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Structural degradation of polyurethane-based elastomeric modules

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Degradative characteristics were studied using specimens of three polyurethane-based elastomeric modules that were treated in solutions of varying acidity, oxygen content and temperature. After periods of 10 and 100 days, molecular weight distribution changes, mechanical property changes and elemental chemistry changes were studied using gel permeation chromatography (GPC), stress-relaxation testing and X-ray photoelectron spectroscopy (XPS), respectively. As determined through analyses of the molecular, mechanical, and elemental changes after treatment, the degradative mechanism was influenced by whether the polyurethane was polyester-based or polyether-based, and the degree of structural degradation was influenced by the type and duration of conditioning treatment. Degradation of the polyester-based materials after treatment was dominated by a chain scission mechanism; conversely, the degradation of the polyether-based material was dominated by a crosslinking mechanism. Among the conditioning treatments, the combined effects of an increase in acidity, oxygen content and temperature most influenced the degree of degradation with time, with the increase in temperature having the greatest effect of any of the single variables investigated.

1. Introduction

Polyurethanes were introduced in the 1930s and were initially manufactured as fibres for use in synthetic fabrics and as foams for use in aircraft propellors and landing flaps [1]. Because of favourable characteristics such as toughness, wear resistance, and versatility, polyurethane applications were expanded to include adhesives, surface coatings, sports equipment, furniture, and automotive components [2].

Presently, because of their biocompatibility, performance, and ease of manufacture, polyurethane elastomers are used extensively in health care. Medical applications include artificial heart systems, catheters, dressings, and drug delivery systems [1]. Dental applications include elastomeric modules and chains that are used in orthodontics to ligate the archwire to the bracket on each tooth and to position teeth, respectively. These elastomers can be manufactured to be colourless, allowing for an aesthetically pleasing appearance, especially when used with transparent brackets.

An inherent problem with polyurethane materials is that degradation may occur over time, affecting mechanical properties (e.g. tensile strength, stiffness, fatigue strength, and toughness), causing colour changes, initiating surface cracking, and reducing biocompatibility. Modes of structural degradation of these materials may include chain scission, which can occur through mechanical, thermal, or chemical means, and/or crosslinking [3]. Previous investigators have focused on the biostability of implanted polyurethanes and their biodegradation in the body [4, 5] and have found that thermal degradation, enzymatic hydrolysis, and oxidation play a major role in polyurethane implant rejection [6–8].

Although orthodontic elastomeric modules are not implanted and therefore pose little danger of soliciting an immune response, their degradation is manifested by an undesirable yellowing as well as by a reduction in stiffness and force retention. In this study, the degradative effects of environmental conditions on three polyurethane elastomeric orthodontic materials that differed in their chemical formulations and manufacturing processes were investigated. Molecular weight distribution changes were studied using gel permeation chromatography (GPC); mechanical property changes were analysed using a stress-relaxation test; and elemental chemistry changes were evaluated through X-ray photoelectron spectroscopy (XPS). Although yellowing was not obvious after treatment of the modules, ample evidence of structural and mechanical degradation was present. Apparently, the mechanism and degree of degradation were influenced by the type and duration of conditioning treatment as well as by whether the polyurethane was polyester- or polyether-based.

2. Materials and methods

2.1. Specimen preparation

A polyether-based polyurethane (Pellethane 2363-80A, Dow Chemical Company, Midland, MI, USA)

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and two polyester-based polyurethanes (Nihon HS90A, Nihon Unipolymer Company, Tokyo, Japan and Texin 480A, Miles Corporation, Pittsburgh, PA, USA) were processed into elastomeric modules (Ormco Corporation, Glendora, CA, USA) by injection moulding (Pellethane) and extrusion (Nihon and Texin). The Pellethane and Texin materials are currently used in medical applications, and the Nihon material is being considered as a possible biomaterial. To reduce any thermal or ultraviolet deterioration of the materials, the modules were stored in the dark at − 10 °C.

2.2. Conditioning treatments

The "untreated control" specimens were non-prestressed and stored in the dark at − 10 °C (conditioning treatment 0). All other specimens of each polyurethane material were prestressed on stainless steel rods during the conditioning treatments. This procedure, which was done to amplify the effects of the conditioning treatments, elongated the specimens by 50% and corresponded to a force of approximately 300 g. The "treated control" specimens were placed in a neutral environment of pH 7, 0% oxygen, and 34 °C (conditioning treatment 1). Additional specimens were stored under conditions that tested the effects of increases in environmental acidity (conditioning treatment 2), oxygen content (conditioning treatment 3), and temperature (conditioning treatment 4), and any synergistic effects of increases in all three variables (conditioning treatment 5, the "combined effects" treatment) (Table I). Specimens in conditioning treatments 1, 2, and 4 were maintained in phosphoric buffer solutions under argon, an inert gas. The specimens in conditioning treatments 3 and 5 were stored under the same conditions, except compressed air was substituted for argon.

Two sets of specimens were treated in parallel for 10-day and 100-day durations and were periodically checked for pH changes, temperature variations, or solution contamination. At the end of the 10-day and 100-day periods, the samples were dip-rinsed in deionized water, vacuum dried, and stored in the dark at − 10 °C for later analysis.

2.3. Molecular weight determination

The number average molecular weight (M_n), weight average molecular weight (M_W), and polydispersity ($PD = M_W/M_n$) were determined by GPC. The system consisted of a Waters R410 Differential Refractometer and a Waters 590 Programmable HPLC Pump interfaced with a Waters Dynamic Solutions Baseline 810 Chromatography Workstation. The column was a linear μStyragel HT with an effective molecular weight range of 5000 to 1×10^7. The system was calibrated with a set of seven narrow polystyrene standards, providing a linear calibration curve over a molecular weight range of 5000 to $> 2 \times 10^6$. The polyurethane samples were dissolved in N,N-dimethylformamide (DMF, Aldrich, 99.9 + %, HPLC grade) at a concentration of approximately 2 mg/ml. The solutions were filtered through 45 μm poly(tetrafluoroethylene) (PTFE) filters before injection. The mobile phase was DMF, which had a flowrate of 1 ml/min. The injection volume was 50 μl, and all samples had retention times of less than 12 min. All tests and any replicates were done at ambient temperature (21 °C).

2.4. Mechanical analysis

The stress-relaxation profiles of the three-link module specimens (Fig. 1) were measured with an Instron Universal Testing Machine (Instron Model TTCM, Instron Corp., Canton, MA, USA). Force magnitudes were measured with a 500 kg load cell with the full-scale loads set to 1000 g for the untreated, non-prestressed specimens, and to 400 g for the treated, prestressed specimens. Compliance of the testing apparatus was negligible relative to that of the elastomeric specimens.

At ambient temperature (21 °C), each chain was extended at 20 mm/min from an initial displacement of 8 mm to a final displacement of 20 mm. This position was maintained while the force decay was recorded from the maximum, peak force until a constant, residual force was attained after approximately 5 min. Stiffnesses were computed using the force onset curve, as defined by the slope of the secant to the curve.

2.5. Elemental analysis

For each module, the binding energies and atomic percentages were determined by XPS using a Physical Electronic PHI Model 5400 electron spectrometer. The source was a 1253.6 eV X-ray beam from

TABLE I Conditioning treatments for polyurethane modules[a]

Conditioning treatment number	Conditioning treatment description	Increased acidity (from pH = 7 to pH = 5)	Increased oxygen content (from 0% to 21%)	Increased temperature (from 34 °C to 44 °C)
0	Untreated control	n/a	n/a	n/a
1	Treated control			
2	Increased acidity	X		
3	Increased oxygen		X	
4	Increased temperature			X
5	Combined effects	X	X	X

[a] Untreated control specimens were non-prestressed and were merely stored in the dark at − 10 °C; all other specimens were elongated by 50% and treated as stated.

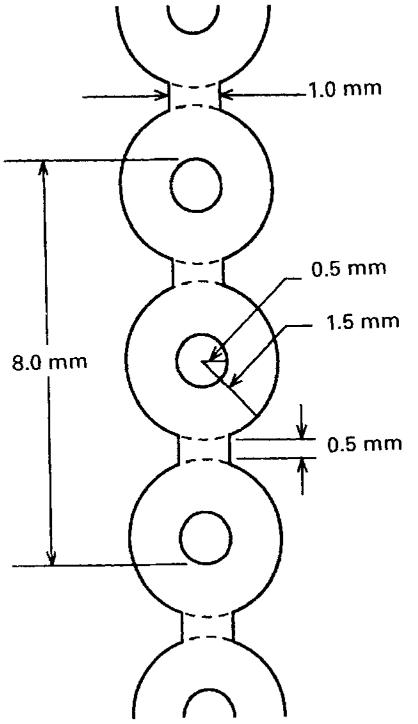


Figure 1 Schematic illustration of the three-link polyurethane elastomeric chain segment used in the mechanical analysis. Thickness of the segment was 1 mm. Measurements were taken before prestress. Drawing is not to scale.

a standard magnesium anode. Low-resolution survey scans were done on a 600 μm diameter spot size at 89.45 eV pass energy at a take-off angle of 45°. After the survey spectra were obtained, higher-resolution scans were done at a pass energy of 35.75 eV, again at a 45° take-off angle. Operating pressure during analysis was approximately 1 μ Pa. Acquisition times varied with peak intensity. Binding energies and atomic percentages were corrected by referencing the hydrocarbon C 1s peak centred at 285.0 eV. Subpeaks were deconvoluted using curve-fitting methods.

TABLE II Molecular weights of polyurethane specimens

Prod/treatment		Number average ($\times 10^{-5}$)	Weight average ($\times 10^{-5}$)	Polydispersity
Pellethane				
0 day	0	1.50	2.41	1.61
10 day	1	1.67	2.70	1.62
	2	1.78	2.78	1.56
	3	1.57	2.53	1.62
	4	1.75	2.64	1.51
	5	1.71	2.60	1.52
100 day	1	1.70	2.64	1.56
	2	1.71	2.73	1.59
	3	1.77	2.73	1.54
	4	1.71	2.70	1.58
	5	1.56	2.49	1.60
Nihon				
0 day	0	1.37	2.49	1.82
10 day	1	1.28	2.39	1.87
	2	1.24	2.32	1.87
	3	1.24	2.27	1.83
	4	1.23	2.27	1.86
	5	1.20	2.21	1.84
100 day	1	1.10	2.06	1.88
	2	1.08	2.00	1.85
	3	1.07	1.98	1.86
	4	0.90	1.68	1.86
	5	0.87	1.64	1.88
Texin				
0 day	0	1.63	2.75	1.68
10 day	1	2.05	3.20	1.56
	2	2.06	3.23	1.57
	3	2.13	3.26	1.53
	4	2.08	3.17	1.53
	5	2.10	3.20	1.53
100 day	1	1.96	3.02	1.54
	2	1.92	2.97	1.55
	3	1.85	2.84	1.53
	4	1.55	2.47	1.59
	5	1.59	2.44	1.53

3. Results

3.1. Molecular weight characterization

GPC profiles were obtained for the untreated control Pellethane, Nihon, and Texin modules, the modules after 10 days of treatment, and the modules after 100 days of treatment (Table II). The untreated Pellethane module had a M_n and M_W of 150 000 and 241 000, respectively. After 10 days of treatment, the M_n and M_W of all specimens increased, with the largest increase seen in the specimen that underwent the "increased acidity" conditioning treatment ($M_n = 178\,000$ and $M_W = 278\,000$). All *PD*s were similar and ranged from 1.51 to 1.62. After 100 days of treatment, all samples increased in M_n and M_W relative to the "untreated control" but varied slightly upward or downward relative to the values after 10 days of treatment. In this regard, only the "increased oxygen" treatment significantly and consistently increased by about 20 000 from 10 to 100 days. After 100 days, the *PD*s were generally comparable to the 10-day treatments.

Among the three untreated samples, Nihon had the highest *PD* at 1.82 and a M_n and M_W of 137 000 and 249 000, respectively. After 10 days of treatment, Nihon molecular weights decreased to a mean of 124 000 in M_n and 229 000 in M_W; the *PD*s increased slightly. The "combined effects" treatment presented the most significant decrease in molecular weights. After 100 days of treatment, all molecular weights further decreased, with the largest decreases seen in the molecular weights of the specimens that underwent the "increased temperature" and "combined effects" conditioning treatments, whose M_ns decreased to about 89 000, and whose M_Ws decreased to about 166 000. *PD*s again increased slightly relative to the untreated module.

Among the untreated samples, Texin had the highest initial M_n and M_W at 163 000 and 275 000, respectively, with a *PD* of 1.68. After 10 days of treatment, all molecular weights increased and the *PD*s dropped to about 1.54. After 100 days of treatment, specimen M_ns for the "treated control", "increased acidity", and "increased oxygen" treatments decreased slightly relative to their 10-day values. The "increased temperature" and "combined effects" treatments produced even greater decreases to the extent that 100-day molecular weight values for these samples dropped below the values for the "untreated control" sample. *PD*s remained close to 1.54 except for the "increased temperature" condition for which *PD* equalled 1.59.

3.2. Mechanical characterization

Representative force–time plots for untreated and treated specimens are presented as force onset (up to 0 min) and decay (from 0 to 5 min) regions in Figs 2 and 3. Stress-relaxation curves for the three "untreated control" specimens were similar. The Pellethane specimen displayed the largest peak load of 525 g and had the greatest stiffness (43.8 g/mm) among the three untreated materials (Table III, columns 2 and 3). The "untreated control" Nihon specimen displayed the greatest residual force (370 g) after 5 min of relaxation (Table III, column 4).

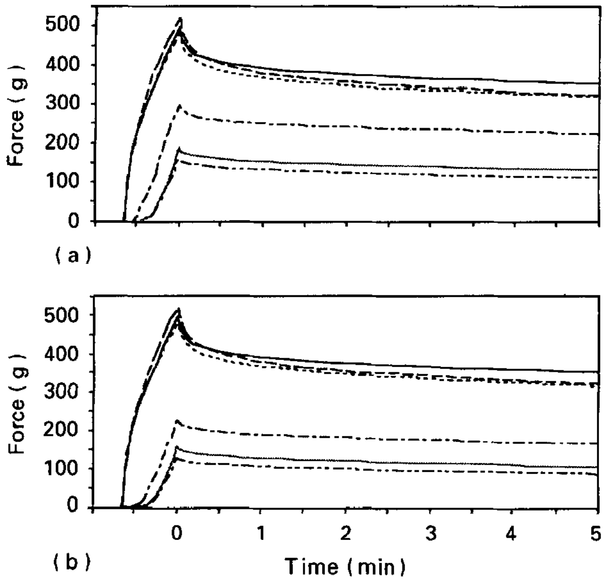


Figure 2 Force–time plot for Pellethane (— - - —) , Nihon (— - —), and Texin (——) specimens that underwent the "increased temperature" treatment for 10 days (a) and 100 days (b). The untreated Pellethane (– —), Nihon (——), and Texin (- - -) control specimens are also shown, at the top of each frame.

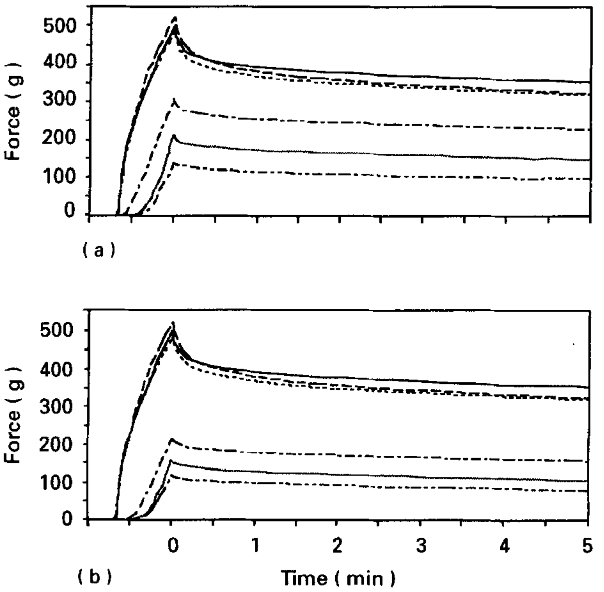


Figure 3 Force–time plot for specimens that underwent the "combined effects" treatment for (a) 10 days and (b) 100 days (— - - — Pellethane; — - — Nihon; —— Texin). The three untreated control specimens are also shown (– — Pellethane; —— Nihon; - - - Texin).

Pellethane, Nihon, and Texin specimens that underwent the "increased temperature" treatment are shown after 10 (Fig. 2a) and 100 days of treatment (Fig. 2b) in comparison with the untreated specimens of all three materials. Specimens that underwent the "combined effects" treatment are shown after 10 (Fig. 3a) and 100 days (Fig. 3b). The treated specimens exhibited permanent deformation of nominally 50% (4 mm) after both 10 and 100 days of treatment. Consequently, during initial Instron loading, a time lag was noted before force onset for the treated samples, thereby decreasing peak and residual force values for the treated, prestressed samples as compared with the force values for the non-prestressed specimens of the untreated control group.

Although the largest changes due to treatment were attributable to prestressing, the magnitudes of the decreases in peak forces, stiffnesses, and residual forces were partially dependent upon conditioning treatment

TABLE III Mechanical characteristics of polyurethane specimens

Prod/treatment		Peak force (g)	Stiffness[a] (g/mm)	Residual force (g)
Pellethane				
0 day	0	525	43.8	340
10 day	1	188	23.5	146
	2	180	22.5	138
	3	174	21.8	134
	4	164	20.5	130
	5	140	17.5	110
100 day	1	154	19.3	120
	2	156	19.5	124
	3	138	17.3	108
	4	130	16.3	106
	5	122	15.3	96
Nihon				
0 day	0	500	41.7	370
10 day	1	340	42.5	268
	2	286	35.8	224
	3	320	40.0	256
	4	300	37.5	240
	5	310	38.8	246
100 day	1	278	34.8	224
	2	266	33.3	216
	3	284	35.5	226
	4	230	28.8	184
	5	216	27.0	172
Texin				
0 day	0	485	40.4	340
10 day	1	224	28.0	170
	2	238	29.8	180
	3	240	30.0	182
	4	190	23.8	150
	5	214	26.8	162
100 day	1	204	25.5	158
	2	198	24.8	154
	3	204	25.5	158
	4	162	20.3	124
	5	160	20.0	124

[a] Stiffness = slope of force onset curve, as defined by the slope of the secant to the curve.

type, material, and treatment duration. Among the conditioning treatments, 4 and 5 generally had the greatest effect on peak force, stiffness, and residual force for all materials after 10 and 100 days. Of the three materials, Pellethane was most affected and displayed mean decreases of 356 g in peak force, 22.6 g/mm in stiffness, and 208 g in residual force after 10 days and 385 g in peak force, 26.3 g/mm in stiffness, and 229 g in residual force after 100 days. Texin exhibited mean decreases of 264 g in peak force, 12.7 g/mm in stiffness, and 171 g in residual force after 10 days and 299 g in peak force, 17.2 g/mm in stiffness, and 196 g in residual force after 100 days. Nihon was affected least and displayed mean decreases of 189 g in peak force, 2.8 g/mm in stiffness, and 123 g in residual force after 10 days and 245 g in peak force, 9.8 g/mm in stiffness, and 166 g in residual force after 100 days (Table III, columns 2–4).

3.3. Elemental characterization

Carbon and oxygen were the dominant elements detected on the surface of all samples (Tables IV–VI); nitrogen and silicon were also detected. Carbon binding energies of approximately 285.0, 286.7, and 289.0 eV corresponded to aliphatic (or aromatic), ether, and carbonyl carbons, respectively. Oxygen binding energies of 531.5, 532.7, and 534.0 eV corresponded to C–O, Si–O, and C = O, respectively. Binding energies were approximately 400.0 eV for nitrogen and 101.9 eV for silicon.

Quantitatively, surfaces of all "untreated control" specimens consisted of approximately 78% carbon, 17% oxygen, 1% nitrogen, and 2% silicon (at %). Silicon was used in the module production process as a lubricant. Small amounts of sulfur were found on the "treated control" sample of Pellethane after 10 days (Table IV), and sulfur and sodium contaminants were detected on the Nihon "treated control" sample after 10 days (Table V).

Surface oxygen-to-carbon (O/C) ratios increased after treatment for all specimens, except for the specimens that underwent the 100-day "increased temperature" and the "combined effects" treatments for Pellethane (Table IV) and the 100-day "combined effects" treatment for Nihon (Table V). All surface

TABLE IV Surface elemental makeup of Pellethane polyurethane elastomers (at %)

		Structural elements							Contaminants	Component ratios	
Component		Carbon			Oxygen			Nitrogen	Si/S/Na		
Bond type		C–C	C–O	C=O	C–O	Si–O	C=O	N–			
Binding energy (eV)		285.0	286.7	289.0	531.5	532.7	534.0	400.0	101.9/169.0/1072.0	O/C ratio	N/C ratio
Treatment											
0 day	0	58.5	19.8	2.3	1.3	3.1	12.5	1.6	1.0/ND[a]/ND	0.21	0.020
10 day	1	53.1	11.7	0.8	5.4	17.6	1.9	1.0	7.8/0.9/ND	0.38	0.015
	2	58.0	10.6	2.6	4.2	15.6	1.1	3.0	5.0/ND/ND	0.29	0.042
	3	53.7	17.5	1.2	4.9	15.4	0.9	1.8	4.6/ND/ND	0.29	0.025
	4	61.8	11.2	3.8	3.2	13.0	0.7	3.1	3.4/ND/ND	0.22	0.040
	5	56.5	16.0	3.3	5.6	11.9	0.6	3.0	3.1/ND/ND	0.24	0.040
100 day	1	52.5	13.8	1.1	5.2	17.3	0.7	1.4	8.2/ND/ND	0.34	0.021
	2	56.4	12.4	3.7	4.8	13.2	2.3	2.5	4.8/ND/ND	0.28	0.034
	3	55.8	15.8	2.8	4.1	13.7	1.1	2.2	4.5/ND/ND	0.25	0.030
	4	75.9	5.5	3.0	4.4	5.5	0.6	2.8	2.3/ND/ND	0.12	0.033
	5	68.3	7.7	4.0	4.9	7.7	1.0	3.8	2.7/ND/ND	0.17	0.048

[a] ND = none detected

TABLE V Surface elemental makeup of Nihon polyurethane elastomers (at %)

		Structural elements							Contaminants	Component ratios	
Component		Carbon			Oxygen			Nitrogen	Si/S/Na		
Bond type		C–C	C–O	C=O	C–O	Si–O	C=O	N–			
Binding energy (eV)		285.0	286.7	289.0	531.5	532.7	534.0	400.0	101.9/169.0/1072.0	O/C ratio	N/C ratio
Treatment											
0 day	0	64.5	6.9	2.9	6.9	6.2	5.2	0.9	2.7/ND[a]/ND	0.25	0.012
10 day	1	60.5	7.3	2.0	5.0	15.9	2.5	1.2	5.6/2.1/0.8	0.34	0.017
	2	56.0	10.6	3.6	6.9	12.6	2.0	1.8	5.9/ND/ND	0.31	0.026
	3	55.3	11.2	3.0	5.3	13.9	2.9	1.5	5.9/ND/ND	0.32	0.022
	4	60.3	9.4	4.3	5.3	12.1	2.7	2.3	3.7/ND/ND	0.27	0.031
	5	57.9	12.5	4.1	5.1	12.2	2.1	2.9	3.2/ND/ND	0.26	0.039
100 day	1	54.7	7.1	2.8	4.5	17.4	3.3	1.2	8.9/ND/ND	0.39	0.019
	2	53.4	10.3	3.9	6.8	13.3	4.1	1.5	6.7/ND/ND	0.36	0.022
	3	48.5	13.2	4.8	8.1	14.7	2.4	2.0	6.4/ND/ND	0.38	0.030
	4	52.6	11.6	4.8	6.1	12.8	3.7	1.9	6.5/ND/ND	0.33	0.028
	5	64.1	8.2	3.5	6.2	9.3	3.1	2.9	2.8/ND/ND	0.25	0.038

[a] ND = none detected

TABLE VI Surface elemental makeup of Texin polyurethane elastomers (at %)

Component		Structural elements Carbon			Oxygen			Nitrogen	Contaminants Si/S/Na	Component ratios	
Bond type		C–C	C–O	C=O	C–O	Si–O	C=O	N–			
Binding energy (eV)		285.0	286.7	289.0	531.5	532.7	534.0	400.0	101.9/169.0/1072.0	O/C ratio	N/C ratio
Treatment											
0 day	0	69.3	6.2	3.7	4.6	9.1	3.5	0.7	3.0/ND/ND[a]	0.22	0.009
10 day	1	56.9	8.6	2.1	5.5	16.3	2.2	0.7	7.7/ND/ND	0.36	0.010
	2	52.3	11.1	6.5	5.3	15.1	4.5	1.3	3.9/ND/ND	0.36	0.019
	3	59.4	8.6	5.6	3.5	12.4	4.9	1.8	3.1/ND/ND	0.28	0.024
	4	56.7	13.0	5.3	4.6	11.3	2.2	1.7	3.3/ND/ND	0.24	0.023
	5	57.3	4.8	1.9	8.6	13.9	1.6	1.7	10.2/ND/ND	0.38	0.027
100 day	1	54.3	6.6	3.2	6.0	17.0	2.2	1.4	9.3/ND/ND	0.39	0.022
	2	55.3	6.8	4.7	7.2	13.4	3.7	1.8	7.2/ND/ND	0.36	0.027
	3	51.7	9.4	5.5	5.3	15.8	4.3	1.7	6.3/ND/ND	0.38	0.026
	4	56.1	11.6	3.0	6.5	13.1	2.2	2.5	5.2/ND/ND	0.31	0.035
	5	58.2	11.0	3.8	4.9	12.1	2.0	3.6	4.4/ND/ND	0.26	0.049

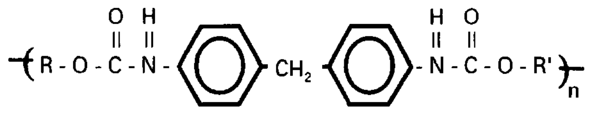
[a] ND = none detected

nitrogen-to-carbon (N/C) ratios increased, except for the 10-day "treated control" specimen for Pellethane (Table IV).

4. Discussion

4.1. General structure

A segmented polyurethane, an example of which is represented by the following formula [9], is a block copolymer made up of a linear series of amorphous soft segments and crystalline hard segments [1].



R–O is the polyol soft segment such as a linear polyether or polyester; the hard segment, methylene bis(p-phenylisocyanate) in this example, consists of the urethane and aromatic groups of a diisocyanate. A low molecular weight difunctional chain extender (R′–O) such as polyethylene oxide may also be reacted with the diisocyanate, resulting in a higher molecular weight hard segment with improved physical properties [10].

4.2. Degradation mechanisms

Methods of degradation of polyurethanes may include crosslinking and/or scission [3]. Hydrolysis at the carboxylic ester linkage is an important mechanism in the degradation of polyester-based polyurethane [10]. Because the hydrolysed group is part of the main chain structure, scission and a reduction in molecular weight result [3]. Polyether-based polyurethanes, however, are generally considered to be hydrolytically stable [11].

4.3. Correlation of molecular weight changes with molecular degradation

The increase in molecular weight for treated as compared to untreated Pellethane indicated that crosslinking, which occurs at the urethane linkages [12], was the dominant mechanism. Crosslinking could not have been very extensive, however, since the treated specimens were completely soluble in DMF. After 10 days of treatment, the "increased acidity" treatment most affected molecular weight by degradative crosslinking; the "increased temperature" treatment had the second largest effect (Table II). Since the molecular weights of specimens continued to increase to the end of the 100-day period for conditioning treatments 1 and 3, the same degradation mechanism probably occurred, except that the largest effect was now due to an increased oxygen content. Pellethane samples that underwent treatments 2 and 5 decreased in molecular weight over the period 10 to 100 days, which may indicate that scission was now dominant. The "combined effects" treatment showed the greatest degradative scission relative to the other conditioning treatments after 100 days.

Nihon exhibited a consistent decrease in molecular weight over time, confirming the hypothesis of hydrolytic chain scission in polyester-based polyurethanes. Using molecular weight changes as an indication of the extent of molecular degradation, the "combined effects" treatment (which incorporated increases in acidity, oxygen content, and temperature) had the greatest effect on the molecular degradation of Nihon modules. The "increased temperature" treatment had the most significant effect of any of the three single variables (Table II).

Texin, also a polyester-based material, exhibited an initial increase in molecular weight. In the bulk material, the increase may have been the result of crosslinking of the carbonyl double bonds in the soft segments during the early stages of oxidative degradation [13]. Once the scission mechanism was dominant (after 100 days), the "combined effects" and the "increased temperature" conditioning treatments had the greatest degradative effects (Table II). As in the case of Nihon, the increase in temperature may be an important factor in increasing the degree of chain hydrolysis at the ester linkages [6, 14].

4.4. Correlation of mechanical property changes with mechanical degradation

Differences among materials as well as the type and duration of conditioning treatment were also factors that contributed to the magnitude of mechanical degradation. As defined by a decrease in stiffness, the "increased temperature" and "combined effects" treatments were found to have the most significant effect on mechanical degradation of the three materials (Table III). Stiffness was always less after 100-day than after 10-day treatments (Figs 2 and 3, cf b and a, respectively, and Table III, column 3), indicating that a longer treatment period had a greater deteriorative effect on the materials. Treated Pellethane specimens had the least stiffness, followed by Texin and Nihon (Table III).

Note: The differences in stiffness may have been augmented by the testing process. If the Instron crosshead speed of 20 mm/min was greater than the rate at which relaxation could occur and the final displacement of 20 mm was greater than the distortion limit of the molecular covalent bonds, then mechanical bond scission may have occurred, causing decreased stiffness [3, 15].

4.5. Correlation of elemental property changes with structural degradation

Although O/C and N/C ratios for Nihon and Texin sheets are not found in the literature, the surface of Pellethane sheet has been reported to have an O/C ratio of 0.12 and a N/C ratio of 0.05 [16]. In the present study, XPS indicated that untreated Pellethane modules, which were injection moulded from Pellethane sheets, had an O/C ratio of 0.21 and a N/C ratio of 0.020 (Table IV). Values for O/C and N/C ratios reported by Han *et al.* [16] for Pellethane sheet are similar to ratios obtained in the present study for Pellethane modules after 100 days of treatment at elevated temperature (Table IV). This suggests that the thermal technique used to process modules from polyurethane sheet may have altered the chemical structure of the material surface.

Since nitrogen is only present in the hard segment, the ratio of N 1s to C 1s corresponds to the relative surface concentration of hard segments [17]. Only one of the treated elastomer specimens did not have its N/C ratio increased (Tables IV–VI). These results imply that the treated modules had an increased proportion of hard segments on the surface when compared to the untreated specimens [7], with the largest increase generally attributable to conditioning treatment 5 after both 10 and 100 days. Rearrangement of the hard segments to the polyurethane surface is facilitated by hydration fostered by the conditioning treatments [17]. With the amount of degradation during treatment indicated by the change in N/C ratio [7], the "combined effects" treatment caused the greatest degradation among the polyurethane modules.

4.6. Correlation of mechanical property changes with molecular and elemental changes

Through increased molecular weight values, the GPC results for Pellethane indicated that a crosslinking mechanism had dominated. Analyses of stress-relaxation data indicated that all Pellethane specimens (and all but one specimen overall) systematically decreased in stiffness over the period 0 to 10 to 100 days of treatment (Table III). Although, in general, an increase in stiffness should be observed if significant crosslinking had occurred [2], the coupled effect of a decrease in stiffness and an increase in molecular weight suggests that both scission and crosslinking must have occurred. The net crosslinking effect simply was not extensive enough to overcome the conformational changes associated with the scission events.

Mechanical testing also indicated that untreated Pellethane had a higher stiffness than either the untreated Nihon or Texin. This correlates with the higher hard segment proportion of Pellethane, as indicated by its higher N/C ratio (Tables IV–VI). Hard segments significantly affect mechanical properties [1]; stiffness increases with increasing hard segment proportion [12].

5. Conclusions

The ester linkages in polyester-based polyurethanes are susceptible to hydrolytic attack, and the mechanism of structural degradation differs from that of polyether-based polyurethanes. The treatment-induced decreases in the molecular weights of the polyester-based materials suggest that a chain scission mechanism dominates. Conversely, the increases in the molecular weights of the polyether-based materials suggest that a crosslinking mechanism dominates. Molecular, mechanical, and elemental analyses indicate that the type and duration of conditioning treatment affect the magnitude of polyurethane degradation; the treatment combining increases in acidity, oxygen and temperature has the greatest effect. Among the three single variables investigated, an increase in temperature appears to influence most the mechanisms responsible for the deterioration of polyurethane elastomers.

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References

1. M. SZYCHER, *J. Biomater. Applic.* 3 (1988) 297.
2. P. WRIGHT and A. P. C. CUMMING, in "Solid polyurethane elastomers" (Gordon and Breach, New York, 1969) p. 38.

3. N. GRASSIE and G. SCOTT, in "Polymer degradation and stabilisation" (Cambridge University Press, New York, 1985) p. 213.
4. Q. ZHAO, N. TOPHAM, J. M. ANDERSON, A. HILTNER, G. LODOEN and C. R. PAYET, *J. Biomed. Mater. Res.* **25**, (1991) 177.
5. M. JAYABALAN, N. SHUNMUGA KUMAR, K. RATHINAM and T. V. KUMARI, *ibid.* **25** (1991) 1431.
6. F. M. BENOIT, *ibid.* **27** (1993) 1341.
7. M. BOUVIER, A. S. CHAWLA and I. HINBERG, *ibid.* **25** (1991) 773.
8. B. J. TYLER and B. D. RATNER, in "Degradation phenomena of polymeric biomaterials" (Springer-Verlag, New York, 1992) p. 9.
9. K. ISAMA, S. KOJIMA and A. NAKAMURA, *J. Biomed. Mater. Res.* **27** (1993) 539.
10. M. D. LELAH and S. L. COOPER, in "Polyurethanes in medicine" (CRC Press, Boca Raton, FL, 1986) p. 27.
11. K. B. STOKES, *J. Biomater. Applic.* **3** (1988) 228.
12. N. HASIRCI, in "High performance biomaterials" (Technomic, Lancaster, PA, 1991) p. 71.
13. A. TAKAHARA, A. J. COURY, R. W. HERGENROTHER and S. L. COOPER, *J. Biomed. Mater. Res.* **25** (1991) 341.
14. G. OERTEL, in "Polyurethane handbook" (Hanser, New York, 1985) p. 385.
15. T. ALFREY, in "Mechanical behavior of high polymers" (Interscience, New York, 1948) p. 493.
16. D. K. HAN, K. D. PARK, K-D. AHN, S. Y. JEONG and Y. H. KIM, *J. Biomed. Mater. Res.* **23** (1989) 87.
17. A. TAKAHARA, N. J. JO and T. KAJIYAMA, *J. Biomater. Sci. Polymer Edn* **1** (1989) 17.

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