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Tensile mechanical properties of polyacetal after one and six months' immersion in Ringer's solution

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The engineering polymer polyacetal (also known as polyoxymethylene) has a long history of clinical use including in the femoral component of the Freeman all-polymer knee replacement. The polymer is a promising material for novel applications including the femoral component of hip resurfacing prostheses. However, no work following the effect on mechanical properties of extended immersion in the physiological environment has been reported.

Samples of five grades of polyacetal were obtained and tested on an MTS Bionix 858 at 37 °C in physiological saline. Three groups of specimens were tested: ''as received''; immersed in Ringer's solution at 37 °C for one month; immersed in Ringer's solution at 37 °C for six months'.

While there were negligible reductions in the ultimate tensile strengths, the Young's moduli of all polymer grades showed significant reductions ($p < 0.01$) of up to 19.5% following one months' immersion. There were negligible changes in ultimate tensile strength and stiffness between one and six months' immersion, however some polymers showed a small, but significant ($p < 0.05$) increase in stiffness. The percentage elongation and true stress for plastic instability showed negligible changes following immersion for one and six months'. These results encourage the use of polyacetal in load-bearing orthopaedic applications.

1. Introduction

While polyacetal is a well-known engineering polymer and has been used previously in orthopaedic implants [1, 2] there is little data on the effect of long-term exposure to the physiological environment on its mechanical properties.

Polyacetal is an attractive material for use in bone-conserving resurfacing hip prostheses. A resurfacing hip prosthesis is a large diameter replacement that retains the bone of the femoral head and neck, replacing only the diseased surfaces of the joint. A femoral resurfacing component made from polyacetal transfers load more evenly to the underlying bone than one made from metal [3]. A large diameter polyacetal on UHMWPE bearing produces 23% less wear volume than a similar CoCr does on UHMWPE bearing in hip simulator tests [4].

Polyacetal is available both as a hompolymer and as a copolymer. The copolymer is generally a cyclic ether (e.g. ethylene oxide) which provides increased resistance to ''unzipping'' degradation of the polymer chain [5]. Reports of the use of polyacetal in the orthopaedic literature have frequently failed to specify which grade has been used and have misused the DuPont homopolymer tradename Delrin® to refer to all grades of polyacetal.

The aims of this study were two-fold: to characterize the static mechanical properties of polyacetal before and after one and six months' immersion in Ringer's solution and to use these properties to differentiate between homopolymer and copolymer grades. This information may then be used to help select the most suitable material for a polyacetal on UHWMPE hip resurfacing prosthesis.

2. Materials and methods

Five samples of polyacetal sheet extrusion were obtained and machined to standard tensile testing specimens (Fig. 1). The polyacetal samples obtained were: copolymer from BASF (''Ultraform®'' or ''Pomalux®''), homo- and co-polymers (''Ertacetal®'') from DSM and homo- (''Delrin®'') and copolymers from Du Pont. None of the polymer samples obtained were ''medical grade''.

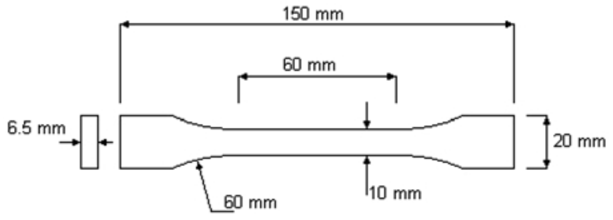

Figure 1 Polymer mechanical test specimen (BS 2782:3, 1976).

However, the sample of BASF copolymer was identical to material supplied to Corin Medical Limited for the manufacture of orthopaedic instrument handles except for the more stringent lot control applied to the medical material. All of the polymers were unpigmented and unfilled.

Flat dumbbell specimens were machined from the polyacetal sheet with dimensions given by BS 2782:3 (1976) and shown in Fig. 1. The test specimens were divided into three groups, the first to be tested immediately, the second to be tested after one month's soaking in Ringer's solution and the third after six month's soaking. There were five specimens of each polymer grade per group. The specimens were soaked in half-strength Ringer's solution at 37 °C. The solution was obtained by dissolving BDH Ringer's solution tablets in de-ionized water. Full-strength Ringer's solution typically has a composition of: 111 mMol NaCl, 1.9 mMol KCl, 1.1 mMol $CaCl_2$, 2.4 mMol $NaHCO_3$, 0.8 mMol NaH_2PO_4.

Tensile testing was undertaken on an MTS Bionix 858 with a 25 kN axial load cell. An environmental chamber which sprayed the specimens with physiological saline at 37 °C was used. Specimen strain was calculated from cross-head displacement using a geometric correction factor as waterproof extensometers were not available. The cross-head speed was 1 mm s^{-1} and data were recorded at 0.05 mm intervals. Manually operated immersible stainless steel specimen grips were used.

The specimens were weighed before and after soaking. Young's moduli were calculated from data over the first 0.8 mm displacement. Nominal stress and strain were recorded at failure. Considère's criterion was used to calculate the true stress (load/instantaneous cross-sectional area) at which necking of the specimen began and this stress was compared with the maximum true stress to assess plastic instability. The significance of changes to properties following immersion in Ringer's solution was tested using two tailed t-tests assuming unequal variances.

3. Results

All the specimens fractured and the fracture surfaces were perpendicular to the loading axis. The fracture surfaces were rough and the regions around the fracture were more opaque than the rest of the material. A typical group of stress strain curves is shown in Fig. 2. The form of the curves and the scatter are similar in all other curve groups. The ultimate tensile strengths of all polymer grades were slightly decreased by immersion in Ringer's solution (Fig. 3). In five cases the decrease after immersion for one or six months' was statistically significant with $p < 0.05$ including two with $p < 0.01$. However, the decreases are so small that in practice they may be neglected. There were no statistically significant differences between tensile strengths after one and after six months' immersion. The homopolymer grades showed the highest strengths while the BASF copolymer showed the greatest variability in strength.

The Young's modulus decreased significantly $(p < 0.01)$ by between 9% and 20% in all polymer grades after immersion in Ringer's solution (Fig. 4). The homopolymers showed the highest stiffnesses before and after immersion, but the DuPont homopolymer showed the largest percentage decrease (19.5%). The BASF copolymer showed the smallest reduction in stiffness. There were small, but significant $(p < 0.05)$, increases in stiffness between one month and six months' immersion in DSM copolymer and both the DuPont homo- and co-polymers.

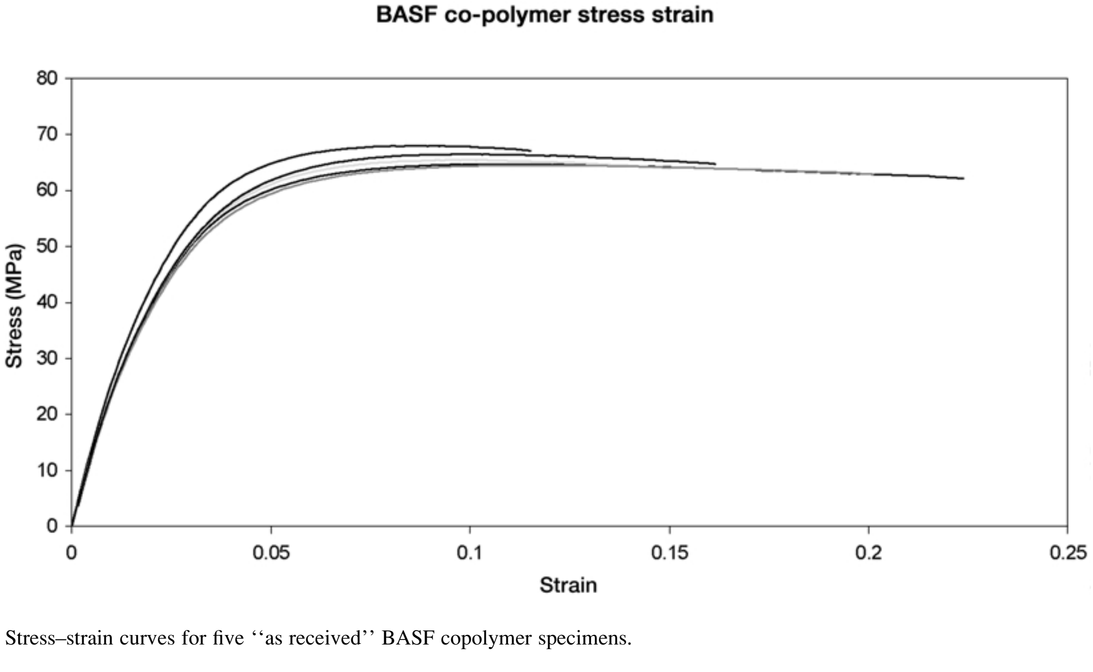

Figure 2 Stress–strain curves for five ''as received'' BASF copolymer specimens.

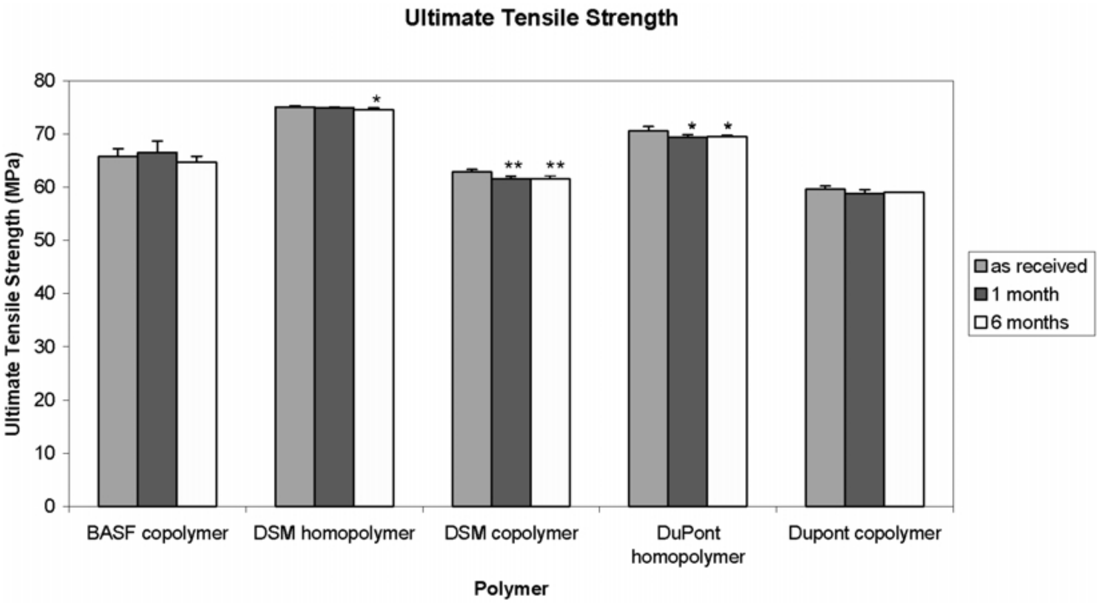

Figure 3 Ultimate tensile strength of polyacetal ''as received'' and after one and six months' immersion in Ringer's solution. Significant differences with the ''as received'' group are indicated * $p < 0.05$ and ** $p < 0.01$. Error bars show one standard deviation.

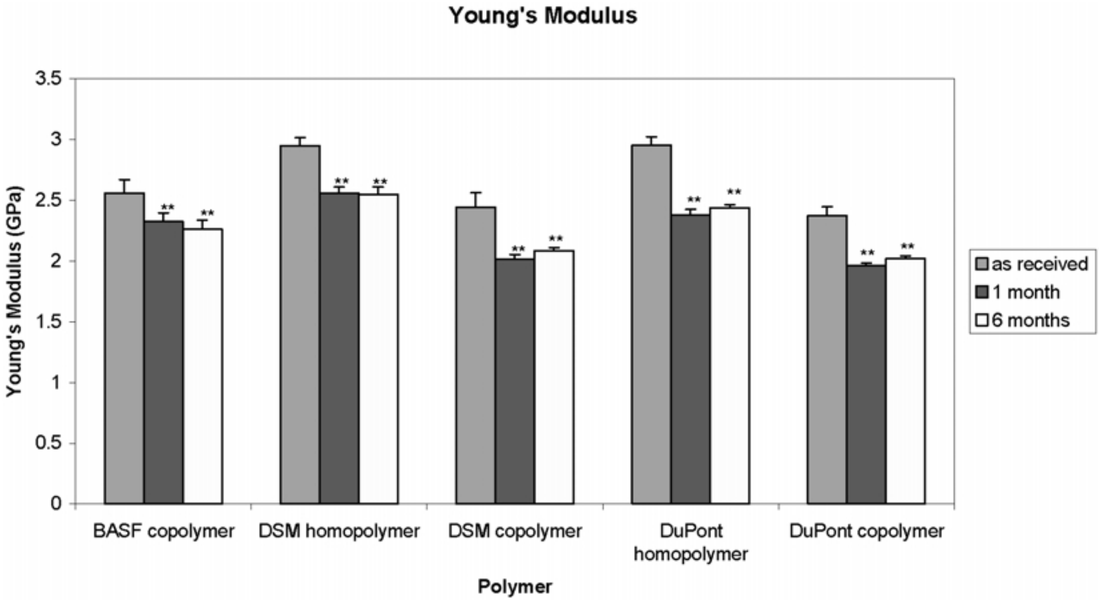

Figure 4 Young's modulus of polyacetal ''as received'' and after one and six months' immersion in Ringer's solution. Significant differences with the ''as received'' group are indicated * $p < 0.05$ and ** $p < 0.01$. Error bars show one standard deviation.

The DSM homopolymer showed very large (up to 56%) elongation at failure (Fig. 5). There were significant increases in elongation in the two DuPont polymers ($p < 0.05$) after one months' immersion, but the same grades showed no significant changes after six months' immersion. There were no significant changes in elongation between one and six months' immersion and no clear increasing or decreasing trends.

The homopolymers showed the highest true stresses for onset of plastic instability (Fig. 6). There were small, but significant, reductions after one month's immersion in the DuPont homo- and copolymers ($p < 0.05$) and in the DSM copolymer ($p < 0.01$) and after six months in the DuPont homopolymer and the DSM copolymer ($p < 0.01$). There was a significant ($p < 0.05$) increase in the Considère stress in the DSM homopolymer between one and six months' immersion. All other grades showed slight reductions. Comparing the Considère stress with the maximum true stress showed greatest plastic instability in the DSM polymers, but all polymers demonstrated some instability before fracture. The plastic instability in the DuPont copolymer increased from ''as received'' to one and six months' immersion.

The water uptake measurements are presented in Table I. The water content increased significantly between one and six months' in the DuPont copolymer only. There were no correlations between water uptake and the changes in any of the measured mechanical properties. The homopolymer specimens showed significantly greater water uptake than the copolymer specimens at one and six months' ($p < 0.01$).

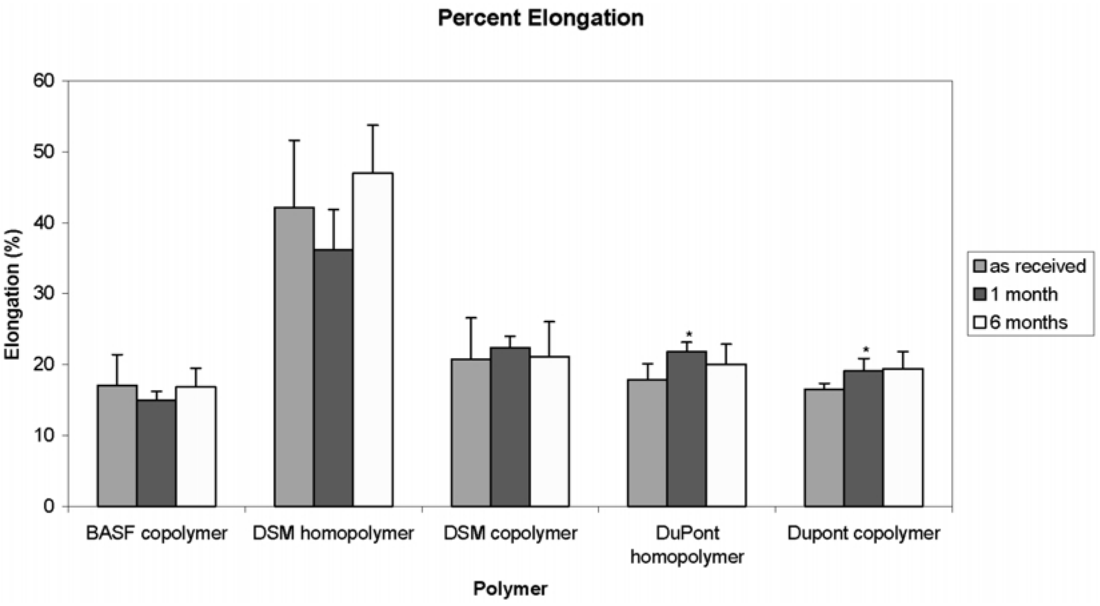

Figure 5 Percentage elongation of polyacetal ''as received'' and after one and six month's immersion in Ringer's solution. Significant differences with the ''as received'' group are indicated * $p < 0.05$ and ** $p < 0.01$. Error bars show one standard deviation.

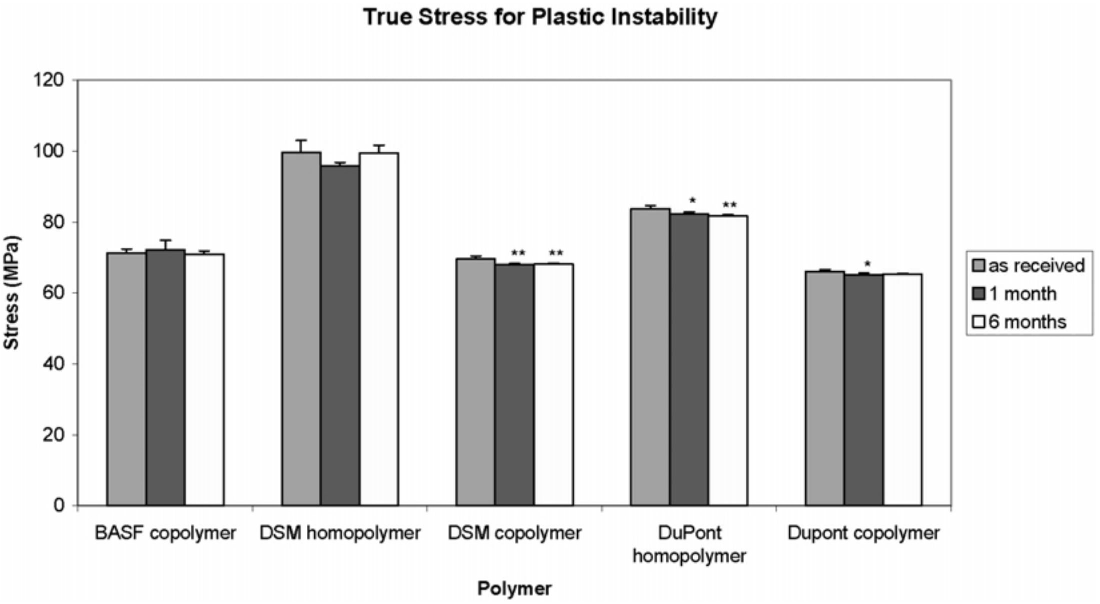

Figure 6 True stress for onset of plastic instability (Considère's criterion) of polyacetal ''as received'' and after one and six months' immersion in Ringer's solution. Significant differences with the ''as received'' group are indicated * $p < 0.05$ and ** $p < 0.01$. Error bars show one standard deviation.

TABLE I Water uptake (mean ± SD) following one and six months' soak in Ringer's solution

Polyacetal	Water-uptake/wt %	
	1 month	6 months
BASF copolymer	0.69 ± 0.04	0.65 ± 0.03
DSM homopolymer	0.78 ± 0.06	0.86 ± 0.11
DSM copolymer	0.63 ± 0.04	0.67 ± 0.03
DuPont homopolymer	0.72 ± 0.02	0.75 ± 0.03
DuPont copolymer	0.68 ± 0.02	0.74 ± 0.04*

* indicates significant difference $p < 0.05$.

4. Discussion

The mechanical properties of the ''as received'' polymer specimens tested at 37 °C in saline are not markedly lower than ultimate strengths of 70 MPa and 58 MPa and stiffnesses of 2.8 and 2.5 GPa for the homo- and copolymer respectively reported for tests at 23 °C in air [5], although this may be due to improvements in polymer technology since these tests took place. As expected the copolymers have lower stiffnesses and strengths than the homopolymers. The variability of the percentage elongation at failure is characteristic of a semi-crystalline polymer which fails in a brittle rather than ductile mode. The rough fracture surfaces confirm this. The increased opacity around the fracture surfaces is evidence of strain-induced crystallization.

The water absorbed into the polyacetal may be expected to have two separate effects on its mechanical properties. The first effect is as rapid as the diffusion of the water into the polymer. The diffusion coefficient of water in polyacetal, measured in a preliminary experiment, was found to be approximately

$D = 8 \times 10^{-12}$ m^{2}s^{-1}. For a specimen of thickness 6.5 mm this gives a characteristic time of $(3.25\,\text{mm})^2/D = 15$ days. Therefore, water uptake by diffusion will be at equilibrium in the specimens immersed for one month. The water molecules in the amorphous regions within the polymer will act as plasticizers, increasing the free volume per polymer molecule and leading to a reduction in stiffness. The uptake of water appears to produce significant, but small, immediate reductions in the strength of some of the polymers. The reduced stiffnesses produce a larger strain at the same stress.

The second effect expected following water uptake is the degradation of the polymer by the water itself and by solutes in the water. These processes produced no significant reductions in mechanical properties between one and six months'. However, there were significant increases in the stiffness of three polymers and a significant increase in the Considère stress for the DSM homopolymer. The increase in stiffness may be due to a secondary process of crystallization facilitated by the increase in free volume per molecule. The increase in stress for plastic instability is interesting and may benefit from further investigation.

The differences observed between polymer grades in the reduction of stiffness following immersion may be due to differences in crystallinity. A polymer with more amorphous material will show a greater effect of water-uptake on its stiffness. However the polymer with the highest stiffness (DuPont homopolymer), which might be expected to have the highest crystallinity, also shows the largest percentage reduction in stiffness. The effect of water-uptake on stiffness is confounded by the presence of different additives (e.g. plasticizers) in the polymer, which may themselves be water soluble.

5. Conclusions

The lack of significant reductions in the mechanical properties between one and six months' after immersion in Ringer's solution demonstrates the suitability of polyacetal for use in the physiological environment. The small differences between properties measured at 37 °C in physiological saline and those reported at 23 °C in air also encourage the use of the polymer.

The stiffness of all polyacetals is significantly decreased following immersion due to the plasticizing action of the absorbed water. Effects other than those due to the increase in free volume per molecule appear to produce increases in stiffness and Considère stress in some polyacetals.

The mechanical tests showed that homopolymers had higher stiffnesses and strengths than the copolymers. The lack of significant differences between one and six months' immersion prevents differentiation between polymer grades on the basis of their lack of degradation in the physiological environment. On the basis of high strength, stiffness and strain to failure, the DSM homopolymer appears to be the most suitable grade for the resurfacing application.

Acknowledgments

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