

Effects of Simulated Clinical Fabrication Heat Treatment and Artificial Weathering on Degree of Crystallinity of Prosthetics/Orthotics Polymers Monitored by X-Ray Diffraction

MICHAEL D. WALDMEIER,^{1,4,*} EVAN H. GREENER,² EUGENE P. LAUTENSCHLAGER,² and MARIO VOLPI^{3,4}

¹University of Connecticut Health Center, Department of Restorative Dentistry & Endodontology, MC-2017, BSAC CSM-011, 263 Farmington Ave., Farmington, Connecticut 06030, ²Northwestern University, Department of Basic & Behavioral Sciences, Chicago, Illinois, ³University of Connecticut Health Center, Department of Biostructure and Function, Farmington, Connecticut, and ⁴University of Connecticut Health Center, Biomolecular Structure Analysis Center, Farmington, Connecticut

SYNOPSIS

The effects of simulated clinical fabrication heat treatment and artificial weathering on the degree of crystallinity for three prosthetics/orthotics polymers were monitored by wide-angle x-ray diffraction. The polymers selected, polypropylene (PP), Subortholen (polyethylene, SB), and Surlyn (polyethylene methacrylate copolymer, SR), represent commonly used semicrystalline materials. Analysis of the as-received polypropylene showed no preferred orientation of the crystallites. The materials 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. The artificial weathering consisted of exposure to cycles of ultraviolet light and heated condensation. The degree of crystallinity was calculated and correlated with the materials structure, and ranged from 13.7 to 64.5% with an order from low to high of SR < SB < PP. The x-ray diffraction technique was demonstrated to be a useful tool for detecting environmental influences on prosthetics/orthotics polymers.

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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

Generally, limb-replacement prosthetic devices contain a central metal shaft or tube and are covered

with a plastic material. Biocompatibility problems, although important, are usually minimal. More frequently, aesthetics and function do 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.²

It has been indicated³ 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 brace⁴ 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.

* To whom correspondence should be addressed.

Thermoplastic means that the braces can be post-formed under moderate heat and pressure, permitting the orthotist to adjust the shape of the brace to precisely fit the needs of the patient. However, no standards for performance existed at this time, so engineers developed their own performance requirements.⁴

Both the American Society for Testing and Materials (ASTM)⁵ and the International Organization for Standardization (ISO) have been moving toward writing standards that deal with performance rather than design. This is due to the concern about the need to provide prostheses and orthoses that are safe. The ISO has continued work leading to the development of an international standard.⁶ This standard 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.⁶

Due to the fact that prosthetics/orthotics polymers are usually heated and molded (thermoplastic) to plaster casts and must function in the environment, influences of processing conditions and environmental factors, such as heat treatments and artificial weathering, are important to the mechanical properties. Many structural aspects related to currently used prosthetics/orthotics polymers have been investigated using x-ray diffraction, such as, unit cell d-spacings and peak positions,^{7,8} crystallinity,⁹⁻¹⁵ and cluster structures.¹⁵ Processing conditions and environmental factors have been shown to produce structural changes such as oxidation-induced crosslinks¹⁶ and ultraviolet irradiation crystallinity changes.¹⁷ In engineering applications, careful characterization of morphology is necessary for developing structure-processing-property relationships to crystallinity.¹⁸ In order to achieve these results, there has been an evolution of procedures for calculating degree of crystallinity^{11,19-22} from approximation techniques.²³⁻²⁵ An apparent degree of crystallinity has been defined on the basis that the solid is composed of an ideal perfectly ordered crystalline phase and an ideally disordered liquid-like phase whose properties are additive.¹¹

Therefore, x-ray diffraction is a suitable technique to monitor the effects on apparent degree of crystallinity due to simulated clinical fabrication heat treatment and accelerated weathering conditions for currently used prosthetics/orthotics polymers.

MATERIALS

The following materials were investigated: Polypropylene (PP), Subortholen (SB), and Surlyn (SR). The PP material was purchased from Durr-Fillauer Medical, Inc., Chattanooga, TN. The SB and SR materials were purchased from PEL Supply Co., Cleveland, OH. The suppliers list the PP, SB, and SR materials as being polypropylene, polyethylene, and ethylene methacrylate ionomer, 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 204°C for the PP material, 177-204°C for the SB material, and 177°C for the SR material.

Artificial Weathering (AW) Treatment

For the artificial weathering (AW) treatment, a Q-U-V Accelerated Weathering Tester (Q-Panel Co., 26200 First St., Cleveland, OH 44145) 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. 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. 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, except for servicing and inspection of the specimens. The weathering cycled with the following times and temperatures: 8 h UV at 60°C, and 4 h 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.

X-Ray Diffraction (XRD)

Two experiments were designed to assess the existence of a preferred orientation of the as-received PP material. Two 2D films, were obtained using an Elliot GX-18 x-ray generator with a rotating anode and a double mirror Frank camera. In the first case, the specimen was held such that the incident beam grazed the surface of the material. In the second case, the specimen was held such that the incident beam was transmitted through the specimen. The settings were 30 mA, 40 KV, using Copper K_{α} radiation of wavelength 1.54 Å and a collection time of 1 h. The measured specimen to detector distance was 53 mm. The Kodak XAR film was used as the detection system. The image was digitized in 2D with an Optronic scanner, Model 72, with a resolution of 100 μ . The digitized image was analyzed with software developed in the Biomolecular Structure Analysis Center, School of Medicine.

X-ray diffraction (XRD) analyses of all treated and untreated materials were performed on an automated Philips x-ray diffractometer, with a Phillips XRG 3100 x-ray generator. The diffractometer was controlled by a microcomputer using Philips Automatic Powder Diffractometer (APD) software. Voltage, current, and wavelength was the same as above. The receiving slit was 0.02 cm. The Philips system used a step scan goniometer and a scintillation detector. A 1" \times 1" block of the specimen was placed flat such that the incident beam grazed the surface of the material. A 2θ angle range was scanned from 10 to 35° (i.e., from 0.1132 to 0.3905 Å⁻¹) at a rate of 0.01°/s. Angles of diffraction peaks were converted to d-spacing values from Bragg's Law.²⁶

Degree of Crystallinity (DC)

To determine the apparent degree of crystallinity for the polypropylene material, a straight line was drawn to connect the points of the diffraction pattern from 0.1132 Å⁻¹ ($2\theta = 10^\circ$) to 0.3361 Å⁻¹ ($2\theta = 30^\circ$). The height of the maximum of the background corresponded to that of the minimum between the two 110 and 040 crystalline peaks, which occur at 0.1583 Å⁻¹ ($2\theta = 14^\circ$) and 0.192 Å⁻¹ ($2\theta = 17^\circ$). The maximum of the background was taken to lie at the reciprocal space of 0.184 Å⁻¹ ($2\theta = 16.3^\circ$), as that in the diffraction curve of an entirely amorphous sample. The background curve was finished as a smooth curve tangential to the diffraction pattern at 0.1414 Å⁻¹ and 0.2590 Å⁻¹. The following equation was used. $DC = (1)/(1 + 1.297(O_{am})/(O_{cr}))$, where O_{am} is the integrated intensity of the amorphous fraction, and O_{cr} is the integrated intensity of the crystalline fraction.²³

To determine the apparent degree of crystallinity for the polyethylene-based materials, SB and SR, a straight line was drawn to connect the points of the diffraction pattern from 0.1132 Å⁻¹ ($2\theta = 10^\circ$) to 0.3361 Å⁻¹ ($2\theta = 30^\circ$). A curve was fitted to the data with a maximum at approximately 0.2177 Å⁻¹ ($2\theta = 19.3^\circ$). The following equation was used. $DC = (1)/(1 + 2.17(O_{am})/(O_{cr}))$, where O_{am} is the integrated intensity of the amorphous fraction and O_{cr} is the integrated intensity of the crystalline fraction.²⁴

Some of the limitations²⁵ of this method occur because an entirely crystalline substance shows diffuse coherent scattering and a loss in intensity of the diffraction peaks occurs due to thermal vibrations and lattice imperfections. However, the importance of the method employed was that it is a

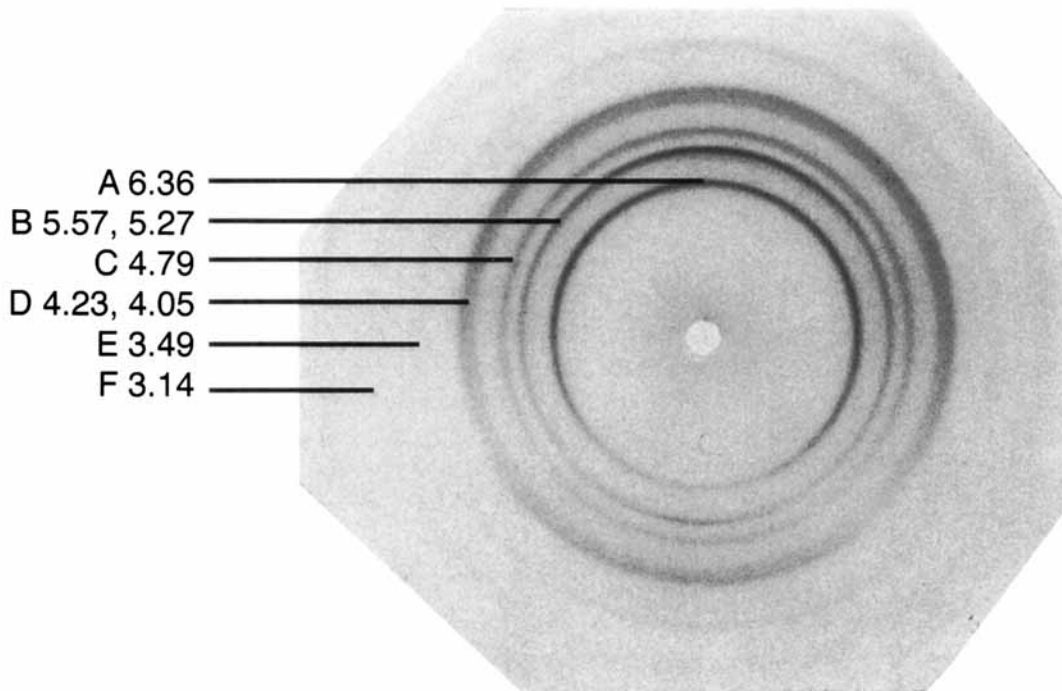


Figure 1 Polypropylene as-received 2D diffraction pattern, with d-spacing.

simplified method allowing for relative comparisons between the materials.

RESULTS

A 2D diffraction pattern with associated d-spacings of the PP material (AR condition) using photographic film was obtained by mounting the specimen tangentially to the beam as shown in Figure 1. A similar transmission experiment produced an analogous diffraction pattern (data not shown). From the digitized 2D pattern, a 1D intensity profile for the PP material was obtained from a rectangular section 1 mm in height and centered on the 2D diffraction pattern. Relative intensities were plotted vs. $(2\sin\theta/\lambda)$ [\AA^{-1}], as shown in Figure 2. The presence of concentric rings both for the tangential and transmission experiments indicated the presence of bundles (crystallites) lacking preferential orientation (an amorphous scatter). This allowed the use of a 1D detection system. The reason for selecting experiments with the x-ray beam tangential to the surface was that weathering, especially to ultraviolet irradiation would initially affect, mostly, the surface of the materials.

The 1D diffraction patterns collected with the Philips x-ray system are shown for the PP, SB, and SR materials, respectively, in Figures 3, 4, and 5.

For clarity, each figure shows the integrated intensities for the as-received (AR), simulated clinical fabrication heat treatment (SC0W), and 8-week weathered (SC8W) conditions for each material. A complete set of data for all conditions has been reported elsewhere.²⁷ The main differences in the characteristics of the diffraction patterns for the three polymers correspond to peak broadening and marked changes in the integrated intensities. Table I was calculated from the equations reported in the methods and compares the degree of crystallinity (in percent) of the three materials, PP, SB, and SR,

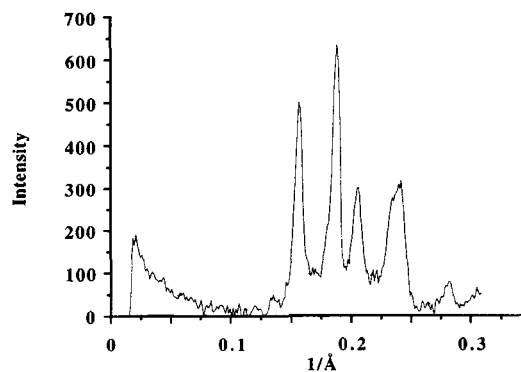


Figure 2 1D diffraction pattern from the 2D polypropylene diffraction pattern, relative intensity vs. reciprocal angstroms (\AA^{-1}).

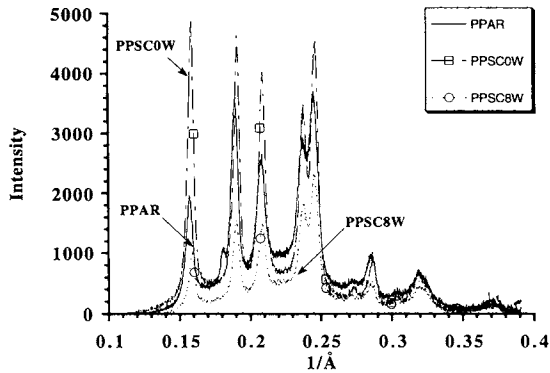


Figure 3 Polypropylene 1D diffraction patterns: 1) as-received; 2) simulated clinical fabrication heat treatment and not weathered (SC0W); and 3) simulated clinical fabrication heat treatment and 8 weeks weathered (SC8W), relative intensities vs. reciprocal angstroms (\AA^{-1}).

vs. the treatment conditions, AR, SC0W, SC2W, SC4W, and SC8W. The extent and direction of the changes is a function of the chemical characteristics of the materials tested. The ultraviolet irradiation of the polymers produced initially an increase in the integrated intensities, followed by a decrease at longer time periods, as shown in Figure 6.

A peak at $\sim 0.18 \text{\AA}^{-1}$ was not seen in the diffraction pattern for the PP material in the simulated clinical fabrication heat-treated nonweathered condition, but was seen in the 2 week weathered diffraction pattern (see Fig. 3). It is unclear if this was due to a specimen orientation effect, to the simulated clinical fabrication heat treatment or artificial weathering, or the formation of bimodal crystal textures in polypropylene.²⁸ For the PP material AR diffraction patterns, the 040 (0.1897\AA^{-1}) and 131

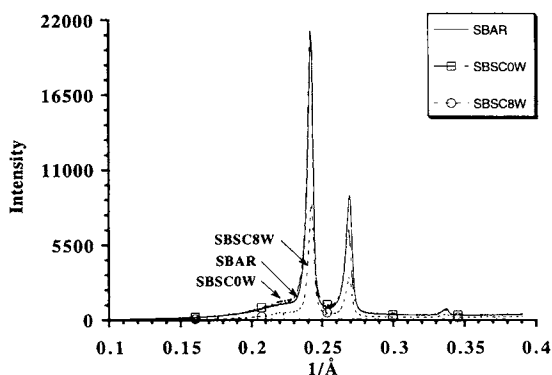


Figure 4 Subortholen 1D diffraction patterns: 1) as-received; 2) simulated clinical fabrication heat treatment and not weathered (SC0W); and 3) simulated clinical fabrication heat treatment and 8 weeks weathered (SC8W), relative intensities vs. reciprocal angstroms (\AA^{-1}).

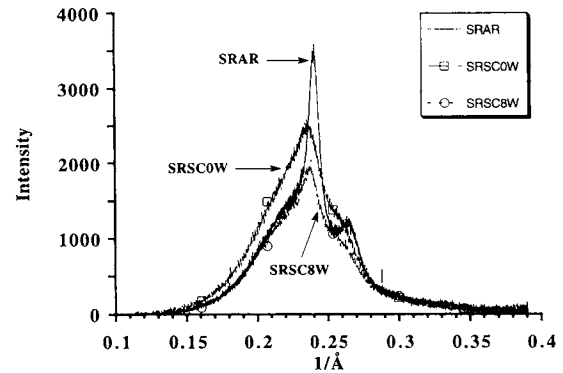


Figure 5 Surlyn 1D diffraction patterns: 1) as-received; 2) simulated clinical fabrication heat treatment and not weathered (SC0W); and 3) simulated clinical fabrication heat treatment and 8 weeks weathered (SC8W), relative intensities vs. reciprocal angstroms (\AA^{-1}).

(0.2465\AA^{-1}) peak intensities were approximately the same. In the diffraction pattern for the PP material, SC0W condition, the 040 (0.1906\AA^{-1}) and 131 (0.1906\AA^{-1}) peaks intensities decreased in intensity. There was a decrease in 2-week 110 (0.1635\AA^{-1}) peak intensity as compared to the 4-week 110 (0.1584\AA^{-1}) peak intensity in the PP weathered specimens using the 040 (0.1932\AA^{-1} , 2-week) (0.1905\AA^{-1} , 4-week) peak as a reference. The heat treatment for the SB material did not affect the 210 (0.3361\AA^{-1}) peak intensity. The AW treatment produced a decrease in the intensity of all of the SB peaks, 110 (0.2426\AA^{-1}), 200 (0.2697\AA^{-1}), and 210 (0.3368\AA^{-1}), at the 8-week weathered period. For the SR material, the 110 (0.2408\AA^{-1}) peak was initially at a higher intensity than the 200 (0.2656\AA^{-1}) peak. The effect on the SR material due to the SCF treatment was to broaden both the 110 (0.2408\AA^{-1}) and 200 (0.2656\AA^{-1}) peaks. The SR 200 (0.2609\AA^{-1}) peak increased in peak intensity in comparing the SC0W to the AR diffraction patterns. The SR SC8W 200 (0.2629\AA^{-1}) peak showed a gradual in-

Table I Comparison of Degree of Crystallinity (%), Condition vs. Material

Condition	Material		
	PP	SB	SR
AR	60.8	38.6	19.8
SC0W	59.2	39.8	14.3
SC2W	64.5	48.5	14.8
SC4W	63.8	45.5	15.6
SC8W	58.4	41.7	13.7

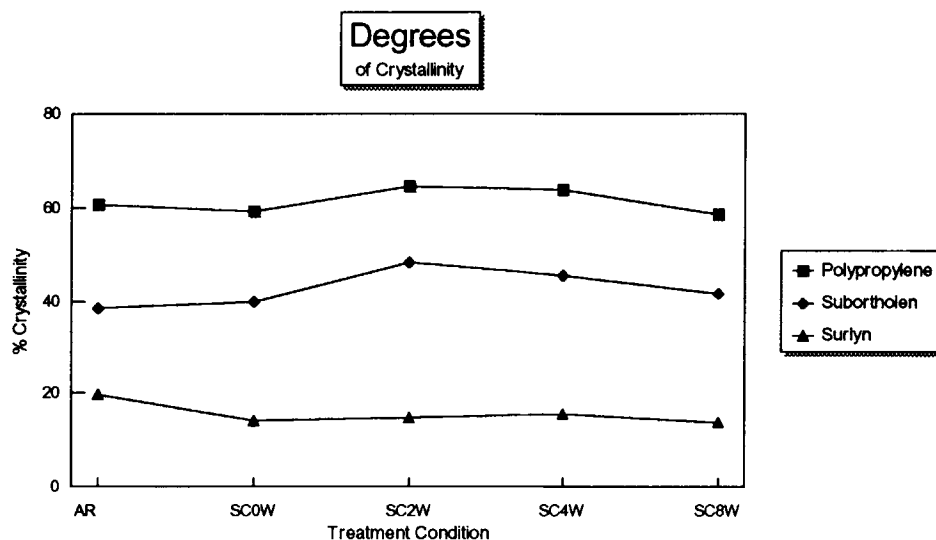


Figure 6 Degree of crystallinity of the polypropylene, Subortholen, and Surllyn materials at the five treatment conditions: AR, SC0W, SC2W, SC4W, and SC8W.

crease in intensity in comparing the 2, 4, and 8 weeks weathered diffraction patterns (data not shown).

DISCUSSION

The diffraction pattern for polypropylene taken in a tangential incidence (Fig. 1) showed a series of concentric rings indicating no preferred orientation, identical to the diffraction pattern obtained for a transmission mode.

Miller indices were in agreement with the literature for the PP material,²³ and the SB material.^{7,20,24} The differences seen in the SR diffraction patterns as compared to the SB diffraction patterns can be explained by a two-phase structural model for the ethylene-methacrylate copolymer.²⁹ The structural features form a basis for their response to clinical fabrication heat treatments and artificial weathering.

Photochemical reactions may cause degradation of functional groups in a polymer without affecting the main chain. New functional groups emerging during these reactions may be carbonyl groups and carbon to carbon double-bond groups. These groups can possess higher reactivity in chemical reactions such as in oxidation processes than carbon to carbon single-bond groups.³⁰ In addition, photochemical reactions may cause degradation of the main chain and, thus, produce the maximum effect on the change of physico-chemical properties.³⁰ Also, the photochemical reactions may cause secondary rad-

icals or intermediate species resulting in polymer crosslinking.³⁰

The peak intensity changes for the PP material may be most evident in the 110 (0.1572 \AA^{-1}), 040 (0.1894 \AA^{-1}), and 130 (0.2084 \AA^{-1}) peaks. The relative intensity of the 200 (0.2689 \AA^{-1}) peak in the SB material may be a significant contributor when determining the curve used in calculating the degree of crystallinity as compared to the 110 (0.2430 \AA^{-1}) peak. The effect of composition for the SR material could explain the broadening of both the 110 (0.2408 \AA^{-1}) and 200 (0.2656 \AA^{-1}) peaks as compared to the peaks in the SB material. The AW treatment in the SR material may have caused broadening in the peaks by increased branching, which is known to decrease crystallinity.³¹

Degree of Crystallinity

Each material had a distinctly different DC range. The DC order was from lowest to highest, SR < SB < PP. Overall, the degree of crystallinity ranged from 13.7 to 64.5%. The DC for the samples of the PP material ranged from 58.4 to 64.5%. The DC for the samples of the SB material ranged from 38.6 to 48.5%. The DC for samples of the SR material ranged from 13.7 to 19.8%. The lower value of DC for the SR material appears to be due to the incorporation of the methacrylate as a copolymer, which does not pack as well into the unit cell as does polyethylene, represented by the SB material.

The SC treatment did not appear to substantially change the DC for the PP or the SB materials, but

did reduce the DC for the SR material. For the SB material, the DC increased in the SC 2 weeks samples by 21.9%, then the DC decreased as the time of weathering increased to 4 and 8 weeks, -6.2% and -8.4% . The resulting DC for the AC nonweathered to AC 8 weeks weathered time period was 41.7%, an increase of 4.8%. After being molten, the SB material may not have had sufficient time and temperature to maximally recrystallize as a result of the air cooling process, which on the bench top may not allow for as much organization as the manufacturing process does.

A crystallinity stability index sequence where the most desirable situation is the least amount of change due to the artificial weathering treatment was from most desirable to least for the time period from 0–2 weeks: SR > PP > SB, and for the time period from 0–8 weeks: PP > SR > SB. Further studies are needed to extrapolate to an expected lifetime of the material.

The trend suggested by the AW treatment was to initially increase the DC for the SC0W specimens and later decrease the DC, depending on the material. The PP and the SB materials were similar in reaching a maximum at 2 weeks of weathering; the SR maximum was at 4 weeks. The heating aspect of the weathering may allow for growth of the crystallites, increasing the DC. The AW process may induce further recrystallization until chain scission and oxidation become the predominant effects. The irradiation-induced chain scission could initially cause crosslinking, increasing the DC. Irradiation in a moist environment causes oxidation, decreasing the DC.¹⁶

Upon exposure to high-energy radiation, ultra-high molecular weight linear polyethylene (UHMW PE) and conventional high density polyethylene (HDPE) polymers experience a significant increase in the degree of crystallinity.³² The irradiated polyethylenes exhibit an "aging effect"; their heat of fusion and, hence, their degree of crystallinity increases monotonically with the aging time (since initial irradiation) at ambient conditions. The magnitude of the "aging" effect is a strong function of the initial molecular weight of the unirradiated polymers and the irradiation dose. The magnitude of both effects is the largest in UHMW PE material that has the highest molecular weight ($M_w > 3 \times 10^6$) and the smallest in the HDPE material that has the lowest molecular weight ($M_w \sim 0.21 \times 10^6$). The crystallinity effect can be explained by the two-step process of irradiation causing scission of strained molecules, such as tie-chain molecules, followed by recrystallization of the broken chains. This

effect was demonstrated over a 1-year period with changes in tensile behavior, ultimate tensile strength, and elongation at break.³³ Correlation with infrared spectroscopic evidence indicated that the carbonyl concentration initially rises, but falls again during the latter part of the "aging" period while unsaturation remained relatively constant.³³

SUMMARY

As a part of examining accelerated environmental influences on prosthetics/orthotics polymers, x-ray diffraction is a useful technique. This methodology examined degree of crystallinity structural changes in prosthetics/orthotics polymers as a function of simulated clinical fabrication heat treatment and artificial weathering. Structural changes were suggested by peak broadening and intensity changes in x-ray diffraction patterns. The trend suggested by the AW treatment was an initial increase in the DC followed by subsequent decreases in the DC. The degree of crystallinity order was from lowest to highest, SR < SB < PP. A stability index sequence for the crystalline materials due to the artificial weathering treatment, based on the amount of degree of crystallinity changes, from most desirable to least, was: for the time period from 0–2 weeks: SR > PP > SB, and for the time period from 0–8 weeks: PP > SR > SB.

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