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Characterisation of Bionate polycarbonate polyurethanes for orthopaedic applications

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Abstract Two polycarbonate polyurethanes, Bionate 75D and Bionate 80A, have been characterized for application in biomimetic joint replacement systems. Procedures involved measurement of the effects of compounding and moulding on molecular weight, melt rheometry, and mechanical testing using conditioned and aged specimens. The effects of compounding with hydroxyapatite and carbon fibres were also evaluated. With Bionate 75D moulding reduces the molecular weight by 30%. Passing the material through a twin screw extruder without filler has similar molecular weight reduction effects to injection moulding. Inclusion of carbon fibre has little additional effect on molecular weight, although moulding of the fibre filled compound causes some further degradation, and Mw is almost halved compared with the original value. Inclusion of hydroxyapatite reduces Mw in a moulded component to less than a quarter of the original value and some form of chemical interaction between the polymer and filler is presumed. The apparent melt viscosity of the Bionate 75D was reduced by the addition of both carbon fibres and hydroxyapatite and this is thought to arise from reduction in molecular weight during the compounding process and the development of shear planes at the polymer-filler interface. The polymer glass transition temperatures are shifted to slightly higher values by the inclusion of filler. The tensile test results show the reinforcing effect of the carbon fibres, but poor wetting and pull out of the fibres was evident. Water absorption results suggest that the materials stabilise after 2 weeks, but the tensile results indicate that property change occurred between 1 month and 5 months of exposure. However the shape of the stress–strain curves is not altered, but with extended water exposure is translated to lower stress levels.

1 Introduction

The development of in vivo biomedical devices has been marked by a clear trend towards the use of biomimetic materials. Replacements for diseased or damaged joints have traditionally relied upon hard metals or ceramics articulating against ultra high molecular weight polyethylene, and although these materials have served well it has always been appreciated that mismatches existed between their properties and those of the natural systems being replaced. An alternative approach is to replace one or both parts of a joint with a more compliant material, thus coming closer to natural cartilage and thereby facilitating liquid film lubrication [1–3]. Benefits of proprioception and reduced wear should ensue, and so development of such systems is being actively pursued.

One of the few candidates for in vivo compliant layer applications is polycarbonate polyurethane which has outstanding hydrolysis and ageing resistance [4]. A typical structure is shown below.

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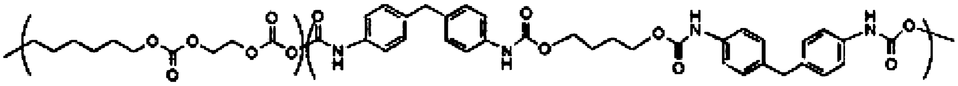


Polyurethanes of this type are constructed, at the molecular level, using hard and soft segments and this allows control of the glass transition temperature and the 37°C modulus. They are synthesized using a hydroxyl terminated polycarbonate, an aromatic diisocyanate such as methylene diphenyl diisocyanate, and a low molecular weight glycol chain extender, and the stiffness is controlled through molar ratios. The high oxidative stability comes from the proximity of the carbonate linkages to the hydrocarbon groups. Commercially these materials are available from The Polymer Technology Group, Berkeley, California, under the trade name Bionate.

Design criteria have now been developed [5] for joint systems using these types of materials and extensive simulator and animal trials carried out [6, 7]. Specifically Bionate 75D, a harder material, is used to provide structural support to a softer and compliant bearing face layer of Bionate 80A, the numbers referring to Shore hardness. Figure 1 shows a typical application, in this case a glenoid component for a shoulder joint system [8, 9]. The component is made by a two step injection moulding process in which the softer layer is over-moulded onto the harder backing to give a strong fusion joint between the two polymers.

For such property critical applications the process stability of these materials is clearly of interest and is one of the concerns of this paper. The polymers are very hygroscopic and it is necessary to pre-dry the material, exposing it to heat in air. It then has to withstand heat and shear conditions as it passes through the injection moulding process. A further concern is the possibility of degradation when compounding with particulate or fibre reinforcement, and hydroxyapatite and carbon fibres are of particular interest in this respect; the former giving the advantage of better osteo-integration and the latter giving considerable stiffness increase. However, compounding with fillers is only likely to be carried out using the harder backing polymer, and not the softer face polymer.

Fig. 1 Glenoid moulded using Bionate 75D backing and then over-moulded with Bionate 80A face layer

The rheological properties of the melt are also clearly important for product fabrication and these have been assessed using capillary rheometry, and in the case of the harder polymer this was done using both unfilled and filled compound. Final moulded material properties of interest for joint replacement are compressive and tensile strength and modulus. These have been measured using conventional tensile testing, cyclic compression testing and dynamic mechanical analysis. Although the primary mode of loading is compressive, changes in tensile properties have been found to be useful measures of fundamental changes at the molecular level, particularly indicative of polymer degradation [10]. The procedures used are described in detail in Sect. 2.

The overall objective of this work was to give a comprehensive material characterization relevant to orthopaedic device applications. Wherever appropriate, final property tests were carried out at 37°C using conditioned materials. Interpretation of the results is in the context of orthopaedic device components manufactured by injection moulding.

2 Experimental

2.1 Materials and processing

Bionate® 75D and 80A were obtained from The Polymer Technology Group. Bionate 75D was compounded with 15 wt% of 4 mm long carbon fibres and also with 20 wt% hydroxyapatite. Drying was performed in an air-circulating oven at 80, 90 and 100°C for 6, 12, 18 and 24 h. Injection moulding was carried out at melt temperatures of 200, 220 and 240°C. Compounding was carried out using a bench-top 16 mm Prism twin-screw extruder and in the context of this paper refers to the process of inclusion of additives such as fillers and fibres using the twin screw extruder and also to the process of passing the polyurethane through the compounding extruder, without additives, as a control process. After compounding the extrudate was pelletised for further processing. Conditions used for compounding are summarized in Table 1.

Table 1 Compounding extruder conditions

Parameter	Setting
Zone 1 temperature	190°C
Zone 2 temperature	205°C
Zone 3 temperature	210°C
Zone 4 temperature	220°C
Die temperature	220°C
Screw speed	29–33 rpm
Haul-off	2 m/min
Water bath temperature	Ambient
Torque	50–55%

Zones refer to the sections of the barrel counting from the feed end

Samples for testing were produced by injection moulding using an Arburg 'All-Rounder' 70 ton machine. Tiles with dimensions of 150 mm × 105 mm × 2.5 mm were moulded using a centre gated mould. Rectangular sections measuring 154 mm × 20 mm × 3.1 mm were also moulded with an end gate. Moulding conditions are detailed in Table 2.

Test specimens were stamped from these mouldings with appropriate dies and sterilised by exposure to gamma radiation. Irradiation was performed in air using a ^{60}Co source at a dose rate of approximately 0.15 Mrad/h to give a received dose of 2.5 Mrads. Samples were then incubated in phosphate buffered saline (PBS) at 37°C for at least 1 month prior to testing to ensure that measured properties were comparable to those expected to arise in vivo.

2.2 Test methodology and procedures

Gel permeation chromatography (GPC) was performed using a Polymer Laboratories gel permeation chromatograph equipped with a set of two Plgel 10 μm Mixed-B Columns. A Gilson 132 refractive index detector with a sensitivity of 0.3 was used and was held at room temperature. Calibration of the chromatograph was achieved with polystyrene standards. The samples were dissolved overnight in a few drops of dimethylacetamide and then made up to concentration with tetrahydrofuran (THF) which was also used as the mobile phase. The parameters measured were the weight average molecular weight (Mw) and the number average molecular weight (Mn). Mw is sensitive to the higher molecular weight end of the chain length distribution whilst Mn is more sensitive to the numbers of shorter chains. Change in the polydispersity, that is the ratio Mw/Mn, can be indicative of the mechanisms of degradation. As a large number of samples had to be tested it was not practical to carry out multiple determinations and the results presented come from one sample under each condition.

Polymer melt flow was investigated using a single-bore Rosand® RH-14C mini capillary Rheometer fitted with a

Table 2 Injection moulding conditions

Rectangular specimen			
	80A @180°C	80A @200°C	80A @220°C
Nozzle temperature (°C)	182	202	222
Melt temperature (°C)	185	202	222
Temperature (°C)	183	195	215
Throat temperature (°C)	167	187	185
Inj. pressure (Bar)	65	50	35
Inj. time (s)	5	5	5
Hold time (s)	5	5	5
Cooling time (s)	25	25	25
Screw speed (rpm)	200	200	200

Tile specimen						
	80A	CF	HA	75D @ 200°C	75D @ 220°C	75D @ 240°C
Nozzle temperature (°C)	203	210	208	203	218	238
Melt temperature (°C)	205	204	208	206	219	237
Temperature (°C)	200	200	205	206	218	237
Throat temperature (°C)	180	185	193	200	190	190
Inj. pressure (Bar)	60	70	70	70	70	70
Inj. time (s)	4.8	5	5	5.7	5	5
Hold time (s)	5	5	5	5	5	5
Cooling time (s)	20	20	20	20	20	20
Screw speed (rpm)	200	200	200	200	200	200

80A = Bionate 80A at three different moulding temperatures. CF = Bionate 75D + 15% carbon fibre by weight. HA = Bionate 75D + 20% hydroxyapatite by weight. 75D = Bionate 75D at three different moulding temperatures

1 mm × 16 mm capillary. All polymers were dried at 80°C for approximately 12 h before testing and the dwell period after charging the barrel was 6 min. The flow curves were captured for various temperatures ranging from 200 to 240°C. The Rosand® software automatically applied the Rabinowitsch correction.

The dynamic mechanical analysis was carried out using a Polymer Laboratories MKII instrument operated in constant displacement mode with multiplexed frequencies of 1, 5, and 10 Hz. Scans were conducted over the temperature range −100 to 150°C, at a heating rate of 1.8°C/min. Test samples were guillotined from the moulded sheets and dried for 8 h at 80°C prior to testing.

To examine the rate of water uptake 25 mm diameter discs were punched from injection-moulded plaques and were incubated in deionised water at 37°C for 2 weeks. The samples were removed from the water, patted dry using lint free tissue and weighed at regular intervals.

Change in fibre length, in the Bionate 75D compounded with carbon fibres, was determined by dissolution and optical measurement. Samples were held in THF at room temperature for 24 h and then smeared onto a glass specimen mount and viewed under an optical microscope. Fibres were optically isolated and measured using a Buehler Omnimet microscope with Version 5.20 image analysis software and to ensure validity of the results, over 350 fibres were measured after compounding and 150 fibres after injection moulding.

Tensile testing was carried out using dumb-bell Type 2 geometry (BS903-A2) with specimens stamped from the injection moulded plaques with a hydraulic press and die. Samples were always cut in the longitudinal direction and were conditioned in PBS solution at 37°C for a period of one month. Tensile testing was performed using an Instron 4302 universal testing machine with Instron Model 3111 temperature chamber. During testing the specimens were gripped with pneumatic jaws and sandpaper to minimise slippage. Separation between the jaws was set at 25 mm and a test speed of 100 mm/min was employed to allow accurate cycling to predetermined strain levels. Oven temperature was maintained at 37°C. A video extensometer was used on the narrow central section of the more elastomeric Bionate 80A specimen.

In order to evaluate the effect of hygrothermal ageing, tensile specimens were tested both dry and conditioned for a 5 month period. Calculated parameters included ultimate tensile strength, secant modulus and ultimate elongation.

The stress–strain curve for elastomers softens significantly during the first number of times the material is loaded to a particular strain, a behaviour commonly known as the Mullins effect [11]. Considering the cyclic loading experienced in an orthopaedic implant, the single pull to failure or first time stretch (FTS) data for Bionate 80A is of limited use. Large strains that greatly exceed those that the part will experience in vivo will also alter the material properties to such an extent that they will become unrealistic for the application of interest. Testing of the softer Bionate 80A was therefore carried out in accordance with test standard GMN6814 [12]. Although this standard is not intended for biomaterials application it is considered by the authors to offer a useful methodology. The tensile specimens were loaded to 20%, 40%, 60%, 80% and 100% strains for three repetitions creating a stress sequence curve loop. The decrease in stress (stress relaxation) was also captured while the strain was held constant at each level for 600 seconds.

Compression testing used cylindrical samples, 12 mm diameter by 6 mm thick, cut from the injection-moulded plaques, with this thickness achieved by superposition of layers bonded with THF. Subsequent to the tensile results, samples were conditioned for 5 months in PBS at 37°C. Testing was performed in a temperature controlled chamber at 37°C using an Instron 4302 universal testing machine coupled with a Monsanto B10 compression cage. Frictional effects were minimised and conditions of unconfined compression were approached by polishing the anvils and lubricating them with silicone grease. In accordance with BS 903-A4, samples were cyclically compressed to 50% strain at a speed of 10 mm/min. The calculated parameter was compression modulus.

3 Results and discussion

3.1 Process stability

Tables 3 and 4 show the effect of drying on molecular weight of both polymers and the results indicate that temperature

Table 3 Effect of drying on the molecular weight of Bionate 80A

Temperature (°C)	Time (h)	Mw	Mn	Mw/Mn
Control—not dried		148,640	61,721	2.408
80	6	169,022	57,649	2.932
80	12	175,491	63,996	2.742
80	18	160,304	61,002	2.628
80	24	167,975	60,962	2.755
90	6	147,945	57,787	2.56
90	12	155,155	61,317	2.53
90	18	167,085	71,968	2.322
90	24	156,402	61,778	2.532
100	6	138,287	60,793	2.275
100	12	144,846	63,445	2.283
100	18	154,537	61,912	2.496
100	24	138,730	56,322	2.463

Table 4 Effect of drying on the molecular weight of Bionate 75D

Temperature (°C)	Time (h)	Mw	Mn	Mw/Mn
Control—not dried		126,026	43,045	2.928
80	6	111,544	37,632	2.964
80	12	113,890	42,752	2.664
80	18	123,640	53,162	2.326
80	24	110,168	60,312	1.827
90	6	102,482	37,336	2.745
90	12	101,283	49,879	2.031
90	18	92,914	46,123	2.014
90	24	103,802	38,514	2.695
100	6	90,400	33,760	2.678
100	12	95,617	35,698	2.679
100	18	93,343	37,430	2.494
100	24	96,329	37,943	2.539

Table 5 Effect of compounding and moulding on molecular weight of Bionate 75D

	Mw	Mn	Mw/Mn
Control	126,026	43,045	2.928
Dried @ 80°C for 12 h	113,890	42,752	2.664
Compounded—no additive	74,723	38,134	1.959
Re-dried	75,203	38,356	1.961
Moulded @200°C	78,238	34,528	2.266
Moulded @220°C	80,166	35,285	2.272
Moulded @240°C	72,813	30,575	2.381
Compounded with CF	76,917	29,028	2.65
Moulded 75D + CF	64,947	26,138	2.485
Compounded with HA	41,436	17,109	2.422
Moulded 75D + HA	31,177	13,516	2.307

Compounded, no additive, refers to material which has been passed through the compounding extruder without the inclusion of other ingredients

rather than time is the critical parameter. Drying at 100°C for any of the time periods evaluated appears to drop the Mn value by about 10% in the case of the 80A material and by almost 25% in the case of the 75D. It is considered that this difference in response arises from the differing thermal stabilities of the hard and soft segments.

Table 5 shows the effects of compounding and moulding on the molecular weight of Bionate 75D. Passing the material through the twin-screw extruder reduces Mw by 40% and Mn by about 11%, moving the dispersity index very close to two. Such results are consistent with shear induced chain scission processes, in which the longest chains are preferentially broken. Re-drying and moulding has little additional effect on molecular weight, suggesting that the initial molecular weight loss on drying may come from weak links in the chain.

Inclusion of carbon fibres during compounding has a marked effect in reducing Mn, but little effect of Mw; an observation that is difficult to explain. A molecular weight reduction is consistent with the increased shear occasioned by the fibres, but it would be expected that Mw would show the greatest sensitivity to this.

Moulding of the carbon fibre re-inforced material further reduces both Mw and Mn and this is presumed to arise from intensification of shear within the injection moulder barrel. As the polymer volume fraction is reduced the effective shear rate, for any given screw speed, is increased. Hydroxyapatite has the most dramatic effect on chain length with severe molecular weight degradation occurring, presumable again through intensification of shear, although results presented later suggest the possibility of filler induced polymer degradation.

3.2 Melt rheology

The flow curves for Bionate 80A, Bionate 75D and for the Bionate 75D compounds are presented graphically in Fig. 2. Consistent with the power law relation, generally adopted with polymer melts [13], linear trendlines were added to the plots for visualisation and to forecast polymer flow behaviour beyond the tested shear rate range.

Overall, the quality of the melt extrudate was good for the pure Bionate 80A and Bionate 75D and the flow curves show acceptable viscosities for moulding at the recommended processing temperatures of 200–230°C. The results are also in close agreement with those of Quigley 1999 [14]. As would be expected, increasing the melt temperature reduces apparent viscosity and moves the flow behaviour closer to Newtonian.

Both the carbon fibre and hydroxyapatite blends demonstrated large die swell and melt fracture. In particular at temperatures over 200°C severe frothing and swelling hampered measurements of the Bionate 75D-hydroxyapatite

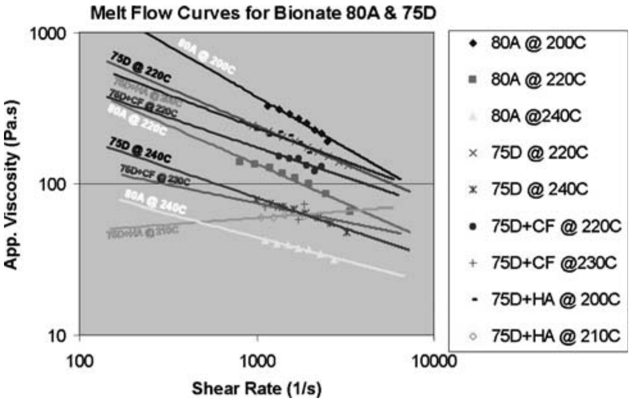


Fig. 2 Melt flow curves for Bionate 75D unfilled and filled, and Bionate 80A

compound. As dehydroxylation of hydroxyapatite does not occur until relatively high temperatures [15] it is presumed that the swelling indicates either post-compounding water absorption by the filler or the polymer, however the polymer had been dried for 12 h at 80°C prior to testing. A possibility is that after compounding the polymer matrix encapsulated the moisture laden, aerated hydroxyapatite which subsequently released vapour during rheometry. An extruder may also allow released vapours to escape back through the hopper while a capillary rheometer may force these vapours out through the die. The hydroxyapatite blend may also have exceeded a critical shear stress passing through the capillary die inducing polymer degradation. Surprisingly, the addition of both 15% carbon fibres and 20% hydroxyapatite reduces the apparent melt viscosity of the Bionate 75D and increases temperature sensitivity. Two factors may be responsible for this. Reduction in molecular weight during the compounding process and the development of shear planes at the polymer filler interface [16].

3.3 Dynamic mechanical thermal analysis

The DMTA results shown in Fig. 3 show that for Bionate 80A and 75D the glass transition temperatures are 17 and 76°C, respectively. Interestingly the damping curves do not show any evidence of the two-phase behaviour that would be expected if there was significant phase separation of hard and soft segments [17]. The reinforcing ability of both filler materials is apparent in the less abrupt drop in storage modulus as the temperature is increased. The addition of carbon fibres to the Bionate 75D increases the glass transition to 84°C and the 37°C modulus is increased significantly, from 866 to 1944 MPa. However the addition of hydroxyapatite only increases the Tg to 78°C and modulus to 968 MPa. With both fillers the damping values are greatly reduced.

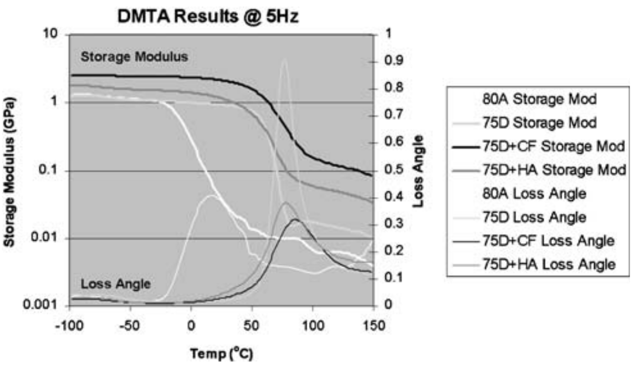


Fig. 3 5 Hz dynamic mechanical response of Bionate 75D unfilled and filled, and Bionate 80A

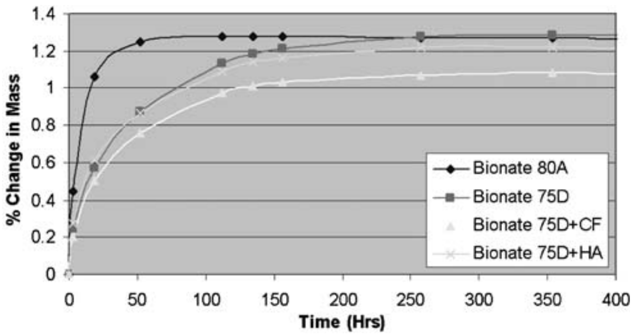


Fig. 4 Water absorption curves for Bionate 75D unfilled and filled, and Bionate 80A

3.4 Water absorption

Water absorption results are shown in Fig. 4. While the softer Bionate 80A material shows the fastest rate of water uptake, it stabilises at approximately 1.27 wt%, a value similar to the harder Bionate 75D. Khan 2002 reports a 0.85% increase in weight for Bionate 80A but it is not clear if the samples were dried beforehand. The addition of 15% by weight carbon fibres to the Bionate 75D results in a 15.6% reduction in water uptake (1.28–1.08%) consistent with the polymer volume fraction change, whereas the hydroxyapatite filler only incurs a 5% reduction in water absorption relative to Bionate 75D. Overall the results suggest that all four materials reach equilibrium after approximately 2 weeks.

3.5 Tensile testing

The tensile stress–strain results for all four materials are presented in Table 6 and Fig. 5. The size constraint of the temperature chamber prevented testing of Bionate 80A samples to rupture and so ultimate tensile strength and elongation could not be calculated. While Bionate 80A demonstrates elastomeric behaviour, typical of materials above their glass transition temperature, Bionate 75D shows more of a yield point before drawing to ultimate elongation. The reinforcing effect of the carbon fibres on the Bionate 75D is reflected by a 80% increase in ultimate tensile strength, from 21.55 to 38.84 MPa, and a 74% reduction in ultimate elongation. The generally adverse effects of 20% hydroxyapatite filler are highlighted by a 22% reduction in UTS and a 10% reduction in ultimate elongation.

The effect of hygrothermal ageing on the tensile properties of Bionate 80A and Bionate 75D is also summarised in Table 6 and it is apparent that ultimate tensile strength and ultimate elongation decrease with ageing. While the absorption results suggest that water content of the Bionate stabilises rapidly, the tensile results indicate that the material is undergoing property change for much longer. However the

Table 6 Tensile properties of Bionate 75D and Bionate 80A, dry and conditioned for 1 month and 5 months (FTS = first time stretch, SSCL = stress sequence curve loop)

	UTS (MPa)	UE (%)	50% Mod (MPa)		100% Mod (MPa)	
			FTS	SSCL	FTS	SSCL
Bionate 80A Dry	–	–	5.51 ± 0.09	4.91 ± 0.12	7.51 ± 0.22	6.52 ± 0.25
Bionate 80A 1 M	–	–	4.04 ± 0.23	4.04 ± 0.15	5.04 ± 0.82	–
Bionate 80A 5 M	–	–	3.38 ± 0.01	3.31 ± 0.08	4.29 ± 0.09	4.17 ± 0.28
Bionate 75D Dry	49.48 ± 3.22	352.06 ± 0.33	21.10 ± 0.96	–	24.92 ± 1.22	–
Bionate 75D 1 M	21.55 ± 0.96	123.56 ± 9.06	16.52 ± 0.23	–	19.75 ± 0.27	–
Bionate 75D 5 M	–	–	15.60 ± 0.58	–	17.94 ± 0.40	–

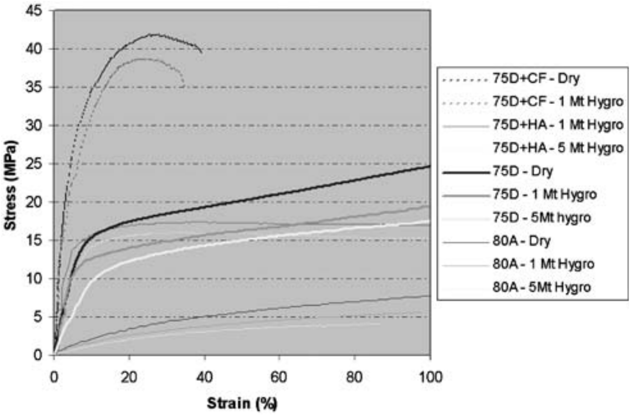


Fig. 5 Tensile stress–strain results for Bionate 75D unfilled and filled, and Bionate 80A, dry and wet aged

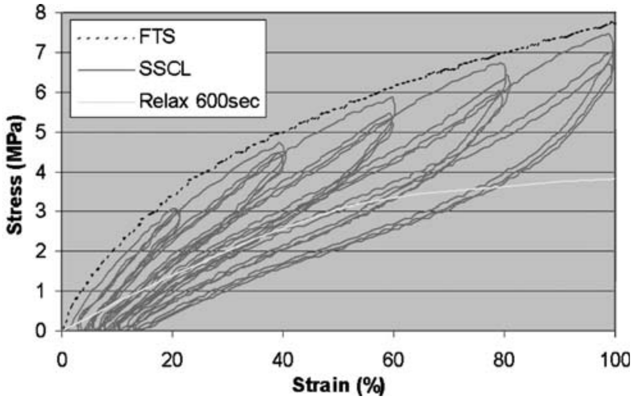
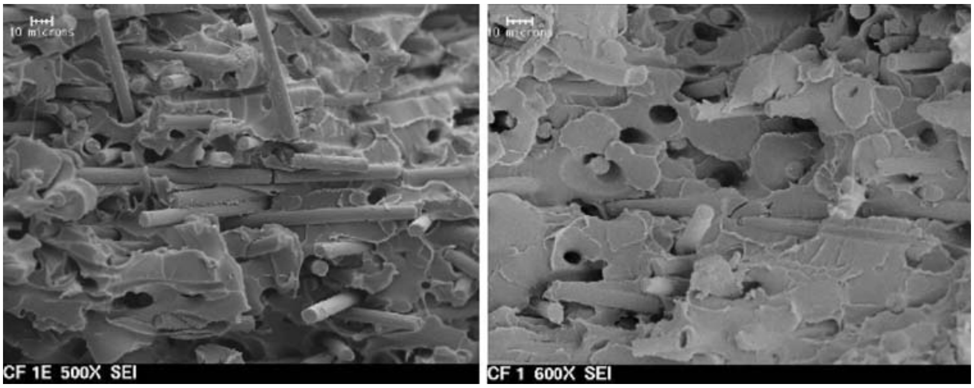


Fig. 7 The tensile test results for Bionate 80A, in accordance with GMN6814, take the form of a typical first time stretch (FTS), a stress sequence curve loop (SSCL) and 600 s stress relaxation curve

shape of the stress–strain curves is not altered, but is translated to lower stress levels with extended exposure and this is taken to indicate plasticisation. Similar behaviour is shown by the Bionate 75D composite materials. The Bionate 75D-HA became very brittle after drying, causing premature failure of all test pieces outside the narrow central section. This may be due to filler agglomeration, or may arise from polymer degradation. Figure 6 shows electron micrographs of the fracture surface of the carbon fibre reinforced material and significant fibre pull out is evident. Micrographs of the hydroxyapatite filled materials showed a relatively featureless flaky surface.

The tensile test results for Bionate 80A, in accordance with GMN6814, take the form of a typical first time stretch (FTS), a stress sequence curve loop (SSCL) and 600 s stress relaxation curve, and are presented in Fig. 7. Considering the cyclic loading experienced in orthopaedic implants, the stabilised condition after three repeated loading sequences yields more realistic stress–strain data for component design.

Fig. 6 Electron micrographs of the fracture surface of the carbon fibre reinforced material



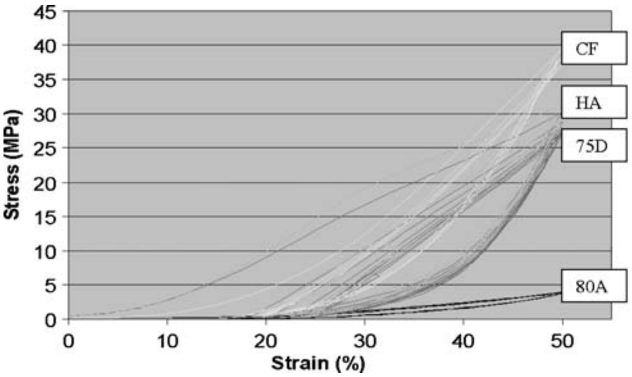


Fig. 8 Compression stress–strain results

3.6 Compression

The compression stress–strain results are presented in Fig. 8 and highlight the difference in compressive strength between the softer Bionate 80A and the harder Bionate 75D and its composites. In agreement with test standard BS903, the compressive behaviour of all materials is taken to stabilise after the third repetition. The shift in zero-strain resulting from the 1st to the 4th compressive cycle has been quantified in Table 7, but not shown graphically in the figure. This shift in zero strain is a combination of the compression set of the material and inaccuracies in the test set-up, such as friction associated with the compression cage. The hydroxyapatite filler had minimal impact on the compressive behaviour of the Bionate 75D and marginally increased the overall strength. The addition of carbon fibres had a much greater impact on the stress–strain curve.

4 Conclusions

Based on the GPC results, optimal drying of the Bionate material is achieved after 12 h in a fan-assisted oven at 80°C, and moulding temperatures should not exceed 220°C. By the time Bionate 75D is converted into a product the combined effects of heat and shear have dropped the molecular weight to around 70% of the raw material value. Passing the material through the twin screw extruder, without added filler has similar molecular weight reduction effects to injection moulding.

Inclusion of carbon fibre has little additional effect on molecular weight, although moulding of the fibre filled compound does cause some further degradation, and by this time the Mw has almost halved compared with the original value. Inclusion of hydroxyapatite has the most dramatic effect on molecular weight reducing Mw in a moulded component to less than a quarter of the original value. Some form of chemical interaction between the polymer and filler must be presumed, and a possibility is that small amounts of released water are causing high temperature hydrolysis of the polyurethane. The polymer breakdown is also evident in the rheology results where lower apparent viscosities are obtained with the filled compounds relative to the original materials. The observation of foaming with the hydroxyapatite filler is further evidence of adverse interaction.

As would be expected the included fillers shift the glass transition temperatures to slightly higher values and slightly increase the dynamic moduli. The proximity of the glass transition temperatures to the operating temperature of 37°C means that with both materials, properties are changing quite quickly with temperature. This may be of greater significance with Bionate 80A which is intended to be used as the bearing face material as any failure of the liquid film lubrication will cause local heating. Frictional heating of the 75D material is not likely.

While the tensile test results clearly illustrate the reinforcing effect of the carbon fibres, the poor wetting and pull out of the fibres, as evident in the SEM micrographs, show that the fibre-matrix bond is not ideal and could be improved. Poor wetting of the carbon fibres may be due to the high viscosity of Bionate 75D and may be improved by plasma or silane treatment of the fibres. Hydroxyapatite filler was considered because of its potential to improve bone in-growth performance of the final product in vivo. While this composite behaved much better in compression than in tension, processing issues leading to embrittlement of the material, possibly moisture content or agglomeration related, need to be resolved before it can be considered as an appropriate filler with this polymer.

The water absorption results suggest that the materials stabilise after 2 weeks, but the tensile results indicate that significant change occurred between 1 month and 5 months of exposure. The results of both Khan [10] and Quigley [14] however indicate that the drop in tensile

Table 7 Summary of the compression results including standard deviations

	Bionate 80A	Bionate 75D	Bionate 75D + CF	Bionate 75D + HA
E10% (MPa)	3.33 ± 0.14	92.41 ± 5.23	84.00 ± 5.58	97.25 ± 3.09
E20% (MPa)	6.20 ± 0.46	91.7 ± 5.9	103.75 ± 4.99	101.63 ± 2.40
Zero-strain shift (%)	8.21 ± 0.73	22.57 ± 2.62	20.61 ± 1.24	23.15 ± 1.52
	n = 11	*n* = 15	*n* = 4	*n* = 3

modulus levels off after approximately two months and begins to recover with continued ageing. It is therefore considered that this slow change in tensile properties is a reflection of local transport of plasticizing water, perhaps into segment domains.

The results presented here were obtained using materials and mouldings manufactured under processing conditions closely corresponding to those which would be used for production of orthopaedic components. They therefore provide a useful guide to the use of these and similar polycarbonate urethanes in biomedical applications.

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