# Effects of Simulated Clinical Fabrication Heat Treatment and Artificial Weathering on the Tensile Testing of Prosthetics/Orthotics Polymers

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SYNOPSIS

The tensile behavior was compared for five prosthetics/orthotics polymers: Durr-Plex (copolyester), Polypropylene (polypropylene), Subortholen (polyethylene), Surlyn (ionomer), and Uvex (and cellulose acetate butyrate). Tensile properties, yield strength, and modulus of elasticity are related to a number of factors including composition and condition of polymers. The polymers were examined in the as-received and simulated clinical fabrication heat-treated conditions. The simulated clinical fabrication heat-treated specimens were subsequently treated to 2 weeks, 4 weeks, and 8 weeks of artificial weathering conditions, consisting of exposure to cycles of ultraviolet light and heated condensation. Tensile testing was performed on an Instron mechanical testing system, until fracture occurred. The ranges and respective rankings of yield strength and modulus of elasticity in tension were determined. Analysis of Variance (ANOVA) and post hoc Scheffé statistical analyses were performed for different polymers of the same treatment condition, and different treatment conditions of the same polymer. The analysis of variance (ANOVA) showed significant yield strength and modulus differences for the five polymers. The choice of material significantly influences the tensile properties for prosthetics/orthotics polymers. The Uvex polymer had the highest yield strength and elastic modulus, and the Surlyn polymer had the lowest yield strength and elastic modulus. The ranking trend was Uvex > Durr-Plex > polypropylene > Subortholen > Surlyn. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Several million individuals have impaired limb or spinal functions that can be ameliorated by appropriate use of external prostheses and orthoses. When replacement of entire limbs is necessary, a prosthesis should be made with some level of functionality. Efforts to improve design and use of these prostheses and orthoses are considered important by the Department of Education (DOE) and the National Institute on Disability and Rehabilitation Research (NIDRR).[1]

It has been indicated[2] that the number one priority in prosthetic and orthotic research strategies is the incorporation of modern materials by technology transfer into clinical applications to produce novel and innovative means for the fabrication of improved prosthetic and orthotic devices. An example of this incorporation is a composite orthotic leg brace[3] with one-third the weight, 40% higher stiffness, and twice the strength of its steel counterpart. It is molded from a thermoplastic composite: nylon reinforced with long discontinuous carbon fibers. However, no standards for performance existed at this time, so engineers developed their own performance requirements.[3]

Both the American Society for Testing and Materials (ASTM)[4] and the International Organization for Standardization (ISO) have been working on methods and standards that deal with performance

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rather than design. The ISO has developed an international standard[5] that specifies procedures for simplified static and cyclic strength tests where compound loadings are produced by the application of a single test force. Limitations of this standard and directions for its improvement include laboratory tests dealing with function, wear and tear, and environmental influences. Because there are no standards for such tests, appropriate procedures will need to be specified.[5]

A number of aspects relevant to an understanding of tensile behavior under accelerated environmental conditions have been investigated: (1) effect of polymer structure on the tensile behavior;[6–13] (2) effect of processing on structural degradation;[10,11,14] definitions and values of tensile strength for thermoplastic polymers with strain rates not always specified;[7–8,10,15–22] (3) definitions and values of elastic modulus;[13,15–17,19–22] (4) effect of heat treatment;[7,8,18,23,24] (5) natural or outdoor weathering;[13,21,22] and (6) artificial weathering.[18,20–22,25] In addition, limited statistical analyses[10,15–18,20] and rankings development[19,20,22] have been published.

Difficulties in evaluating previous research include the following: nonstandardized weathering conditions and testing devices, nonoverlapping selection of polymers as compared to those used in prosthetics/orthotics applications, specimen thicknesses not representative of clinical usage, variable strain rates for testing, and a lack of statistics.

## OBJECTIVE

The objective of this study was to systematically examine the effects of simulated fabrication heat treatment and artificial weathering conditions (processing) on the tensile properties for consistent comparisons among currently used prosthetics/orthotics polymers.

## MATERIALS

The following polymers were investigated: Durr-Plex (DP), Polypropylene (PP), Subortholen (SB), Surlyn (SR), and Uvex (UX). The PP material was purchased from Durr-Fillauer Medical, Inc., Chattanooga, TN. The DP, SB, SR, and UX polymers, were purchased from PEL Supply Co., Cleveland, OH. The suppliers list the DP, PP, SB, SR, and UX polymers, as being polyethylene terephthalate, polypropylene, polyethylene, ethylene methacrylate ionomer, and cellulose acetate, respectively.

## METHODS

### Simulated Clinical Fabrication Heat Treatment (SC)

The simulated clinical fabrication heat treatment (SC) method consisted of placing the three materials, 6″ square specimens approximately $\frac{1}{4}$″ thick, on preheated Teflon®-coated aluminum sheets in convection blower ovens (Grieve, Models AB-500 and 3-3-3, Round Lake, IL), heated at the supplier's recommended temperatures for 15–20 min, until bubbles started to form around the periphery, the corners were pliable, and the materials became transparent. The materials were then covered with a second, preheated, Teflon®-coated aluminum sheet, and allowed to air cool on the bench top. This method of oven heating and air cooling reflects only a part of the current processing of the materials. The complete sequence for a "clinical fabrication process" would be: convection oven heating, deforming or molding specimens around curved surfaces on cold and often wet plaster casts, and letting the specimens air cool to room temperature. The use of aluminum sheets allows for a more uniform cooling than cold and/or wet plaster casts. The forming temperatures were 148–163°C for the DP, 204°C for the PP, 177–204°C for the SB, 177°C for the SR, and 148–163°C for the UX polymers, respectively.

### Artificial Weathering (AW) Treatment

For the artificial weathering (AW) treatment, a Q-U-V Accelerated Weathering Tester® (Q-Panel Co., Cleveland, OH) was used. The test chamber was constructed of corrosion-resistant materials enclosing eight fluorescent ultraviolet (UV) lamps, a heated water pan, test specimen racks, and provisions for controlling and indicating operating times and temperatures. The test specimens were mounted in stationary racks with the plane of the test surface parallel to the plane of the lamps at a distance of 50 mm from the nearest surface of the lamps. The lamps were UV-B lamps with a peak emission at 313 nm. Only one side was exposed to the UV light. Water vapor was generated by heating a water pan extending under the entire sample area. Specimen racks and the test specimens themselves constituted the side walls of the chamber so that the back sides of the specimens were exposed to cooling effects of ambient room air. The resulting heat transfer caused water to condense on the test surface. The specimens were arranged so that condensate ran off the test surface by gravity and was replaced by fresh con-

densate in a continuous process. Vents along the bottom of the test chamber were provided to permit an exchange of ambient air and water vapor to prevent oxygen depletion of the condensate. The cycle timer had a continuously operating cycle time for programming the selected cycle of UV periods and condensation periods. The specimen temperature was monitored by a thermometer with a remote sensor. The instrument was operated continuously, repeating the cycle of 8 h with UV light at 60°C, and 4 h without UV light at 50°C.

The specimen conditions were as-received (AR), simulated clinical fabrication heat treatment without weathering (SC0W), simulated clinical fabrication heat treatment and weathered for 2 weeks (SC2W), 4 weeks (SC4W), and 8 weeks (SC8W). Only specimens of the materials in the SC condition were further exposed to artificial weathering. No unprocessed, as-received specimens were weathered.

### Tensile Testing

The materials were obtained in 4 × 6′ sheets, approximately 1/4″ in thickness. The dimensions of the specimens were based on those suggested by the ASTM (American Society for Testing and Materials, Philadelphia, PA), in "Standard Test Method for Tensile Properties of Plastics," D638-87a. Specimens were cut to approximately 5′ in length and 1′ in width with a band saw, and smoothed by milling. To form the narrowed midsection, a 4′ diameter spiked wheel bit was used in the drill press. A paper template was used as a guide for the wheel bit to follow. The thickness and width at the narrow section of each specimen was measured the nearest 0.001 inch prior to placement in the tensile test machine.

An electromechanical tensile test machine, Instron Model (Instron Corp.) was used for the tensile testing. This machine has a constant rate of crosshead movement and comprises essentially the following: a fixed or essentially stationary member carrying one grip, a movable member carrying a second grip, a drive mechanism for imparting to the movable member a uniform controlled velocity with respect to the stationary member, and a load-indicating mechanism, a strip chart recorder, showing the total tensile load carried by the test specimen when held by the grips.

The specimens were placed in the grips of the Instron, taking care to align the long axis of the specimen and the grips with an imaginary line joining the points of attachment of the grips to the machine. The grips were hand tightened evenly and firmly to the degree necessary to prevent slippage of the specimen during the test. The crosshead speed, 2′/min, was selected by considering the ASTM standard test method D638-87a and choosing a rate that would cause all materials to fracture within the same parameters.

The yield (ultimate) tensile strength was calculated by dividing the maximum load in pounds-force (from the strip-chart recorder) by the original minimum cross-sectional area of the specimen and then converting to MPa. The modulus of elasticity was calculated by extending the initial linear portion of the load-extension curve and dividing the difference in stress corresponding to the segment of the curve by the corresponding difference in strain. The modulus values were converted to MPa. The averages and standard deviations were calculated. The analysis of variance (ANOVA) and post hoc Scheffé comparisons, at a $p$-value for significance of 0.05, were performed using the Statistica™ software (StatSoft, Tulsa, OK) to determine significance for: (1) yield strength and modulus of elasticity among the different polymers but same condition; and (2) yield strength and modulus of elasticity within the same polymer but different conditions.

## RESULTS

The calculated values of yield stress and elastic modulus in tension for five commonly used prosthetics/orthotics polymers are shown in Figures 1 and 2 as a function of specimen condition, due to the SC and the AW treatments. The ranges (MPa) were 15.7–59.1 for the yield strength and 456–2505 for the elastic modulus. Yield strength and elastic modulus were analyzed for statistical differences. Comparisons were made between different polymers

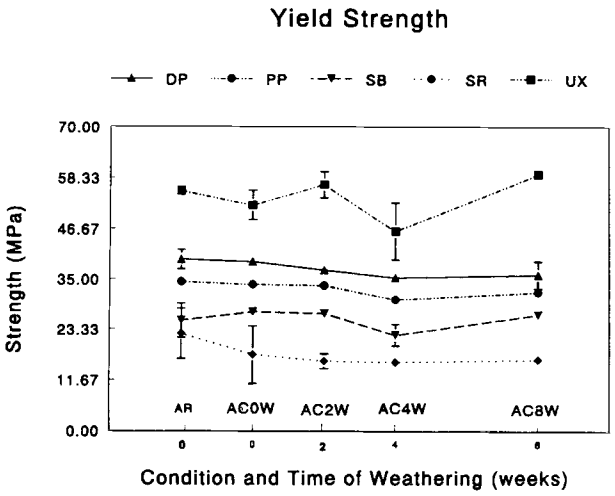


**Figure 1** Yield strength as a function of as-received, simulated fabrication heat-treated, and artificial weathering conditions.

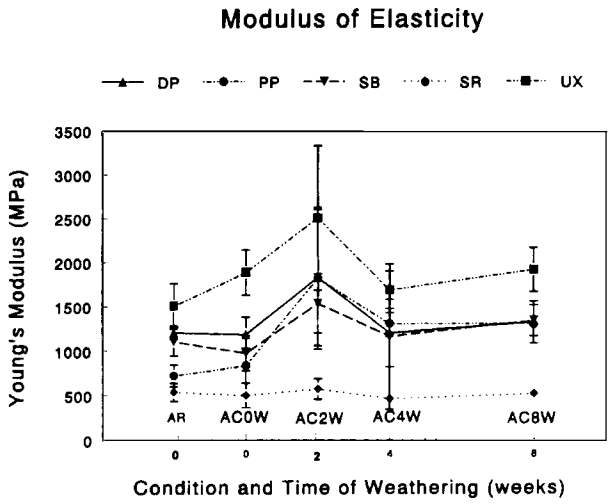


**Figure 2** Elastic modulus as a function of as-received, simulated fabrication heat-treated, and artificial weathering conditions.

and between different conditions of the same polymer. The ranges for the standard deviation divided by the average (in percent) were 0.9–38.2% for the yield strength and 2.5–70.8% for the elastic modulus. The elastic modulus standard deviations were larger in 12 out of 15 condition comparisons than with the corresponding yield strength standard deviations.

## DISCUSSION

The effects of simulated fabrication heat treatment and artificial weathering conditions (processing) applied in a consistent manner, on the tensile properties among currently used prosthetics/orthotics polymers in typical specimen thicknesses, showed significant differences among the polymers due to composition, indicated by an analysis of variance. The Scheffé test showed that not all polymers were significantly different from each other. In the yield strength rankings, the UX and DP polymers had the highest yield strengths and were significantly different from each other, with the UX polymer having the higher strength. The PP and SB polymers were in the middle, with the PP generally having a higher strength than the SB polymer. The SR polymer had the lowest yield strength. In the elastic modulus rankings, the UX polymer had the highest elastic modulus. The trend in the middle was generally DP, SB, and PP, although none were significantly different from each other. The SR polymer had the lowest elastic modulus. The highest and most desirable yield strengths and elastic moduli were generally in the two amorphous materials, DP and UX, and may be due to bulky terephthalate backbone in DP, or side groups, acetate and butyrate groups attached to cellulose in UX, inhibiting chain movement.[26] The PP polymer had a yield strength range of 30–34 MPa, and a modulus of elasticity range of 720–1820 MPa. The literature values for polypropylene were a yield strength range of 29–39 MPa and a modulus of elasticity range of 1032–1720 MPa.[17] Because these polymers exhibit viscoelastic behavior, the strain-rate sensitivity is a concern and should be stated when discussing test results.[15,16] The test parameters were not always specified in the literature. The settings selected allowed for a comparison of the materials under the same conditions. Even though the SR polymer has a relative ease of formability, it would not be suitable for a rapid prototyping application due to surface irregularities produced in milling.

The analysis of variance indicated significant differences among the polymers due to composition. The Scheffé test indicated which polymers were significantly different from each other. Detection of significant differences may have been limited by the low number of samples per group, 3–5, the difficulties in milling, the use of an electromechanical testing machine with chart paper, the intervals selected for testing, and the range of the standard deviations was 0.9–38.2% for the yield strength and 2.5-70.8% for the elastic modulus. The larger standard deviations that occurred in the elastic modulus as compared with the corresponding standard deviations in yield strength may be attributed to the viscoelastic behavior of the polymers and any variability in the region used for the calculations. As this was a pilot study, the number of samples was limited. Only one side of the polymer samples had UV exposure because clinically, one side is in close contact with tissue and not exposed. Clinically used sample thicknesses were used because degradation has been shown to be most extensive at or near film surfaces, and it is unknown if the effect of weathering is more of a cosmetic and hygienic problem than a mechanical properties problem.[29]

### Effect of the SC Treatment

The SC treatment produced decreases in the yield strengths for all polymers, and decreases in the elastic moduli for the DP, SB, and SR polymers. Although there were significant differences in the yield strengths and elastic moduli among the group of polymers, there was no significant difference due to the heat-treatment conditions. This suggests that if chain rearrangement and/or degradation occurred during simulated clinical fabrication heat treatment,

the tensile properties were not significantly influenced. The SC treatment did not incorporate any forming process that would produce molecular orientation.[6] A forming process may result in a section that is prone to failure due to a high concentration of stresses.[19]

### Effect of the AW Treatment

At the end of the 8 weeks AW treatment period, there were decreases in yield strength for all polymers except the UX polymer. Significant yield strength changes were identified at the 4 weeks and 8 weeks weathering periods. While nonsignificant increases in elastic modulus were noted for all polymers at the end of the 8 weeks' AW treatment period, the analysis of variance indicated significant differences in the PP ($p$-level of 0.018) polymer group. The trend changes in the yield strength did not correspond to similar trend changes in the elastic modulus. Degradation due to light may be seen as a two-step process; instantaneous formation of free radicals that are highly reactive; and a series of temperature-sensitive chemical reactions, comparatively slow in rate, having great effects on the mechanical properties.[18]

Although not yet quantified, chemical structure changes have been identified during the AW treatment periods and would be expected to influence the tensile properties via crosslinking and crystallinity changes.[27] In the DP polymer, the changes identified were: unsaturation (C=C, C=C—H, C=C=C, and C≡C—H), oxidation (C=O), and hydroxylation (OH). In the PP polymer, the chemical structural changes identified were: unsaturation (C=C, C=C—H, and C≡C—H), oxidation (C=O), and hydroxylation (OH). In the SB polymer, the changes identified were: unsaturation (C=C, and C=C—H), and oxidation (C=O). In the SR polymer, the changes identified were: oxidation (C=O), hydroxylation (OH), and ester changes (COO). In the UX polymer, the changes identified were: unsaturation (C=C, C=C—H, C=C=C, and C≡C—H), oxidation (C=O), hydroxylation (OH), and ester changes (COO). Chemical structure changes may have either a delayed impact on the mechanical properties or are required to produced extensive structural modifications before the properties are altered.[29]

During the SC0W–SC2W time period, there were decreases in the yield strengths for all polymers, except the UX polymer. There were increases in the elastic moduli for all polymers. None of the changes were significant. There was a significant difference in elastic modulus for the PP polymer between the AR condition and the SC2W condition at the $p$-level of 0.039. There was a significant difference in elastic modulus for the PP polymer between the SC0W condition and the SC2W condition at the $p$-level of 0.072. The enhancement of elastic modulus can result from two structural modifications, both of which are possible, crosslinking and crystallinity.[13] The PP, SB, and SR polymers showed an increase in degree of crystallinity.[28]

During the SC2W–SC4W time period, there were decreases in the yield strengths and elastic moduli for all polymers. Significant differences were detected in the yield strengths for the PP and UX polymers. The degree of crystallinity[28] decreased for the PP and SB polymers, and increased for the SR polymer, which was attributed to a reduced concentration of carbonyl groups.[27]

During the SC4W–SC8W time period, there were increases in the yield strengths for all polymers with the increase significant for the UX polymer. These increases were consistent with the behavior of 4-year naturally weathered polyethylene samples. The tensile strength decreased during the first 3 years, and increased slightly during the fourth year.[22] There were decreases in the elastic moduli for the DP and PP polymers, and increases for the SB, SR, and UX polymers. The elastic moduli were not significantly different. The degree of crystallinity[28] decreased for the PP, SB, and SR polymers.

### Stability Index Rankings After 8 Weeks AW Treatment

Stability index rankings considering the percentage change in yield strengths and elastic moduli after the artificial weathering treatment, from most desirable to least, for the time period from 0–8 weeks, were established. The yield strength rankings with the percent change (%) were, respectively: SB (−2.4), PP (−5.1), SR (−6.6), DP (−7.7), and UX (13.5). The elastic modulus rankings with the percent change (%) were, respectively, UX (1.3), SR (2.8), DP (11.5), SB (37.3), and PP (54.2). An approximate order of weather resistance has been listed for 10 polymers.[29] Even though polypropylene, ethylene methacrylic acid copolymer, and cellulose acetate butyrate were not included, a rating of relative weather resistance was listed as polyethylene terephthalate > polyethylene > cellulose, corresponding to DP, SB, and UX. This ranking was not similar to the yield strength or elastic modulus rankings from this study. The criteria were not specified for the rankings, but the main types of failure in polymers were attributed to discoloration, and loss of mechanical and electrical properties.[29]

When another tensile property, elongation to rupture, was used to evaluate the accelerating performance of various AW testers and a similarity to outdoor exposure, rankings changed with the tester.[22] Problems have been noted in correlating accelerated weathering and outdoor exposure, especially when changes are small and data scattering is large.[22] Further investigation into this area is warranted to develop accelerated environmental methods that would more closely model clinical conditions and to assess the contribution of degradation to fatigue.[14]

## CONCLUSIONS

A consistent method was used to investigate the effects of simulated clinical fabrication heat-treatment and artificial weathering conditions (processing) on the hardness properties among currently used prosthetics/orthotics polymers. The yield strength and elastic modulus parameters and rankings for currently used prosthetics/orthotics polymers in the as-received, simulated clinical fabrication heat-treatment and artificial weathering conditions were established. The SC treatment did not significantly affect the tensile properties comparing the as-received to the heat treated without weathering time periods, AR and SC0W. The AW treatment did not significantly affect the tensile properties comparing the initial to the final weathering time periods, SC0W and SC8W. There were, however, trends and significance differences among the 2-week, 4-week, and 8-week comparisons.

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