wet conditions, respectively (cf. Tables III and IV; Fig. 7, upper left).

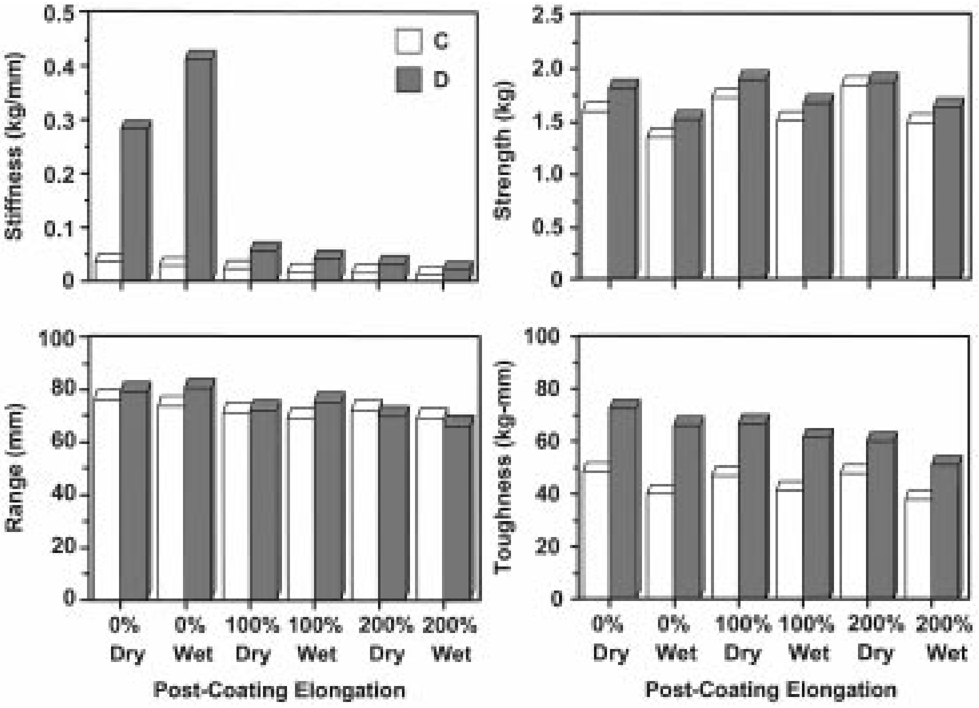

Figure 7 Mechanical properties of **C** and **D** modules showing the effects of post-coating elongations in the dry and wet conditions. For coating modes, see Table I.

TABLE V Mean values of stress-relaxation analysis for chain modules tested with 0% post-coating elongation

Coating mode	Coating label	Peak load (g)	Residual load[a] (g)	Residual/peak (%)
Dry[b]				
As Received	**A**	393 ± 13[c]	297 ± 8	75.3 ± 0.6
0% NC @ −5 °C	**B**	374 ± 12	282 ± 8	75.3 ± 1.1
0% NC @ 23 °C	**C**	391 ± 55	286 ± 45	73.0 ± 1.3
0% S&C	**D**	681 ± 61	432 ± 44	63.3 ± 0.9
100% S&C	**E**	623 ± 42	413 ± 28	66.4 ± 2.0
200% S&C	**F**	422 ± 17	301 ± 11	71.4 ± 0.3
100% C	**G**	658 ± 30	422 ± 24	64.1 ± 0.9
200% C	**H**	450 ± 10	318 ± 7	70.7 ± 1.5
Wet[b]				
0% NC @ 23 °C	**C**	381 ± 17	288 ± 16	75.6 ± 1.2
0% S&C	**D**	677 ± 12	412 ± 9	60.8 ± 1.0
100% S&C	**E**	615 ± 26	393 ± 18	63.9 ± 2.3
200% S&C	**F**	456 ± 15	316 ± 12	70.9 ± 3.2
100% C	**G**	541 ± 25	355 ± 8	65.8 ± 2.3
200% C	**H**	472 ± 28	329 ± 18	69.6 ± 2.1

[a] Residual load reading taken at 15 min.

[b] See Table I for the definitions of dry and wet.

[c] Mean ± standard deviation of five samples per test (see Table I).

TABLE VI Mean values of the stress-relaxation analysis for chain modules tested with post-coating elongation

Coating mode	Coating label	Post-coating elongation (%)	Peak load (g)	Residual load[a] (g)	Residual/peak (%)
Dry[b]					
0% NC @ 23 °C	**C**	100	457 ± 48[c]	348 ± 30	76.4 ± 1.6
0% NC @ 23 °C	**C**	200	284 ± 16	236 ± 12	83.1 ± 0.5
0% S&C	**D**	100	709 ± 20	468 ± 14	66.0 ± 0.1
0% S&C	**D**	200	356 ± 25	274 ± 13	76.9 ± 2.0
Wet[b]					
0% NC @ 23 °C	**C**	100	373 ± 3	309 ± 2	82.7 ± 0.3
0% NC @ 23 °C	**C**	200	223 ± 21	179 ± 21	80.1 ± 2.6
0% S&C	**D**	100	629 ± 60	399 ± 22	63.7 ± 3.3
0% S&C	**D**	200	282 ± 22	211 ± 15	75.0 ± 1.3

[a] Residual load reading taken at 15 min.

[b] See Table I for the definitions of dry and wet.

[c] Mean ± standard deviation of five samples per test (see Table I).

TABLE VII Load-decay coefficients for two-element Maxwell-Weichert model based on mean values of chain module data with 0% post-coating elongation[a]

Coating Mode	Coating Label	κ_1 (g/cm)	τ_1 (min)	κ_2 (g/cm)	τ_2 (min)
Dry[b]					
As received	**A**	27.6	0.62	125.3	186
0% NC @ $-5\,^\circ$C	**B**	25.8	0.90	113.3	194
0% NC @ 23 °C	**C**	31.2	0.66	124.0	170
0% S&C	**D**	79.2	0.46	173.0	192
100% S&C	**E**	70.4	0.49	176.4	192
200% S&C	**F**	39.6	0.53	129.6	214
100% C	**G**	97.1	0.50	235.2	152
200% C	**H**	68.0	0.55	219.3	197
Wet[b]					
0% NC @ 23 °C	**C**	28.3	0.74	119.9	221
0% S&C	**D**	86.7	0.56	170.7	175
100% S&C	**E**	86.8	0.58	200.9	169
200% S&C	**F**	59.6	0.59	186.4	174
100% C	**G**	72.4	0.53	184.5	166
200% C	**H**	64.4	0.57	196.9	187

[a] Mean value of five samples was used to generate each model.
[b] See Table I for the definitions of dry and wet.

When a Tukey-Kramer analysis was used to compare the means of multiple groups (the presence of a coating, the level of post-coating elongation, and the dry or wet condition), the stiffness and toughness properties of the **D** modules were statistically different from the properties of their non-coated counterparts ($p < 0.001$; Tables III and IV; Fig. 7). For dry and wet conditions, even at 200% post-coating elongation the toughness values of the coated **D** modules were higher than the non-coated **C** modules with 0% post-coating elongation (cf. Tables III and IV). In general all mechanical properties gradually decreased from dry to wet and 100% to 200% post-coating elongation (Fig. 7). As with the modules that were stretched during the coating process (**E**, **F**, **G**, and **H**), the properties of the **C** and **D** modules that were elongated after coating decreased due to the permanent set.

4.4. Stress relaxation

The **A**, **B**, and **C** modules were similar to each other, which indicated that minimal degradation had occurred during storage (Table V, **A**, **B**, & **C**; Fig. 8). This information presumably applied to the modules sent for coating, although their specific transit conditions were unknown. Notwithstanding, these modules were considered ''controls'', which compared favorably with earlier publications [24–27].

The coating increased the peak load values but did not otherwise change the stress-relaxation profiles of the modules (Fig. 8, lower, and Fig. 10). Comparison of non-coated and coated modules indicated a substantial difference in both the average peak load produced and the resulting residual/peak value (Table V, top). These differences between **C** & **D** were similar in the wet condition (Table V, bottom) and for post-coating elongation (Table VI). This trend was attributed to the coating, which increases the module's stiffness. All **C** and **D** modules experienced a greater peak load in the dry over the wet condition (Fig. 10). Furthermore, as post-coating elongation increased from 0% to 200%, the residual/peak values increased in dry or wet conditions (cf. Tables V and VI).

TABLE VIII Load-decay coefficients for two-element Maxwell-Weichert model based on mean values of chain module data with post-coating elongation[a]

Coating mode	Coating label	Post-coating elongation (%)	κ_1 (g/cm)	τ_1 (min)	κ_2 (g/cm)	τ_2 (min)
Dry[b]						
0% NC @ 23 °C	**C**	100	32.7	0.63	158.8	176
0% NC @ 23 °C	**C**	200	14.5	0.77	110.0	245
0% S&C	**D**	100	94.6	0.47	240.9	178
0% S&C	**D**	200	32.4	0.53	133.9	333
Wet[b]						
0% NC @ 23 °C	**C**	100	22.4	0.76	141.9	362
0% NC @ 23 °C	**C**	200	14.6	0.94	102.7	173
0% S&C	**D**	100	111.5	0.56	249.4	177
0% S&C	**D**	200	31.4	0.71	143.5	172

[a] Mean value of five samples was used to generate each model.
[b] See Table I for the definitions of dry and wet.

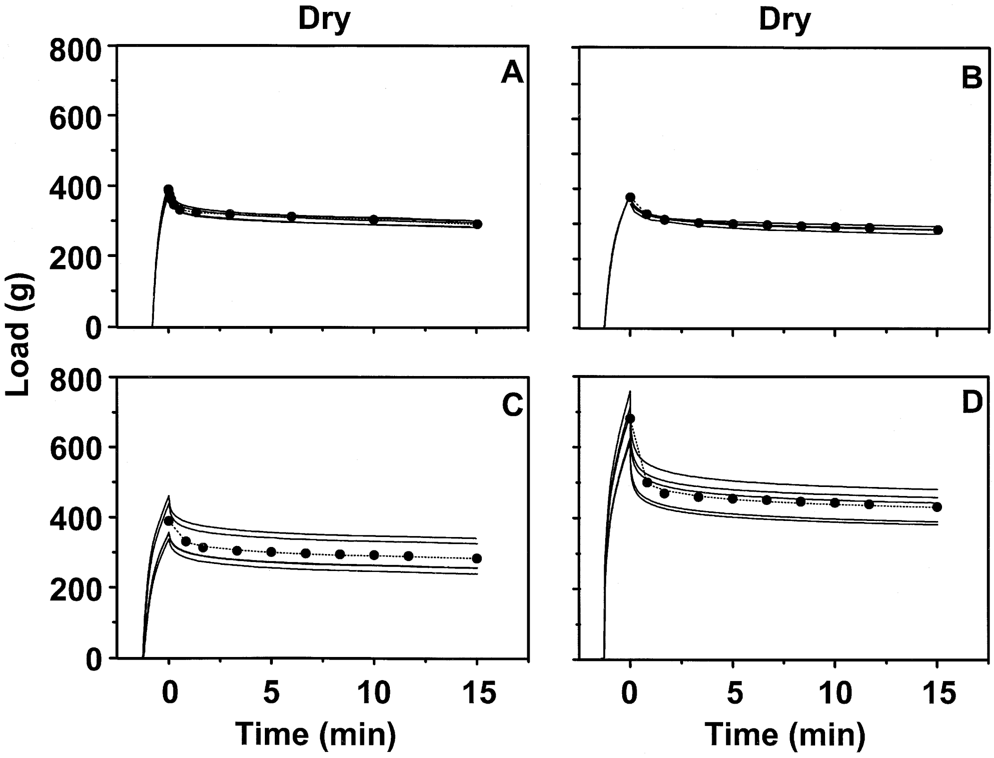

Figure 8 Plots of the stress-relaxation profiles for non-coated (**A** = as received, **B** = 0% NC @ −5 °C, **C** = 0% NC @ 23 °C) and coated (**D** = 0% S&C) modules in the dry condition with 0% post-coating elongation. Note that (—) is the actual data, (- - -) is the mean of the data, and (•) is the model-generated data.

For the modules coated at 100% elongation (**E** & **G**) the residual/peak values were about 65% of the 640 g peak loading (Fig. 9, left column). Increasing the elongation to 200% during coating (**F** & **H**) increased the residual/peak values to approximately 70%, but reduced the peak loads to around 450 g (Fig. 9, right column). This is attributed to the permanent set that occurred when these modules were elongated after

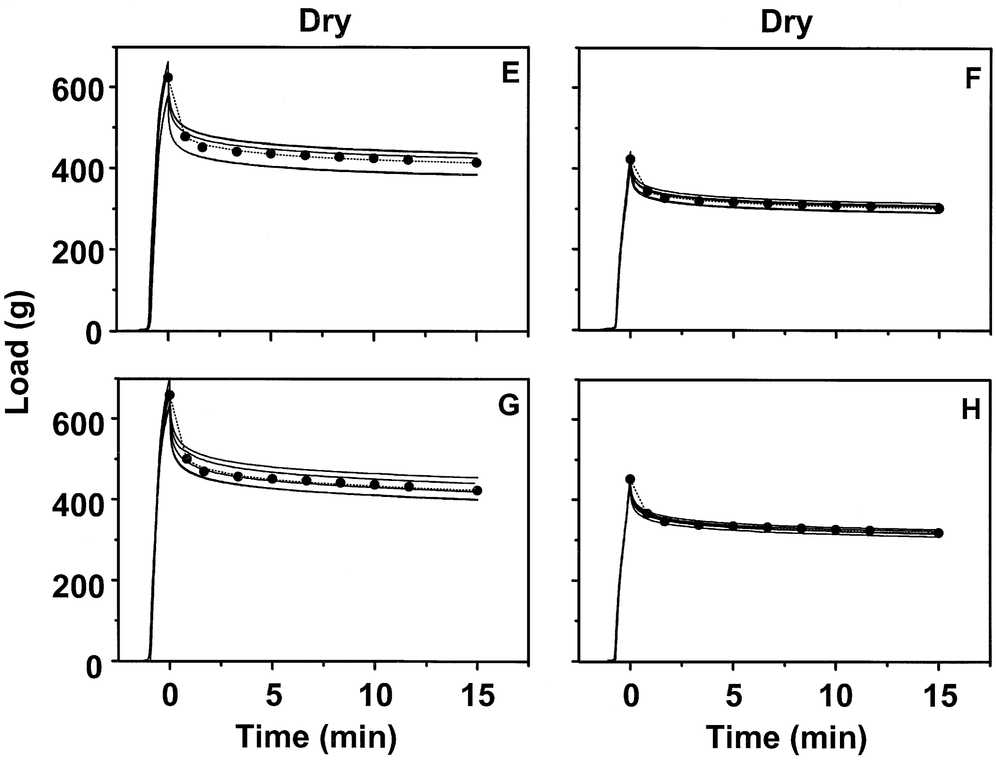

Figure 9 Plots of stress-relaxation profiles for modules in the dry condition that were elongated preceding coating: 100% (cf. left column, **E** = 100% S&C and **G** = 100% C) and 200% (cf. right column, **F** = 200% S&C and **H** = 200% C). Note that (—) is the actual data, (- - -) is the mean of the data, and (•) is the model-generated data.

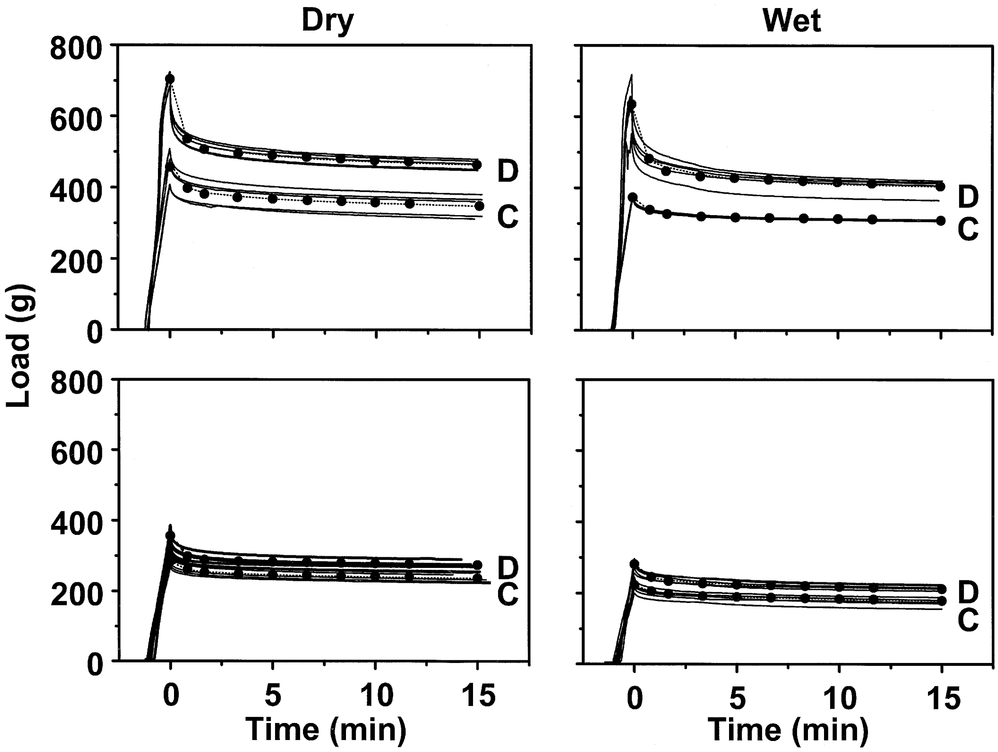

Figure 10 Plots of stress-relaxation profiles for modules with 100% (top row) and 200% (bottom row) post-coating elongation in both the dry and wet conditions (**C** = 0% NC @ 23 °C, **D** = 0% S&C). Note that (—) is the actual data, (- - -) is the mean of the data, and (•) is the model-generated data.

coating. Because the changes in lengths that were imparted to them during testing were not as great, their loads were less.

When comparing dry and wet conditions with 0% post-coating elongation, select dry modules (**C**, **D**, **E**, and **G**) achieved higher initial loading values than their wet counterparts (Table V). For the **F** and **H** modules the initial peak loads were approximately 200 g lower than the other coated modules for the reasons detailed in the previous paragraph (Fig. 9).

Maxwell-Weichert model. Previous research has shown that elastomeric modules experience stress relaxation [5–8, 28]. How the coating could affect the stress relaxation of the modules was not known. Although a response could be developed for a coated module using the ''rule of mixtures'' [28, 29], a continuum approach was chosen that was based on viscoelasticity [22, 30, 31].

The Maxwell-Weichert model was applied to the load-time data from the stress-relaxation curves [32]. Since each module had a unique set of load-decay coefficients, each coating mode required a unique model (Tables VII and VIII). In all cases, the spring coefficients (κ_1, κ_2) for the non-coated (**A–C**) modules were less than those for the coated **D** modules, indicating an increased stiffness from coating (cf. Tables VII and VIII). In the dry condition with 0% post-coating elongation, only the first relaxation coefficient (τ_1) differed greatly between the non-coated (**A–C**) and coated **D** modules. Therefore, the effect of the coating on the chain module's stress-relaxation response was best observed in the fast acting element. Although similar coefficients were generally seen for the other coated modules, the **F** modules exhibited a peculiar response. Due to the permanent set developed during the shipping and coating process, the **F** modules had spring coefficients (κ_1, κ_2) that approached those of the non-coated modules. This trend indicates that, as the modules were elongated to a greater percentage, their resiliencies were reduced.

The Maxwell-Weichert model accurately predicted the long-term ($>$ 2min) decay profile of both the non-coated and coated modules in each mode (cf. Figs. 8–10). Because orthodontic goals are reached in weeks and months, not seconds and minutes, the model can predict the remaining load *in vitro* at any given practical time. When applied *in vivo*, however, the effect of tooth motion must be considered.

5. Conclusions

A chlorine-substituted poly(para-xylylene) coating can generally withstand both normal and excessive elongations. The coating does not change the total amount of water sorbed by the modules. This sorbed water is not detrimental to the mechanical properties. Most of the improvement in the mechanical properties is negated by coating the modules after they are stretched or by elongating the modules after coating. The coating of unstretched modules increases the magnitude of the peak load value, but decreases the residual/peak value. Elongation of modules during or after coating had a mixed effect on the peak and the residual/peak values. A Maxwell-Weichert model can accurately evaluate all coating modes *in vitro*. In the future, such modules should be further evaluated for their staining characteristics.

6. Acknowledgment

We wish to thank the American Association of Orthodontist Foundation for their support of this research. We also wish to thank Mr Michael Wile of GAC for providing the modules and Mr Craig Mattison of Specialty Coatings Systems for his cooperation in the module coating.

Notes

1. Dry condition is defined as storage at either 23 °C (Tests 3.a and 4.a) or 37 °C (Tests 3.b, 3.c, 4.b, and 4.c) and prevailing humidity.
2. Wet condition is defined as storage in 37 °C distilled water for at least five weeks.

References

1. H. G. HERSHEY, *J. Am. Dent. Assoc.* **117** (1988) E29.
2. K. REITAN and P. RYGH, in ''Orthodontics: Current Principles and Techniques, 2nd ed.'' (Mosby-Year Book, St. Louis, 1994) p. 96.
3. C. J. BURSTONE, in ''Orthodontics: Current Principles and Techniques, 2nd ed.'' (Mosby-Year Book, St. Louis, 1994) p. 235.
4. J. L. VADEN, J. G. DALE and H. A. KLONTZ, in ''Orthodontics: Current Principles and Techniques, 2nd ed.'' (Mosby-Year Book, St. Louis, 1994) p. 627.
5. A. K. WONG, *Angle Orthod.* **46** (1976) 196.
6. J. YOUNG and J. L. SANDRIK, *ibid.* **49** (1979) 104.
7. P. C. K. CHUNG, S. H. Y. WEI and L. R. REYNOLDS, *Brit. J. Orthod.* **16** (1989) 265.
8. W. P. ROCK, H. J. WILSON and S. E. FISHER, *ibid.* **13** (1986) 147.
9. L. ZHANG, C. C. CHU and I. H. LOH, *J. Biomed. Mater. Res.* **27** (1993) 1425.
10. R. P. KUSY, O. KEITH, J. Q. WHITLEY and C. R. SAUNDERS, *J. Am. Ceram. Soc.* **76** (1993) 336.
11. K. C. KENNEDY, T. CHEN and R. P. KUSY, *J. Mater. Sci.: Mat. in Med.* **9** (1998) 243.
12. S. W. ZUFALL and R. P. KUSY, ''Water Sorption Properties of a Poly(chloro-*p*-xylylene)-Coated-Fiber-Reinforced Polymeric Biomaterial'', 1999 Annual Meeting of the Society for Biomaterials (1999) April-May.
13. Corporate promotional literature, ''Parylene conformal coatings: Specifications and properties'' (Specialty Coating Systems Technologies) Indianapolis, 1996) p.1.
14. Corporate promotional literature, ''Parylene: A biostable coating for medical applications'' (Specialty Coating Systems Technologies, Indianapolis, 1994) p.1.
15. G. E. LOEB, A. E. WALKER, S. UEMATSU and B. W. KONIGSMARE, *J. Biomed. Mater. Res.* **11** (1977) 195.
16. B. HUMPHREY, *Med. Plastics & Biomater. Mag.* **1** (1996) 28.
17. R. P. KUSY, P. F. HIRSCH and T. -C. PENG, *Alcoholism: Clinical and Exper. Res.* **13** (1989) 185.
18. E. A. SCHOBER, R. P. KUSY, J. Q. WHITLEY and D. A. SAVITZ, *J. Mat. Sci.: Mat. in Med.* **5** (1994) 130.
19. S. L. ROSEN, in ''Fundamental Principles of Polymeric Materials'' (Wiley-Interscience, New York, 1982) p. 236.
20. J. J. AKLONIS, W. J. MACKNIGHT and M. SHEN, in ''Introduction to Polymer Viscoelasticity''(Wiley-Interscience, New York, 1972) p. 143.
21. J. E. MARK, A. EISENBERG, W. W. GRAESSLEY, L. MANDELKERN and J. L. KOENIG, in ''Physical Properties of Polymers'' (American Chemical Society, Washington, D.C., 1984) pp. 12–13.
22. J. VINCENT, in ''Structural Biomaterials, 2nd ed.'' (Princeton University Press, Princeton, 1990) pp. 17–22 and pp. 60–63.
23. W. P. ROCK, H. J. WILSON and S. E. FISHER, *Brit. J. Orthod.* **12** (1985) 202.
24. J. B. PARK and R. S. LAKES (eds), in ''Biomaterials: An Introduction, 2nd ed.'' (Plenum, New York, 1992) pp. 169 and 185.
25. H. F. CHANG, in ''Proceedings of the National Science Council, Republic of China-Part B, Life Sciences'', Taipei 1987 (The Council, Taipei, 1987) p. 45.
26. D. C. DE GENOVA, P. MCINNES-LEDOUX, R. WEINBERG and R. SHAYE, *Am. J. Orthod.* **87** (1985) 377.
27. J. S. STEVENSON and R. P. KUSY, *Angle Orthod.* **64** (1994) 455.
28. D. L. BATY, J. E. VOLZ and J. A. VON FRAUNHOFER, *Am. J. Orthod. Dentofac. Orthop.* **106** (1994) 40.
29. T. C. LU, W. N. WANG, T. H. TARNG and J. W. CHEN, *ibid.* **104** (1993) 373.
30. Z. D. JASTRZEBSKI, in ''The Nature and Properties of Engineering Materials, 2nd ed.'' (John Wiley, New York, 1976) pp. 247–255.
31. L. E. NIELSEN, in ''Mechanical Properties of Polymers, 2nd ed.'' (Reinhold, New York, 1967) pp. 77–83.
32. R. P. MCKAMEY and R. P. KUSY, ''Stress-relaxing, composite ligature wires: Formulations and characteristics'', *Angle Orthod.* **69** (1999) 441.

Received 22 December 1998
and accepted 21 June 1999