Structural Characterization of Selected Prosthetic–Orthotic Polymers by Nuclear Magnetic Resonance Spectroscopy

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SYNOPSIS

The structural characterization for five currently used prosthetic–orthotic polymers, determined by proton (^{1}H) nuclear magnetic resonance spectroscopy, showed residual unsaturation, C=C groups, in all materials, ranging from 1.7 to 15%. The determination of residual unsaturation by ^{1}H-NMR spectroscopy in polymers contributes information that may be useful for: (1) quality control of batches of materials, and (2) the development of standards, test methods necessary to evaluate the effects of environmental influences associated with long-term clinical service. Materials selected for current usage were: Durr-Plex (polyethylene terephthalate), polypropylene, Subortholen (polyethylene), Surlyn (ethylene methacrylate ionomer), and Uvex (cellulose acetate butyrate). © 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. Existing prostheses and orthoses are often cumbersome, uncomfortable, expensive, of limited capacity, or insufficiently versatile for fully satisfactory use in the necessary range of educational, vocational, and independent living settings. 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] The NIDRR considers improvement in these devices so essential that high funding priorities were assigned to research and development in these areas.

Generally, limb-replacement prosthetic devices contain a central metal shaft or tube and are covered with plastic material. Because the prostheses have little contact with the body tissues, biocompatibility problems are minimal. However, aesthetics and function do dictate the choice of plastic materials. Gebelein[2] states that low density, ultraviolet-visible light stability, and resistance to dirt and/or staining are essential properties for the plastics used in external prosthetic systems.

The NIDRR[1] stresses that the state-of-the-art in such fields as electronics, materials development, computer-assisted design, and computer-assisted manufacture is sufficiently advanced to support the development of prosthetic and orthotic devices that are more reliable, adaptable, comfortable, affordable, and provide greater enhancement of function. These devices are needed for disabled persons of all ages.

Burgess[3] has indicated that in his perception, the number one priority in prosthetic and orthotic research strategy 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 the composite orthotic leg brace developed by White,[4] which has 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. Ther-

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moplastic means that the braces can be postformed under moderate heat and pressure, permitting the orthotist to adjust the shape of the brace to precisely fit the needs of the patient. No standards for performance existed at the time, so Sparta engineers developed their own performance requirements.[4]

As a result of concern in the international community about the need to provide prostheses that were safe in use by amputees, and also because of an awareness that test standards would assist the development of better prostheses, the International Organization for Standardization (ISO) Technical Committee 168 has continued work leading to the development of the international standard, ISO 10328, Prosthetics—Structural Testing of Lower Limb Prostheses.[5] This test, ISO 10328, specifies procedures for simplified static and cyclic strength tests where compound loadings are produced by the application of a single test force. The laboratory tests and field trials should be repeated when significant design changes are made to a load-bearing part of the prosthesis. The Committee has recognized the limitations of this standard and identified directions that should be undertaken. Ideally, additional laboratory tests dealing with function, wear and tear, and environmental influences should be carried out as part of the evaluation procedure. There are no standards for such tests, so appropriate procedures will need to be specified.[5]

Future needs of the plastics manufacturers listed by Harkins and Dubreuil[6] in their examination of concurrent engineering in product design/development may be valid for the prosthetic and orthotic manufacturers. These needs include: (1) developing value-added products with improved functionality, features, and performance; (2) bringing products faster to market through better research; (3) shortening the development cycle by making better, more efficient use of technology and human resources; (4) reducing the risk in developing new products; and (5) achieving higher quality levels not only in the manufacturing cycle but in product development.

Nuclear magnetic resonance spectroscopy (NMR) has been shown to be an effective technique in the identification of polymeric materials[7,8] and impurities in raw materials and products.[9] The NMR technique has been used extensively for the specific structural characterization and quantification of unsaturation, carboxyl, ester, and carbonyl groups in polymers.[10] There is a connection between structures, processing (handling and usage), and properties of materials. In the polymerization of ethylene and propylene, a saturated copolymer is formed. Processing of this material requires that some un-

saturation has to be introduced. The amount of unsaturation left in the ethylene propylene diene terpolymer is of great interest, because the properties will be affected.[10] Unsaturation has been associated with sites for polymer degradation.[11,12]

Structural characterization of five commercially available thermoplastic prosthetic and orthotic polymers, in the "as-received" condition (AR), was performed by ^{1}H-NMR spectroscopy to assess one aspect of manufacturing processing, residual unsaturation (RU). The determination of RU by ^{1}H-NMR spectroscopy in polymers contributes information that may be useful for: (1) quality control of batches of materials, and (2) the development of standards, test methods necessary to evaluate the effects of environmental influences associated with long-term clinical service.

MATERIALS

The following materials in the AR condition were investigated: Durr–Plex (DP) (Pel Supply Co., Cleveland, OH), Polypropylene (PP) (Durr–Fillauer Medical, Inc., Chattanooga, TN), Subortholen (SB) (Pel Supply Co.), Surlyn (SR) (Pel Supply Co.), and Uvex (UX) (Pell Supply Co.).

Methods: Proton (^{1}H) NMR Spectroscopy

A Model 400 XL FT-NMR spectrometer (Varian Associates, Palo Alto, CA) was used for the ^{1}H NMR spectroscopy. The materials were purchased as $4 \times 6 \times 1/4''$ sheets. Small portions, $=2 \times =2''$ cubes, were comminuted to specimens of 1–2 mm diameter nodules in a laboratory mill, then cooled with liquid nitrogen to prevent heating of the samples by the rotating knife blades. The samples were placed into the 8″ long glass NMR tubes (Wilmad Glass Co., Buena, NJ). Deuterated tetrachloroethane (1,1,2,2,-$C_2D_2Cl_4$) was added as the solvent but contributed no hydrogen peaks to the spectra. The samples were heated to 80–120°C in the spectrometer. Tetramethyl silane (TMS) (Aldrich Chemical Co., Milwaukee, WI), a commonly used internal standard material in the solvent, was used to provide a zero reference point for peak positions of the various hydrogen environments.

NMR is the form of spectroscopy concerned with radiofrequency-induced transitions between magnetic energy levels of atomic nuclei.[8,13] Nuclei can be induced into a higher energy state by absorption of a radiofrequency (rf) pulse of the appropriate frequency pulse and strength. When this absorption

occurs, the system is said to be in resonance. In resonance, energy is transferred from the rf radiation to the nuclei, which causes a change in the spin orientation of the nuclei, a change in the spin populations in the various energy levels.[14]

After the rf field is turned off, the magnetization returns to its original equilibrium value by emitting energy or by transferring energy to the surrounding molecules.[14] The resulting free-induction decay signal (FID) is modulated by the precessing magnetic moment and decays in intensity as the magnetic moment relaxes back to its equilibrium position. Fourier transformation of the time dependent FID converts it to a frequency spectrum containing information on each nucleus. Because the effective magnetic field experienced by the nucleus, H_{eff}, is sensitive to the immediate environment of the nucleus in the molecule, nuclei in different environments resonate at different frequencies and give structural information on the molecular environment. The location (frequency) of a particular resonance when compared to the frequency of a reference of a reference material is defined as its chemical shift (in parts per million, ppm). The intensity of a resonance is proportional to the number of nuclei in that particular magnetic environment, allowing quantitative measurements.[9] Interactions between nearby magnetically nonequivalent nuclei result in multiple resonances, spin-spin coupling, for each nucleus.[9]

To assign the NMR resonances to specific structural features of the polymer, one method to make structural assignments uses a comparison of the observed chemical shifts with those observed for analogous low-molecular-weight model compounds. Structure elucidation is dependent upon establishing the nature of the chemical bonds between the various atoms in the polymer.[14] Proton (^{1}H) NMR spectroscopy detects structural components containing hydrogen.[14] Unsaturated sites, C=C, in the selected polymers for this study, have hydrogen attached to carbon. Each unique type of hydrogen attached to carbon absorbs energy at a different rf. In interpreting NMR spectra, the x scale represents the qualitative value: peak positions where energy absorption occurred, and the y scale represents the quantitative value: peak intensities, amount of energy absorption in a relative absorption scale. In-
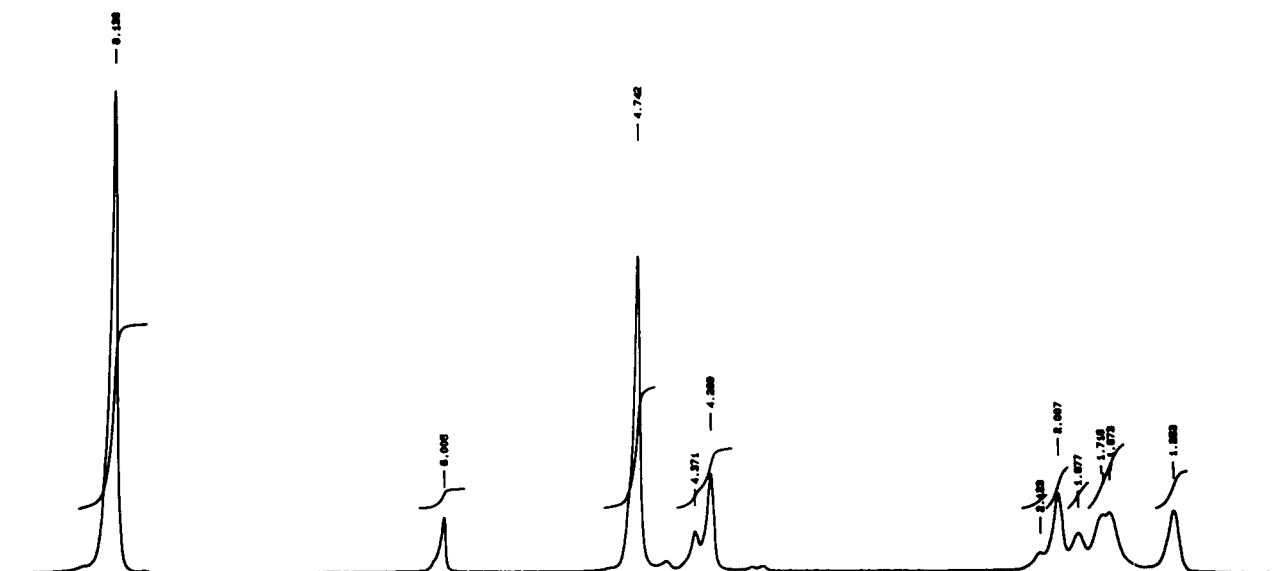
Figure 1 ^{1}H-NMR spectrum of the Durr-Plex material.

Position (ppm)	Assignment	Relative Area	Group
8.1	H bonded to phenyl ring	66.0	A
6.0	H bonded to unsaturated C=C	5.2	B
4.7–4.3	CH₂ bonded to O	67.1	C
2.0–1.2	CH₂ bonded to CH₂	66.6	D

The residual unsaturation was: (H bonded to unsaturated C=C)/(H bonded to unsaturated C=C + CH₂ bonded to O + CH₂ bonded to CH₂) × 100 = ____%. (5.2)/(5.2 + 67.1 + 66.6) × 100 = 3.7%.

terpretation of proton NMR spectra is usually fea-
sible in greater detail than is the case for infrared
or ultraviolet spectra.[15]

Further details regarding the NMR spectroscopic
technique are available.[14,16] *Spectroscopy of Poly-
mers*[14] applies the technique of NMR spectroscopy
to the characterization of polymers and gives a suf-
ficient knowledge to decide the suitability of the
spectroscopic method, the sampling technique, and
the type of results that can be expected.

Calculation of Residual Unsaturation

The residual unsaturation (RU), from the quantity
of hydrogen attached to C=C groups, was calculated
as the % of the total NMR peak areas represented
by the hydrogen attached to C=C group NMR peak
areas. The total NMR peak areas include all hydro-
gen attached to C to C groups that could be fully
hydrogenated. These groups would be alkane, al-

kene, or alkyne, but not phenyl rings or ester (C—
O) groups.

RESULTS

Peak assignments were made through comparisons
with standard references.[16-19] The spectra for the
DP, PP, SB, SR, and UX materials along with their
corresponding peak assignments are shown in Fig-
ures 1-5. The chemical structures, consistent with
the NMR spectra, are shown in Figure 6. The struc-
tures are associated with the NMR peak positions.
The values for percent residual unsaturation are
listed in Table I.

DISCUSSION

Prosthetic and orthotic devices are needed with op-
timal physical and mechanical properties over the
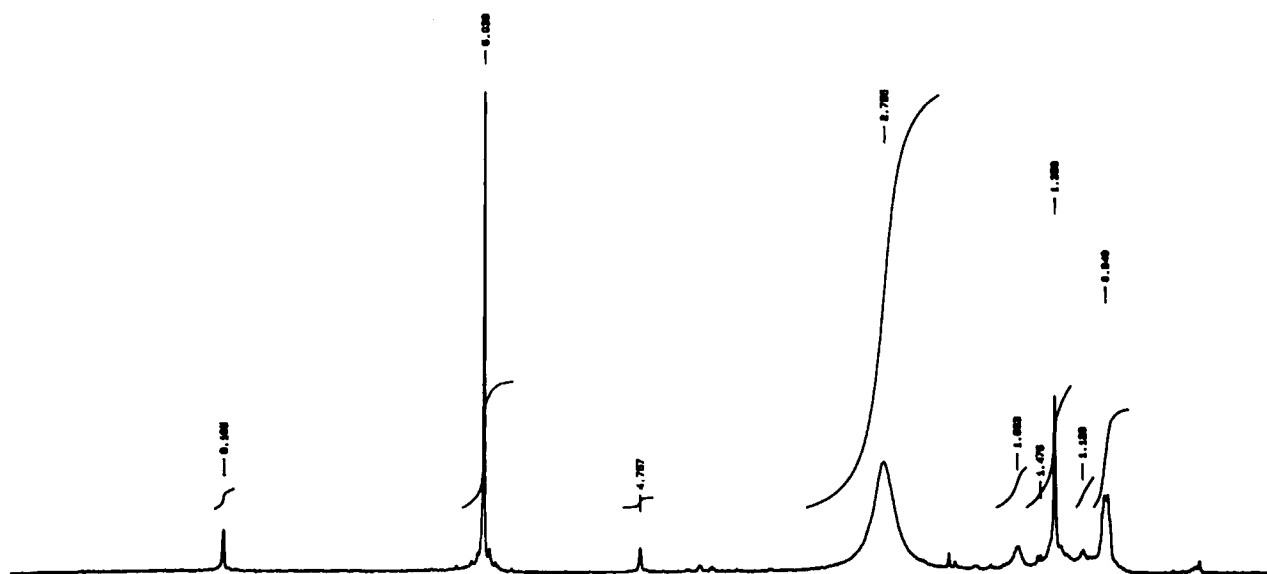
Figure 2 ^{1}H-NMR spectrum of the Polypropylene material.

Position (ppm)	Assignment	Relative Area	Group
6.0	H bonded to unsaturated C=C	39.4	A
2.7	CH$_2$ bonded to saturated CH$_2$	128.1	B
1.3 and 0.8	CH$_3$—C saturated	92.8	C
0.2	terminal CH$_3$—	1.9	D

The residual unsaturation was: (H bonded to unsaturated C=C)/(H bonded to unsat-

urated C=C + CH$_2$ bonded to CH$_2$ + CH3— saturated + terminal CH$_3$) × 100

= ___%. (39.4)/(39.4 + 128.1 + 92.8 + 1.9) × 100 = 15%.
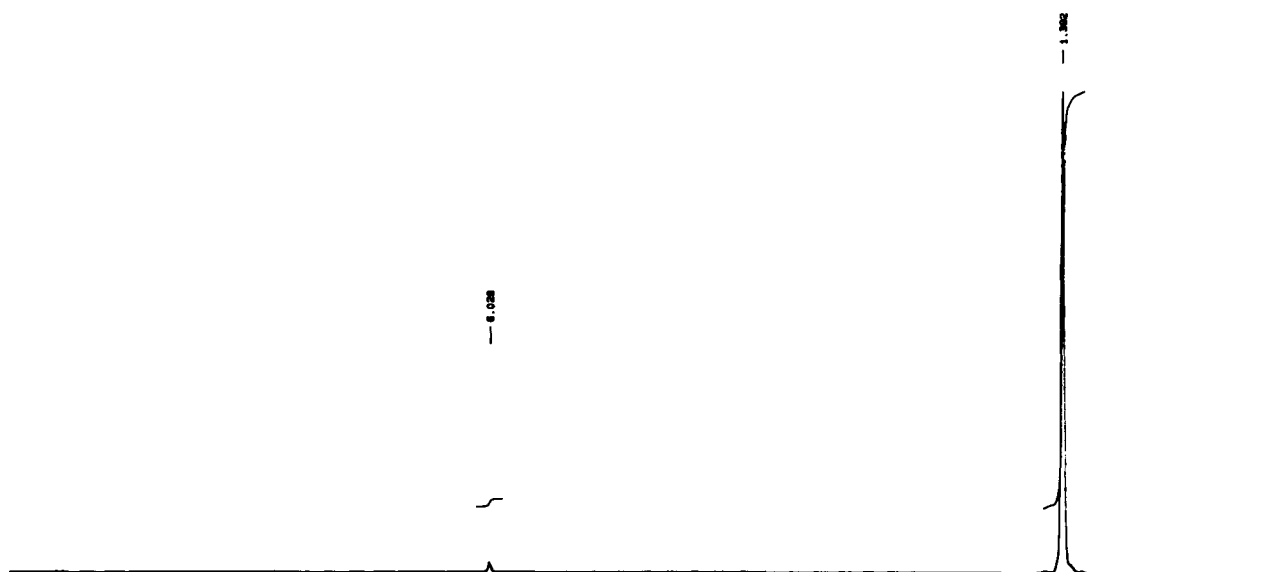
Figure 3 ^{1}H-NMR spectrum of the Subortholen material.

Position (ppm)	Assignment	Relative Area	Group
6.1	H bonded to unsaturated C=C	2.0	A
1.4	CH$_2$ bonded to CH$_2$	115.2	B

The residual unsaturation was: (H bonded to unsaturated C=C)/(H bonded to unsaturated C=C + CH$_2$ bonded to CH$_2$) × 100 = ____%. (2.0)/(2.0 + 115.2) × 100 = 1.7%.
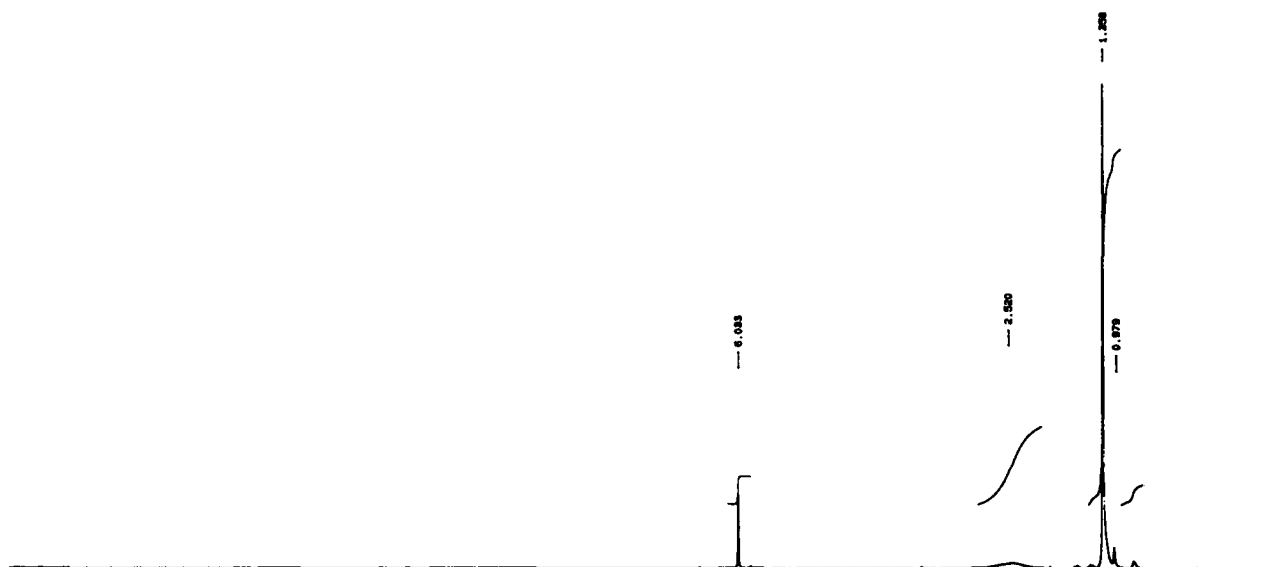
Figure 4 ^{1}H-NMR spectrum of the Surlyn material.

Position (ppm)	Assignment	Relative Area	Group
6.03	H bonded to unsaturated C=C	9.2	A
1.3	CH$_2$ bonded to CH$_2$	99.7	B
0.98	CH$_3$	7.3	C

The residual unsaturation was: (H bonded to unsaturated C=C)/(H bonded to unsaturated C=C + CH$_2$ bonded to CH$_2$ + CH$_3$) × 100 = ____%. (9.2)/(9.2 + 99.7 + 7.3) × 100 = 7.9%.

Figure 5 ¹H-NMR spectrum of the Uvex material.

Position (ppm)	Assignment	Relative Area	Group
6.0	H bonded to unsaturated C=C	7.6	A
5.2	H bonded to oxygen	16.3	B
4.8–4.4	Ch₂ bonded to cellulose chain	142.6	C
4.2–3.6	H bonded to cellulose chain		
2.4–2.3	H bonded to γ C of butyrate	143.8	D
2.2–2.0	H bonded to methyl of acetate		
1.8–1.4	H bonded to β C of butyrate	102.5	E
1.1–1.0	H bonded to α C of butyrate	105.6	F

The residual unsaturation in the cellulose chain was: (H bonded to unsaturated C=C)/
(H bonded to unsaturated C=C + CH_2 bonded to H bonded to cellulose chain) × 100
= _____%. (7.6)/(7.6 + 142.6) × 100 = 5.1%.

range of clinical activities and life span. Therefore, the structural characterization and the influence of structure on the physical and mechanical properties are essential to that goal of optimization. According to the suppliers, the materials and their respective compositions were as follows: Durr-Plex, polyethylene terephthalate; Polypropylene, polypropylene; Subortholen, polyethylene; Surlyn, ethylene methacrylate ionomer; and Uvex, cellulose acetate butyrate. The NMR data were always consistent with the suppliers' compositional claims and did not indicate any other components. The SB material appeared to be pink in color, which suggested incorporation of coloring agents. However, specific peaks for a typical coloring agent, azo chromophore,[20] could not be positively identified. Because of their structures, these five materials do have different temperature working conditions and physical and mechanical properties.[21]

The most significant finding was that the five se-

lected currently used prosthetic polymers, determined by ¹H-NMR spectroscopy, contained RU in all materials, ranging from 1.7 to 15%. The ranking from lowest to highest was: SB < DP < UX < SR < PP. There was no association evident between this batch of materials and RU. Because nylon is a thermoplastic, RU may be present in the matrix component of the White composite device. RU may be important for long-term clinical behavior because unsaturation has been shown to be reactive site for degradation.[11,12]

Investigating the materials in this study in the AR condition and quantifying the RU provides a baseline starting point. This point is necessary to properly assess the effects of simulated clinical fabrication heat treatment and artificial weathering factors on physical and mechanical properties such as color stability, strength, stiffness, and hardness. The incorporation of carbon fibers in the White composite device[4] added a component variable that

(a)

Durr-Plex (Polyethylene terephthalate)

(b)

Polypropylene

(c)

Subortholen (Polyethylene)

(d)

Surlyn (Polyethylene methacrylate)

(e)

Cellulose

Substituent Groups, R:

Acetate

Butyrate
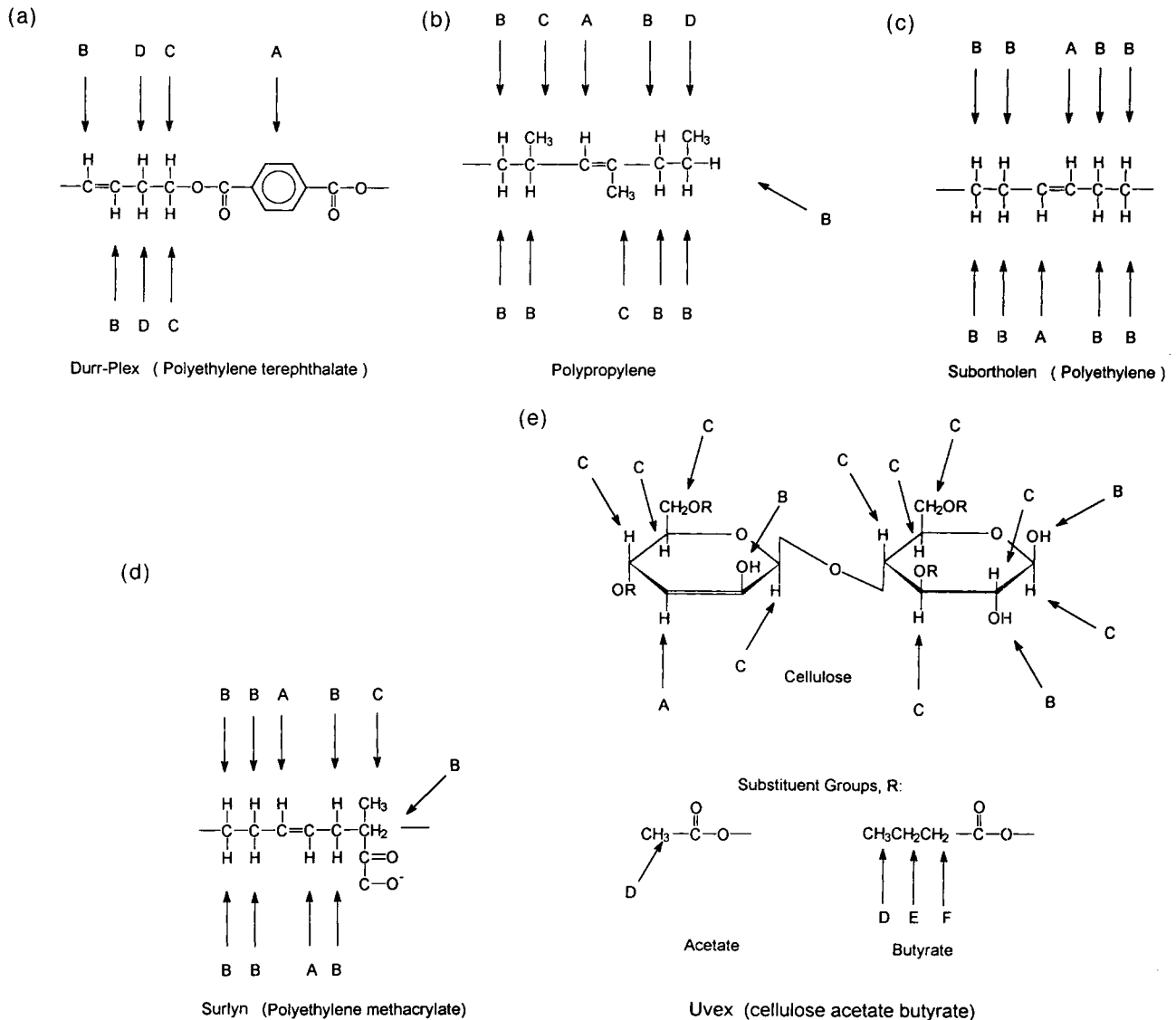
Uvex (cellulose acetate butyrate)

Figure 6 Chemical structures for prosthetic materials.

should be examined, especially because heat treatment was used in the fabrication process.

A systems approach for improvement in prosthetic and orthotic devices advocated by White,[4] incorporating input from medical, engineering, and materials sciences, may be a more valuable route than uncoordinated efforts to optimize the final product for physical and mechanical properties. The trend toward using composite materials for improvements in weight and to customize strength and stiffness characteristics is evident in the White composite device.

The development of appropriate test methodology and standards relating to the effects of environmental influences, identified by the ISO Technical Committee 168, may be addressed in part by techniques such as NMR spectroscopy. Some types of environmental influences, such as exposure to ultraviolet light and heated condensation, which simulate accelerated weathering, produce significant degradation changes.[21]

Table I   Residual C=C Unsaturation (%)

Materials	% Unsaturation
Durr-Plex	3.7
Polypropylene	15.0
Subortholen	1.7
Surlyn	7.9
Uvex	5.1

CONCLUSIONS

The compositions of the polymers were consistent with the suppliers' listing. Residual unsaturation was present in all five prosthetic polymers examined. Quantification of residual unsaturation was achieved by the use of NMR spectroscopy. NMR spectroscopy may be an appropriate technique in monitoring quality control and in the the development of standards for some types of environmental influences.

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