

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

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## SYNOPSIS

The hardness behavior was compared for five prosthetics/orthotics polymers: Durr-Plex (copolyester), Polypropylene (polypropylene), Subortholen (polyethylene), Surlyn (ionomer), and Uvex (and cellulose acetate butyrate). The hardness is related to a number of factors including the composition and condition of the 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. Five measurements were taken for each treatment condition using a Durometer hardness tester. The hardness ranges and the respective rankings for the polymers 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 hardness differences for the five polymers. The choice of material significantly influences the mechanical property of hardness for prosthetics/orthotics polymers. The Durr-Plex polymer had the highest hardness and the Surlyn polymer had the lowest hardness. The ranking trend was Durr-Plex > Uvex > 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).<sup>1</sup>

Generally, limb-replacement prosthetic devices are covered with a plastic material. Esthetics and function, rather than biocompatibility, dictate the choice of plastic materials. Low density, ultraviolet-visible light stability, and resistance to dirt and/or staining are essential properties for the plastics used in external prosthetic systems.<sup>2</sup> It has been indicated<sup>3</sup> 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<sup>4</sup> 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

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discontinuous carbon fibers. However, no standards for performance existed at this time, so engineers developed their own performance requirements.<sup>4</sup>

Both the American Society for Testing and Materials (ASTM)<sup>5</sup> and the International Organization for Standardization (ISO) have been moving toward writing standards that deal with performance rather than design. The ISO has continued work leading to the development of an international standard.<sup>6</sup> 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.<sup>6</sup>

Due to the fact that prosthetics/orthotics polymers are usually heated and molded (thermoplastic) to plaster casts and must function in the environment, the influences of processing conditions and environmental factors, such as heat and moisture treatments,<sup>7</sup> irradiation,<sup>8-11</sup> and both outdoor and artificial weathering<sup>12-18</sup> must be considered on the mechanical properties. Processing conditions and environmental factors have been shown to produce structural changes such as oxidation-induced chain scission and crosslinks<sup>8,19</sup> and ultraviolet irradiation crystallinity changes.<sup>16</sup>

It is the intent of a clinic team to provide an appliance that will stand up under the strain of constant use.<sup>20</sup> During constant use, the outer surface may become indented. Hardness is essentially resistance to indentation and a complex surface property related to mechanical properties of a material as strength, modulus, and plasticity and microstructure.<sup>21,22</sup> However, differing methods of testing, limited coverage of the polymers<sup>23-26</sup> used in prosthetics/orthotics, and varying conditions of the samples, do not allow for effective comparisons, especially in regards to the effects of heat treating and weathering.

## OBJECTIVE

The objective of this study was to systematically examine the effects of simulated fabrication heat treatment and artificial weathering conditions (processing) on the hardness 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 polymer 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 polymers, 6" square specimens approximately  $\frac{1}{4}$ " thick, on preheated Teflon<sup>®</sup>-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 polymers became transparent. The polymers were then covered with a second, preheated, Teflon<sup>®</sup>-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 polymers. 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<sup>™</sup> (Q-Panel Co., Cleveland, OH) was used. The test chamber was constructed of corrosion-resistant polymers 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 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 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 condensate 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 polymers in the SC condition were further exposed to artificial weathering. No unprocessed, as-received specimens were weathered.

### Hardness Testing

The hardness testing was based on ASTM standard D2240 (ASTM, Philadelphia, PA). The sample thickness was approximately  $\frac{1}{4}$  inch. The samples were placed on a bench for support. A Durometer hardness tester (Pacific Transducer Corp) Model 307L Type D meets or exceeds the ASTM D2240 specifications and covers a range sufficient to include these polymers on the same scale. It was held vertically with the point of the indenter at least  $\frac{1}{2}$  inch from any edge. The presser foot was applied to the samples quickly with firm force, without shock and parallel to the surface. Sufficient force was applied to allow for firm contact between the presser foot and the samples. Five readings were taken. The testing scale was 0–100 hardness numbers and has an inverse relationship to indentation; the higher the number, the lower the hardness. At a hardness number of zero, there is an indentation of 0.100 inches into the sample, and at a hardness number of 100, there is no indentation into the sample. Each hardness number represents 0.001 inch of inden-

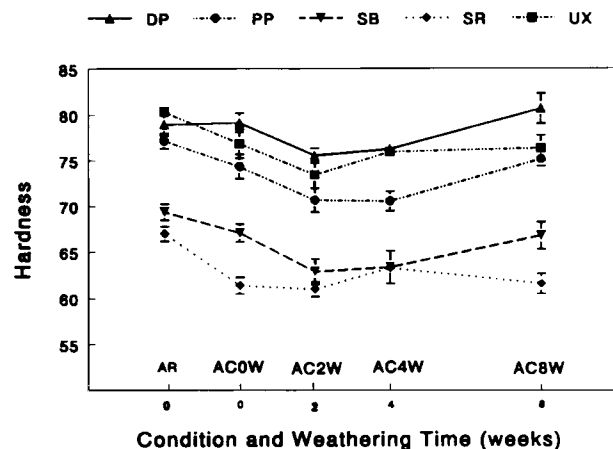
tation. The indenter is a 30° spherocone with an 0.004-inch radius end.<sup>24</sup> The averages, standard deviations, analysis of variance (ANOVA), and post hoc Scheffé tests were performed using the Statistica<sup>®</sup> software (StatSoft, Tulsa, OK). The *p*-value for significance was 0.05.

### RESULTS

The hardness values using a Durometer hardness tester for five commonly used prosthetics/orthotics polymers are shown in Figure 1 as a function of specimen condition, due to the SC and the AW treatments. The Durometer hardness values for all samples ranged from 61–80.7. The hardness ranges were 75.6–80.7 (DP), 70.6–77.2 (PP), 62.9–69.4 (SB), 61.0–67.0 (SR), and 73.5–80.4 (UX). When the hardness values were analyzed by comparisons between different polymers, and between different conditions of the same polymer, statistical differences were noted due to composition and condition. The standard deviation range was 0.35–1.78. The ranges for the standard deviation divided by the average (in percent) were 0.47–2.81%. The rankings of the polymers by condition are shown in Table I. The effects of SC Treatment on the hardness is shown in Table II.

### DISCUSSION

The effects of simulated clinical fabrication heat treatment and artificial weathering conditions (processing) applied in a consistent manner, on the



**Figure 1** Graph of durometer hardness as a function of simulated clinical fabrication heat treatment and artificial weathering treatments.

**Table I** Rankings of Polymers by Condition

AR:	UX $\cong$ DP $\cong$ PP > SB > SR
SC0W:	DP $\cong$ UX $\cong$ PP > SB > SR
SC2W:	DP $\cong$ UX > PP > SB $\cong$ SR
SC4W:	DP $\cong$ UX > PP > SB $\cong$ SR
SC8W:	DP $\cong$ UX > PP > SB > SR

> Is significantly different.

$\cong$  Is not significantly different.

hardness 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 rankings, the DP and UX polymers had the highest hardness, but not significantly different from each other. The PP and SB polymers were in the middle, with the PP polymer having a significantly higher hardness than the SB polymer. The SR polymer had the lowest hardness. The SR hardness range of 61–67 was comparable to the Du Pont Bulletin range of 50–75.<sup>25</sup>

The influence of structural characteristics such as functional groups and crystallinity on the hardness can be noted for the polymers with the two highest hardnesses. The DP and UX polymers were amorphous (low crystallinity)<sup>28</sup> and had bulky backbone or side groups, which may inhibit chain movement. A terephthalate group (phenyl ring with a carbonyl group) is part of the backbone in the DP polymer chain. Acetate and butyrate groups attached a cellulose backbone are part of the UX polymer.<sup>27</sup> The SR polymer is composed of three phases of crystalline and amorphous phases and cluster<sup>30</sup> and showed a lower degree of crystallinity<sup>29</sup> than the SB polymer.

#### Effects of the SC Treatment

The SC treatment decreased the hardness for all polymers except the DP polymer. This effect was significant for the PP, SR, and UX polymers. In the PP polymer, this could be related to the occurrence of unsaturation and oxidation,<sup>28</sup> and a decrease in crystallinity.<sup>29</sup> Unsaturation and oxidation occurred in the SB polymer<sup>28</sup> reflecting degradation, whereas the increase in degree of crystallinity<sup>29</sup> may have been due to realignment of the polymer chains. In the SR polymer, COO functional group was more readily identified, suggesting chain modification, without any indication of oxidation or unsaturation in the FTIR spectrum,<sup>28</sup> and the degree of crystal-

linity decreased.<sup>29</sup> In the UX polymer, unsaturation and oxidation-related peaks in the FTIR spectrum could be associated with degradation processes.<sup>28</sup>

#### Effects of the AW Treatment

At the end of the 8-week weathered (SC0W–SC8W) time period, the final hardness for each of the polymers was not different compared to the initial SC treatment hardness. Short-term weathering (0–2 weeks, 2–4 weeks, and 4–8 weeks) time periods, did demonstrate significant changes. During the 2-week weathered (SC0W–SC2W) time period, all polymers showed a decrease in hardness and were significant except for the SR polymer. During the 4-week weathered (SC2W–SC4W) time period, all polymers except PP showed an increase in hardness, but only the SR polymer increase was significant. During the 8-week weathered (SC4W–SC8W) time period, the hardness increased for all polymers except the SR polymer, with insignificant changes for both the SR and UX polymers.

## 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 Durometer hardness ranges and rankings for clinically used prosthetics/orthotics polymers were established. The choice of material significantly influences the mechanical property of hardness for this group of polymers. The DP polymer had the highest hardness, the PP and SB polymers were in the middle, and the SR polymer had the lowest hardness. The hardness ranking trend (hardest to softest) was generally DP > UX > PP > SB > SR. The SC treatment significantly affected the hardness for the PP, SR, and UX polymers. The AW treatment did not sig-

**Table II** Effects of SC Treatment on the Hardness

DP:	SC0W $\cong$ AR
PP:	AR > SC0W
SB:	AR $\cong$ SC0W
SR:	AR > SC0W
UX:	AR > SC0W

> Is significantly different.

$\cong$  Is not significantly different.

nificantly affect the hardness comparing the non-weathered to the 8-week weathered samples. There were, however, significant differences due to the AW treatment among the 2- and 4-week comparisons.

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