

Prediction of Service Lifetime and Performance of a Prosthetic Thermoplastic

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SYNOPSIS

The service lifetime and performance for a prosthetic and orthotic thermoplastic, Subortholen™, was measured using correlations between artificial and natural weathering degradation data of (1) the accumulated carbonyl compound concentration at the polymer surface, (2) changes in thickness of the surface reaction zone, and (3) changes in hardness and tensile properties. An empirical, mathematical relationship between artificial and natural weathering exposures is presented. Results show that the hardness degradation is a useful parameter to estimate the different stages in clinical performance of Subortholen. Corroborating hardness, tensile properties, and weathering exposure time, the service lifetime for Subortholen was determined to be 4–6 years. This finding indicates that the correlation between artificial and natural weathering degradation may provide an effective way to calculate the most appropriate time to replace a worn prosthetic or orthotic device before the device passes into a dangerous stage. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polymeric prosthetic and orthotic devices are exposed to the outdoor environment during clinical service. Such prolonged outdoor exposure (weathering) can attack these polymers, resulting in the deterioration of their molecular structures and mechanical properties.^{1,2} Occasionally, devices made from such polymers gradually lose their ability to perform and may become unsafe to use.^{3,4} In this regard, there is a need to develop methods and techniques useful for predicting the service lifetime and performance of polymers used for prosthetics and orthotics. The goal of this work was to develop a method for measuring the service lifetime for polymers used in clinics.

Prediction of outdoor performance for a polymer can be obtained by measuring the time required for it to achieve the same incremental or decremental changes in a specific properties that it might under artificial or natural weathering exposure. Correlations between the natural degradation of polymer

properties and results obtained in the laboratory have been reported.^{5–8} Although many variables are involved in influencing the correlations,^{9–14} it appears that a comparative (not absolute) relationship can still be established.^{13–16} Many material properties which are degraded by weathering have been examined: chemical composition,⁵ color,^{6,8} hardness,^{16,17} tensile properties,^{5–8} and impact resistance.⁸ An exponential equation appears to adequately describe the most common type of relationship between artificial and natural weathering.^{6–8} However, since many variables are involved during weathering, the correlations reported in other studies should be restrictively applied to specific polymers. In other words, results obtained from different laboratories for one specific polymer cannot be used to predict the natural lifetime of a different polymer. Thus, experiments were designed in this study to explore the effects of weathering on polymers used in prosthetics and orthotics.

To learn which correlations are meaningful, changes in chemistry within the surface reaction zone and in thickness of the zone were selected, since these two parameters play important roles in dominating the degradation in molecular structures and

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mechanical properties.^{1,2} Therefore, quantitative measurement of weathering products (i.e., accumulated [C=O] and reaction zone thickness) as functions of either artificial or natural weathering exposure were undertaken. In addition, the bulk properties of this material (tensile properties) were examined, because changes in properties at the surface layer can significantly influence overall bulk properties.¹⁸⁻²⁰ Because strength and ductility play an important role in the clinical performance of polymers,^{21,22} changes in the ductility and strength during weathering were monitored to determine the clinically safe or unstable stages of polymer employed.

Prediction of the service lifetime and performance was accomplished by correlating the degradation of bulk properties with the degradation in hardness. Hardness was chosen because it offers two advantages: First, it prevents variations from sample preparations since other properties may vary greatly with the sample sizes and shapes. Second, and more importantly, it tests characteristics that are more sensitive to changes at the surface layer of the exposed material since weathering is absolutely a surface phenomenon.¹⁶

In this study, the clinical safe lifetime of a polymer is defined as the time period during which the polymer had degraded to 50% of its total degraded value. Beyond 50% degradation, the polymer is assumed to be no longer stable for clinical service. The use of "50%" as an index has been reported in some studies.^{8,23} We define the useful lifetime of our polymer to be restricted to the period in which both strength and ductility are reduced to 50% of its total degraded values. After this stage, clinically unacceptability is declared.

In the present study, changes in chemistry and in physical and mechanical properties that resulted from both artificial and natural weathering were quantitatively and qualitatively examined. This study was designed to examine the correlation of changes in properties between artificial and natural weathering to measure and predict the remaining useful lifetime and long-term clinical performance of the polymer employed.

MATERIALS AND METHODS

A commercial semicrystalline thermoplastic, SubortholenTM (medium density ethylene-based copolymer with $\rho = 0.935 \text{ g/cm}^3$, $\bar{M}_w \approx 8.22 \times 10^5 \text{ g/mol}$, $\bar{M}_w/\bar{M}_n \approx 31.7$, Pel Supply, Cleveland, OH) used to fabricate prostheses and orthoses, was em-

ployed in this study. In a previous study,² we characterized Subortholen through FTIR. It has been found that in addition to polyethylene Subortholen consists of numerous additives, impurities, antioxidants, chromophores, and preexisting carbonyl compounds.

Both artificial and natural weathering were applied to machined, tensile test specimens to induce the changes in physical and mechanical properties. Changes in selected properties were correlated to establish the relationship between artificial and natural weathering.

Artificial Weathering

Artificial weathering of samples was performed by placing 144 machined tensile test specimens of Subortholen in an artificial weathering tester (Q-Panel, Cleveland, OH) for 10 weeks, exposing them to repetitive cycles of 8 h of UV light (313 nm wavelength) at 80°C, followed by 4 h at 60°C in water vapor. During the weathering process, seven specimens were removed from the artificial weathering tester every 4 days to examine changes in different properties. The 4 day interval was chosen so that for each weathering condition the population of samples would be more than six.

In the artificial weathering tester, test specimens were mounted on stationary racks with the plane of the test surface parallel to the plane of UV lamps at a distance of 50 mm from the nearest surface. The throughput of UV radiation during the artificial weathering was controlled by replacing the two oldest lamps out of a total of eight lamps every 400 h of total lamp operation to assure the homogeneity of the UV radiation.

Natural Weathering

Outdoor, natural weathering was performed by placing an additional 144 tensile dumbbells in the open air at the Chicago Lake Front between May 13 and November 5, 1991. Temperature and percent humidity were recorded daily. Every 2 weeks, 12 specimens were removed and stored indoors at room temperature until characterization.

Measurements of Property Changes

For both artificially and naturally weathered samples, the accumulation of carbonyl compounds at the exposed sample surface was examined using Fourier transform infrared spectroscopy (FTIR,

Analect, Irvine, CA). Changes in carbonyl compound concentration was measured because it is the most significant weathered product which causes changes in the polymer structure.^{1,2} A FTIR microscope was used to assure that each observation was made within the surface reaction zone area (<0.1 mm). The weathering generated [C=O] was quantitatively measured by taking the ratio of the area under the C=O absorbance peak (1715 cm⁻¹) over the area under the strongest CH₂ stretching peak (2920 cm⁻¹). The strongest CH₂ stretching served as an internal standard,²⁴ since weathering exposure does not influence this peak. In addition, an internal standard was used to eliminate sample-to-sample variations (e.g., geometry or thickness). Before testing, specimens were stored in a vacuum desiccator for 48 h to minimize the moisture content inside the samples. Absorption spectra were obtained at a resolution of 4 cm⁻¹ averaged over 256 scans for each specimen. High-pressure nitrogen gas was purged into the system during FTIR scanning to ensure a clean and stable background.

Thickness of the surface reaction zone as a function of either artificial or natural weathering exposure was monitored using an optical microscope from samples sectioned normal to surface planes. Six readings were taken from six samples (i.e., one reading for each sample) for each weathering condition.

Dumbbell-shaped tensile specimens with the following dimensions were used for tensile tests: gauge length (8.7 mm), thickness (3 mm), width of narrow section (4 mm), and total length (39 mm). Tensile testing was performed on a static testing machine (Instron, Canton, MA) with a crosshead speed of 1.27 mm/min. Tensile strength at yield was calculated by dividing the maximum load by the original cross-sectional area of the specimen. Percent elongation at break was calculated by dividing maximum extension at break by the original gauge length. Specimens treated under different weathering conditions were tested. Six samples were used for each weathering condition.

Hardness measurements were carried out with a Tukon hardness tester (Wilson, Bridgeport, CT) under a 25 g applied load by a Knoop diamond indenter. The 25 g applied load was selected because it gave an optimum indentation length which was easily located optically within the damaged area. Before measurement, the instrument was calibrated into a zero indentation condition under no load applied. Ten readings were randomly taken from six samples for each weathering condition.

A computer statistical software package, (CSS, Statsoft, Tulsa, OK) was utilized to examine the significance of linear regression using a least-square linear approach between the observed and predicted values at the 0.95 confidence level. The correlation coefficient *r* and the probability *p* values calculated from the Pearson correlation are presented.

RESULTS

The logarithmic plots of the accumulated carbonyl concentration as a function of either artificial weathering (Fig. 1) and natural weathering (Fig. 2) were curve-fit by a least-square linear regression method. The time needed to produce a specific amount of [C=O] were determined. In addition, logarithmic plots of the reaction zone thickness as a function of either artificial weathering (Fig. 3) and natural weathering (Fig. 4) were also curve-fit by least-square linear regression. The time needed to produce a specific thickness of the reaction zone was determined. By mathematically maintaining [C=O] or the reaction zone thickness at a constant value and equating the expressions from the least-square linear regression for either [C=O] or zone thickness vs. time curves, a time correlation between artificial and natural weathering was generated (Fig. 5).

The degradation of tensile yield strength and elongation as a function of artificial weathering ex-

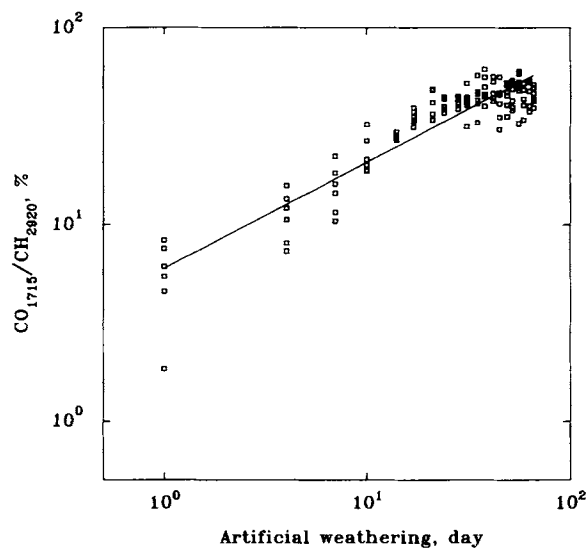


Figure 1 Accumulated [C=O] at the exposed Subor- tholen surface during artificial weathering. Regression equation: $Y = 0.77937 + 0.53684 X$, $r = 0.8751$, $p = 0.0000$.

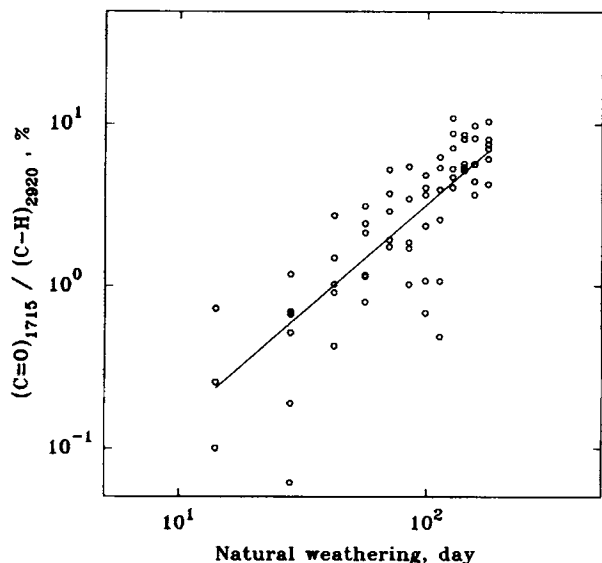


Figure 2 Accumulated [C=O] at the exposed Subortholen surface during natural weathering. Regression equation: $Y = -2.16085 + 1.3352 X$, $r = 0.8811$, $p = 0.0000$.

posure are shown in Figures 6 and 7. From the curves, it is easy to determine the time period when the material had degraded 50% of its total degraded value. From Figures 6 and 7, the time that Subortholen had dropped both 50% of its total degraded yield strength and tensile elongation during artificial weathering is approximately 4 days. This 4 day artificial weathering exposure is defined as the safe service lifetime of this polymer.

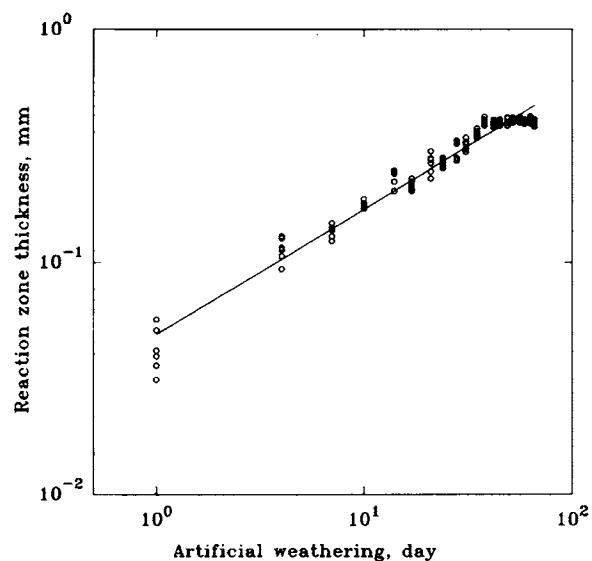


Figure 3 Growth of the reaction zone thickness of Subortholen as a function of artificial weathering. Regression equation: $Y = -1.31028 + 0.5393 X$, $r = 0.9755$, $p = 0.0000$.

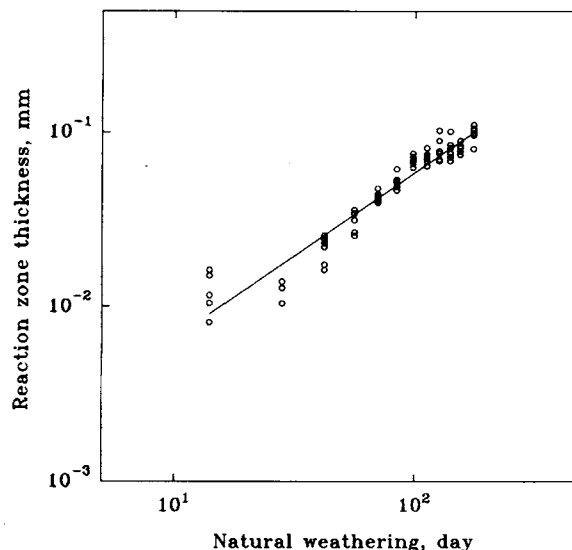


Figure 4 Growth of the reaction zone thickness of Subortholen as a function of natural weathering. Regression equation: $Y = -3.13056 + 0.94892 X$, $r = 0.9836$, $p = 0.0000$.

Figure 8 shows the hardness degradation trend during artificial weathering for Subortholen. In the curve, two regions were observed: an increased hardness region and a decreased hardness region. The time that it took Subortholen to reach its maximum hardness point (i.e., 11 days) was defined as the border between clinically unstable and clinically

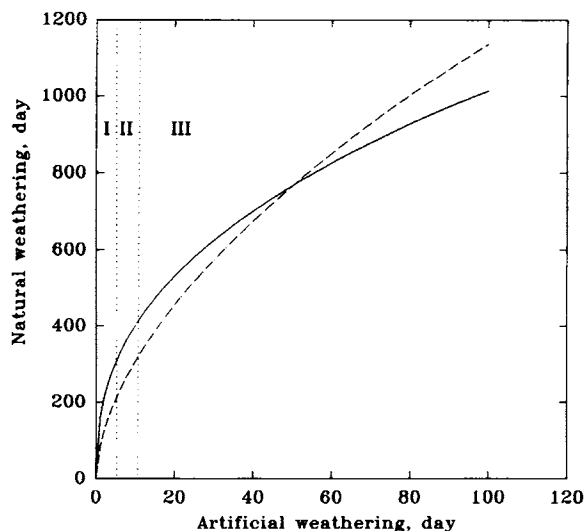


Figure 5 Correlations between artificial and natural weathering for Subortholen: (—) through [C=O] correlation; (----) through reaction zone thickness correlation. Three stages of clinical performance of Subortholen are assumed: (I) safe; (II) unstable; (III) unacceptable stages.

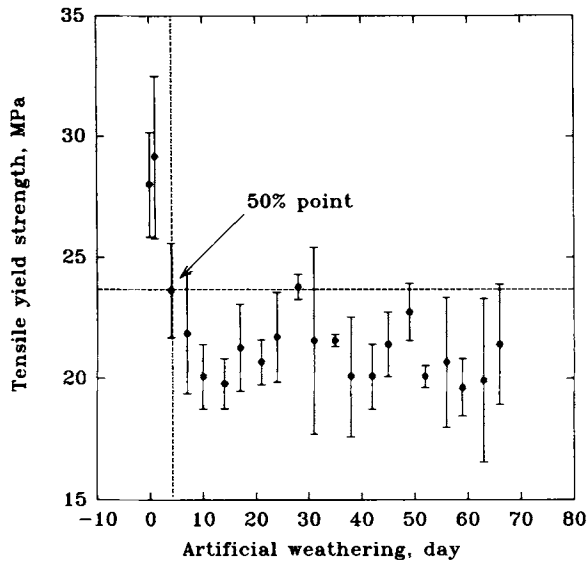


Figure 6 Degradation of tensile yield strength of Subortholen during artificial weathering. Arrow indicates the time when Subortholen had degraded 50% of its total decreased value.

unacceptable stages, since at this point, Subortholen lost most of its original strength and ductility (Figs. 6 and 7). Similarly, the time in which Subortholen had degraded to 50% of its total degraded yield strength and tensile elongation was equivalent to 50% of the total increased value in the increased

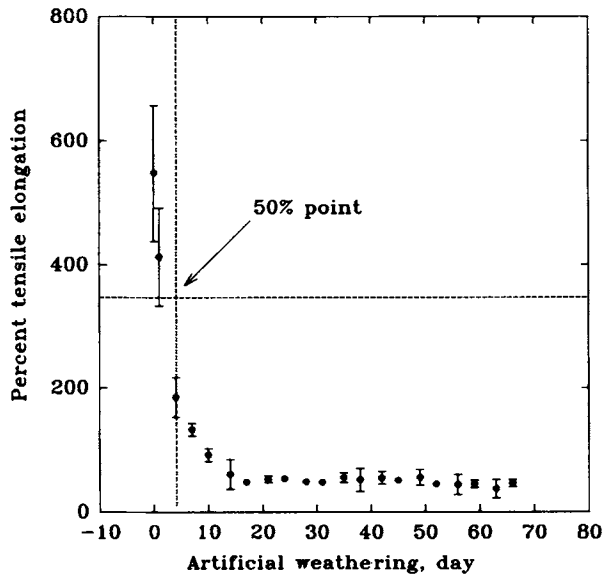


Figure 7 Degradation of tensile elongation of Subortholen during artificial weathering. Arrow indicates the time when Subortholen had degraded 50% of its total decreased value.

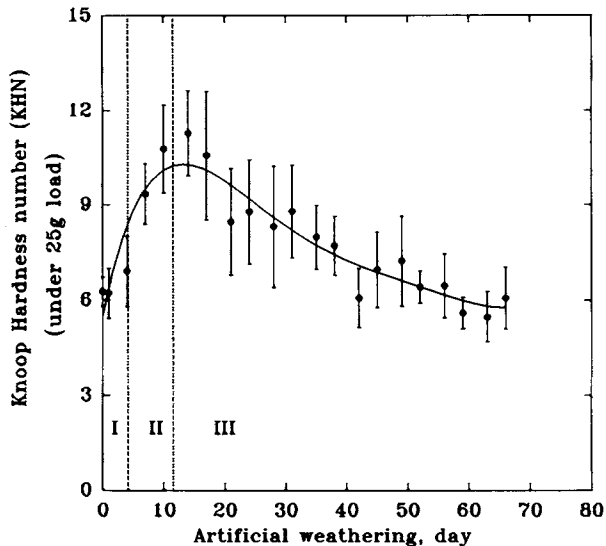


Figure 8 Knoop hardness degradation trends of Subortholen during artificial weathering. Three stages are assumed: clinically (I) safe, (II) unstable, and (III) unacceptable stages.

hardness region. From the above measurements, hardness degradation trends can be divided into three different stages of clinical relevance of Subortholen: clinically safe, clinically unstable, and clinically unacceptable stages (Fig. 8).

PREDICTION OF SERVICE LIFETIME

The duration of the clinically safe period is approximately 4 days with artificial weathering (Figs. 6 and 7). Choosing this point as the clinically safe period, one can calculate the actual device lifetime by fitting the data back to the generated artificial-natural correlation curve (Fig. 5). The corresponding duration for the natural exposure was about 300 days. Therefore, if a normal daily exposure of Subortholen is 3-5 h, the calculated safe life is approximately 4-6 years ($24 \text{ h/day} \div 3-5 \text{ h/day} \times 300 \text{ days} \div 365 \text{ days/year}$). In the above calculation, 24 h exposure per day should ideally consist of nearly 12 h sunlight and 12 h humidity exposure. Similarly, the duration of the clinically unstable stages is approximately 10 days under conditions of artificial weathering (Fig. 5). This material will not reach its clinically unacceptable stage until after 6-8 years of usage ($24 \text{ h/day} \div 3-5 \text{ h/day} \times 400 \text{ days} \div 365 \text{ days/year}$).

DISCUSSION

Results from carbonyl compound accumulation and from thickness of the reaction zone yielded two different equations (Fig. 5). $[C=O]$ data permitted construction of an equation: $\text{Log}(Y_1) = -5.4767 + 2.4872 \times \text{Log}(X_1)$, where Y_1 and X_1 are artificial and natural weather exposure days, respectively. In the case of reaction zone thickness data, another equation was obtained: $\text{Log}(Y_2) = -3.3767 + 1.7595 \times \text{Log}(X_2)$. Although these two equations are not exactly the same, they exhibited strong correlation between each other ($r = 0.99456, p = 0.0000$). Their plots (Figs. 1–4) also exhibit very low p values (all $p = 0.0000$) and high correlation coefficients (all greater than 0.87). This suggests that the logarithmic plots are a reasonable approximation for the weathering data. However, the two correlation equations generated from $[C=O]$ and reaction zone thickness (Fig. 5) predict an approximately 100 day difference in natural weathering exposure (vs. artificial). When one applies the correlation curve for calculation of the three stages of the clinical performance of Subortholen, the 100 day difference approximates a 1 year deviation in overall performance. It should be noted that it is nearly impossible to obtain a universal conversion factor for converting days under artificial weathering into days of natural weathering. Many variables in the weathering environment do not permit a single or a precise prediction of the natural life of a polymeric material. Nevertheless, through this study, we developed a technique to establish a comparative (not absolute) correlation between artificial and natural weathering. However, this result must be restricted exclusively to Subortholen, to Chicago climatic conditions (Figs. 9 and 10), and to tester setup time cycles and temperatures peculiar to this study. For other polymers used in different clinical service area (e.g., Houston), the experiment might be repeated with different results.

The equations presented in this study show that during the early portion of the exposure, a 4–5 day exposure in the artificial weathering tester represents about 1 year in natural weathering. During this period, changes in the accumulated carbonyl concentration and in reaction zone thickness is more rapid in the artificial weathering system than in the natural one. As weathering progresses, the rate of change of Subortholen in the artificial weathering environment becomes slower. So, an additional 4–5 day exposure would represent lesser time periods in natural weathering. Therefore, the overall relation-

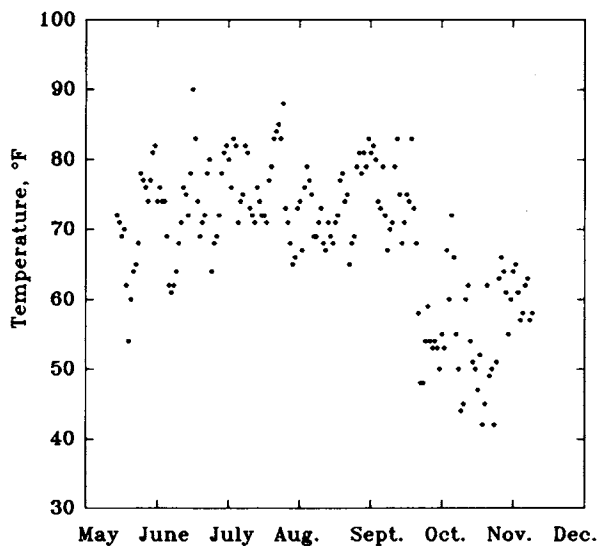


Figure 9 The daily average temperature at the Chicago Lake Front weather station during the weathering testing period (from 5/13/91 to 11/5/91).

ship between artificial and natural weathering is clearly nonlinear. Different exposure periods in artificial weathering would not represent an equivalently proportional time period in natural weathering.

Two distinctive regions in the hardness degradation curve (Fig. 8) were observed. The increased hardness effect may be attributed to the degradation of plasticizer which is commonly added to the polymer during manufacture to make it easier to process. In addition, this effect should be associated with the rapid increase in the crystallinity during the beginning of exposure to weathering,¹ which increases hardness. In the region of decreased hardness, there is a dramatic reduction of molecular weight¹ and the formation of major surface cracks, which may decrease the hardness.²⁵ In our study, the performance of the polymer can easily be monitored from the hardness degradation curve. The time required for Subortholen to degrade to 50% of its total degraded strength and ductility occurs at about the same time as the 50% region of increased hardness, which is assigned as the safe lifetime of Subortholen. However, when examining the clinical performance of Subortholen by measuring its hardness, the same two values will appear in both the clinically acceptable and in the clinically unacceptable regions. Thus, it is necessary to continuously measure the hardness of the polymer over a certain period of time to determine whether the measured hardness is in the region of increase or in the region of decrease. By

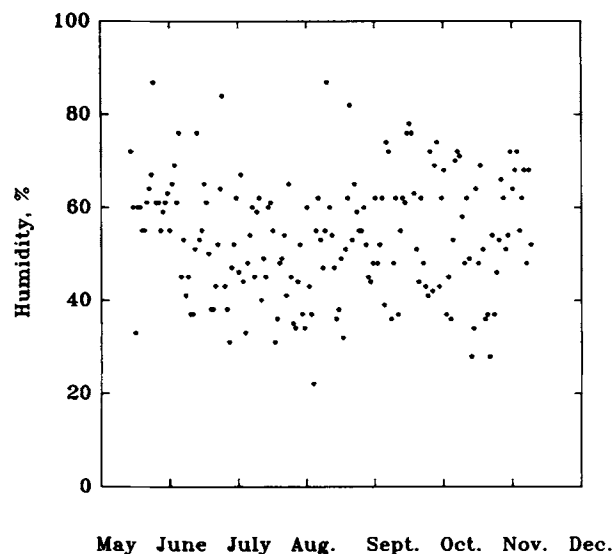


Figure 10 The daily humidity (at noon) at the Chicago Lake Front weather station during the weathering testing period (from 5/13/91 to 11/5/91).

doing this, these regions should still be distinguishable. Since many factors affect the correlation between artificial and natural weathering, the most confident prediction may be achieved by comparing the predicted results generated in this study with data obtained directly from a clinically serviced device made of Subortholen.

The method proposed in this study should be practical since it provides the easiest way to predict the remaining service lifetime and performance of Subortholen. The examination of hardness degradation during weathering provides a convenient technique to assess the quality of the polymer. Only a routine examination of the hardness of the polymer employed need be done in clinical practice. The examination of hardness degradation is prompt and nondestructive. When the correlation for a polymeric device between its hardness degradation curve and its clinical service history is established, the performance of this polymer can be predicted and controlled. Through the method developed in this study, the most appropriate time to replace a worn polymeric prosthetic or orthotic device can be determined quickly and easily before the device degrades to a dangerous stage.

CONCLUSIONS

The correlations in this study allow quick estimations of the time conversion factor between artificial

and natural weathering. Specifically for Subortholen, under the experimental setup used in this study, 4–5 days of artificial weathering equals approximately 1 year of natural weathering, which represents about 6 years of safe service lifetime for Subortholen. Since this estimate is not a linear relationship, other exposure periods under artificial weathering would not represent the same proportional time period as under natural weathering. An empirical, mathematical relationship between two exposures was presented.

Although many factors affect the artificial and natural weathering correlation, it is still possible to provide a comparative relationship which can determine the clinical service lifetime and performance of Subortholen. The hardness degradation is a useful parameter to easily and promptly estimate the different stages in clinical performance of Subortholen. The same method should be convenient for determining the service lifetime of other prosthetic and orthotic polymers.

This work was supported by the National Institute on Disability and Rehabilitation Research (NIDRR), Department of Education, Grant No. H133E80013 (D.S.C.).

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Received June 30, 1994

Accepted August 29, 1994