Contents lists available at ScienceDirect

Polymer

Ultra-high molecular weight polyethylene – Evidence for a three-phase morphology

D. Barron, C. Birkinshaw*

Department of Materials Science and Technology, University of Limerick, Limerick, Ireland

ARTICLE INFO

ABSTRACT

The phase composition of ultra-high molecular weight polyethylene of two different molecular weights has been estimated using Raman spectroscopy. Materials have then been irradiated in air to give a received doses of 3.5 and 10 Mrad, and crystallinity change with time has been monitored by differential scanning calorimetry (DSC), wide and small angle X-ray diffraction (WAX and SAX) and Raman spectroscopy. Analysis by DSC and X-ray diffraction involved melting and re-crystallisation. Raman spectroscopy demonstrated that the material consists of three phases, fully crystalline, fully amorphous and an intermediate all-*trans* non-crystalline phase. Following irradiation the mass fraction of this latter phase reduces as total crystal content increases. SAX results indicate a refinement of the original lamellae and the emergence of a population of smaller crystals. It is thought that the all-*trans* material exists as an interfacial phase and that scission within this phase facilitates the observed crystal changes.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is a linear polymer with number average molecular weight in the range from one to ten million. Although it is supplied in relatively low tonnages by a very small number of manufacturers it has assumed great importance, primarily because of it use as a bearing surface in artificial joints, with well in excess of a million implants per annum using UHMWPE components. Other significant applications include gel-spun fibres and machine bearings. The material properties of particular value in the orthopaedic application are low friction, low creep and bio-inertness in bulk. There are, however, some difficulties to be overcome. First, the implants have to be sterilized and this is usually done by γ irradiation to give received doses of between 2.5 and 5.0 Mrad, and this leads to both immediate and time dependent changes in the material. Secondly the wear debris, which can be present as 10^6 to 10^9 particles/g of local tissue [1], is not bio-inert and through macrophage activity leads to aseptic loosening of the joint [2]. Both of these problems have been the subject of intensive study and have formed the basis of numerous publications.

The thrust of technical development in recent years has been to try to address both problems simultaneously by producing more stable grades of material that are also less prone to wear. Irradiation leads to very high free radical concentrations [3] and if the process

has been carried out in air, oxidative chain scission occurs as well as crosslinking [4]. The chain scission reactions are important because melt crystallisation in UHMWPE is diffusionally hindered and subsequent scission of interlamellae tie chains leads to both immediate and time dependent increases in crystallinity, modulus and brittleness [5–8]. The approach to more stable grades has been through controlling irradiation conditions to drive molecular change in the direction of crosslinking and away from chain scission. This has involved irradiation in the absence of oxygen, thermal annealing, two stage irradiation and melting routines, low irradiation dose rate procedures and the use of mechanical stress to kill radicals [9–11], and for reasons of commercial sensitivity many of these procedures have not been properly described in the literature. However, despite the uncertainty about some of the proprietary methods of producing stable polymer very large numbers of publications have described the chemistry of the irradiation and photo-oxidation processes and have linked these processes to morphology change.

It is usual to describe the morphology of UHMWPE in terms of crystalline and amorphous phases, with commercial compression moulded materials having crystallinity values in the range of 45–60% depending upon molecular weight and history. However, it is the authors' view, based on experimental results already published and new results presented here, that such a description of the material is over simplistic and that a better description of the material can be given, which is relevant to the identified application.

It is well known that in structural analysis the results obtained are strongly influenced by the chosen technique. Differential

* Corresponding author.
E-mail address: colin.birkinshaw@ul.ie (C. Birkinshaw).

scanning calorimetry (DSC) is the commonest technique for crystallinity measurement with UHMWPE and is quick and convenient. Wide angle X-ray diffraction (WAX) will also give percentage crystallinity, whereas small angle X-ray diffraction (SAX) offers the opportunity to measure lamellae thickness, as does transmission electron microscopy (TEM), although both the latter techniques are experimentally more demanding. Recent work [12] using both SAX and DSC has shown that in air irradiated and aged UHMWPE, a bimodal crystal population is present. The mass fraction of the major population, consisting of thicker lamellae, increases only slightly after irradiation and upon ageing, whereas a minor population of smaller crystals, formed after irradiation, grows significantly in importance with ageing.

The new results presented and discussed here were generated using Raman spectroscopy, a technique which is not commonly used for routine crystallography investigation, but which offers some advantages. The Raman spectrum of any polymer is sensitive to chain conformation since the latter influences the vibrational properties. The spectrum of polyethylene between 1400 and 1500 cm^{-1} incorporates the CH_2 bending vibration (I_B) and in the Raman spectrum these peaks are reasonably strong. The orthorhombic unit cell of crystalline polyethylene includes two C_2H_4 groups, and Mutter et al. [13] and Strobl and Hagedorn [14] have shown that the crystalline band becomes split into a doublet (1416 and 1440 cm^{-1}) corresponding to the frequency difference, between the in-phase and anti-phase vibrations of the two groups. In a totally crystalline polymer the peaks of this doublet will be equal in intensity since both vibration modes will occur to an equal extent, but in partially crystalline polymer these absorptions tend towards a single peak at 1440 cm^{-1}, as shown in Fig. 1. It is suggested that this occurs because many chain sections are in an all-trans conformation, but not packed within the orthorhombic unit cell.

Furthermore the I_{1416} peak diminishing and the tendency towards the I_{1440} peak remaining for a partially crystalline sample have been taken to suggest either the existence of an interfacial/transition zone between the crystallites and the disordered regions or that chains have some degree of order, in the all-trans conformation, within the amorphous phase. These observations allow for the use of the Raman spectrum as a means of quantitative structural analysis. For such work an internal standard is provided by the peak centred at 1290 cm^{-1} which arises from the CH_2 twisting vibration (I_T) and is independent of chain conformation. The relationship between highly ordered material contained within the unit cell and semi-ordered material is analysed by measurement of the I_{1416} peak which is then normalised against I_T. Strobl [13,14] calculated the normalised intensity of the I_{1416} peak representing the highly ordered crystalline material in 100% crystalline

polyethylene to be 0.493 and that value has been used here to estimate percentage crystallinity and the relationship between highly ordered material contained within the orthorhombic unit cell and so called interfacial material. Intensities were calculated by inputting a baseline at the extremities of the vibrational peak and integrating above the line. I_{1416} was measured by splitting the band at its maximum in two halves and determining the area of the low-frequency part, which avoids contributions of the higher frequency vibrations. Having calculated the fully crystalline and fully amorphous contents, the all-trans amorphous or interfacial content is obtained as the balance. A detailed study of crystallinity derived from Raman spectra, compared with results from other methods, has recently been published by Lin et al. [15] and this considers the merits of manual versus computer deconvolution of the spectra. Mandelkern and co-workers [16,17] have reported that manual deconvolution is satisfactory and that procedure has been followed here. There is a general consensus in the literature considering polyethylene as a three-phase material that the all-trans phase is interfacial.

Application of Raman spectroscopy in conjunction with information from the previously described DSC and SAX data allows a comprehensive structural analysis of UHMWPE. All of the materials used in this work were either un-irradiated or air irradiated and it is appreciated that most implant materials are now irradiated using inert atmospheres and are often subject to thermal regimes designed to minimise undesirable property change, however, examination of such materials has shown no fundamental differences in terms of the phases present [18].

2. Experimental

Materials used were GUR 1020 and GUR 1050, synthesised by Ticona, and specified to have MW values of 3.5 and 5.5 million, respectively. In the manufacturing process these polymers had been compression moulded into slabs 2 m × 1 m × 60 mm thick. Although it would be desirable to have precise information on the material's thermal history, this information is considered confidential to the manufacturer. Material temperatures of at least 220 °C are presumed and cooling times are of the order of hours. Experience has shown that the materials are morphologically stable with time unless irradiated. Specimens, in the form of blocks approximately 10 mm × 10 mm × 50 mm, were cut from the larger slabs, irradiated in air using a ^{60}Co source at a rate of 0.15 Mrad/h to give received doses of 3.5 and 10 Mrad and were first analysed within five days of irradiation. Ageing was carried out at room temperature in darkness for 25 months.

Differential scanning calorimetry was carried out using a Perkin–Elmer Pyris 1, using a sample size of approximately 5 mg and a heating rate of 10 °C/min under nitrogen. Samples, taken from the centre of the irradiated blocks, were heated to 200 °C, recording the initial melting event and then cooled at 10 °C/min to record the recrystallisation. A heat of fusion of 291 J/g was used to calculate percentage crystallinity with integration limits determined by inspection typically being between 118 and 148 °C for un-irradiated material.

X-ray diffraction was carried out using the Daresbury, UK, Synchrotron Radiation Source (SRS) beamline number MPW 6.2, described in detail elsewhere [19,20]. The configuration used allowed synchronised SAX and WAX measurements to be made. The SAX camera length was 3.5 m. The standard energy of 8.865 keV (1.40 Å) was used. A Linkam hot stage system was mounted in the beam and was programmed to heat and cool the sample at 10 °C/min giving a similar melting and cooling regime to that used for DSC. The programming and synchronization of the heated stage and the output from the two one-dimensional rapid response detectors were achieved via SRS in-house software. Analysis of data was
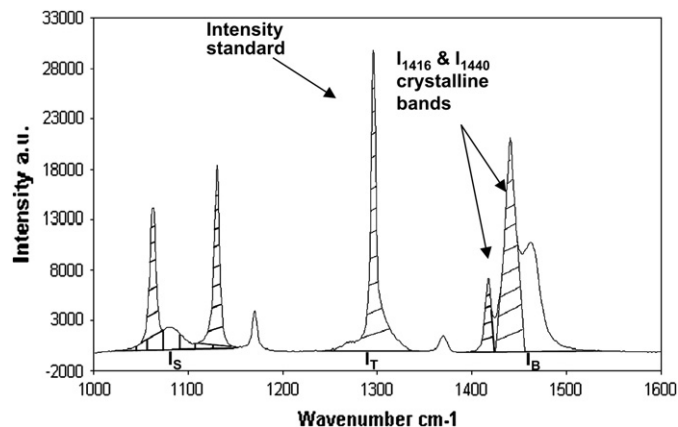

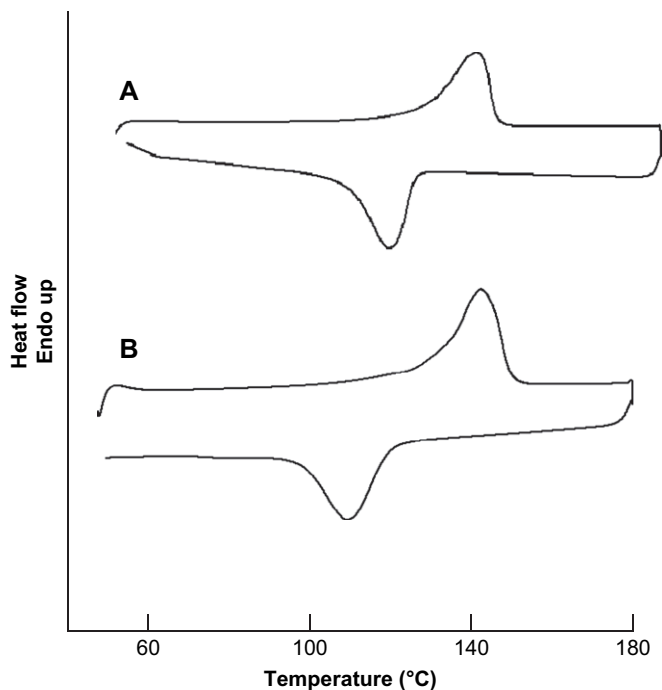Fig. 1. Typical Raman spectrum for polyethylene.

Fig. 2. DSC responses of un-irradiated GUR 1020 control material (A) and GUR 1020 10 Mrad 25-month aged material (B).

Fig. 3. Raman spectrum for control (un-irradiated) GUR 1020 UHMWPE.
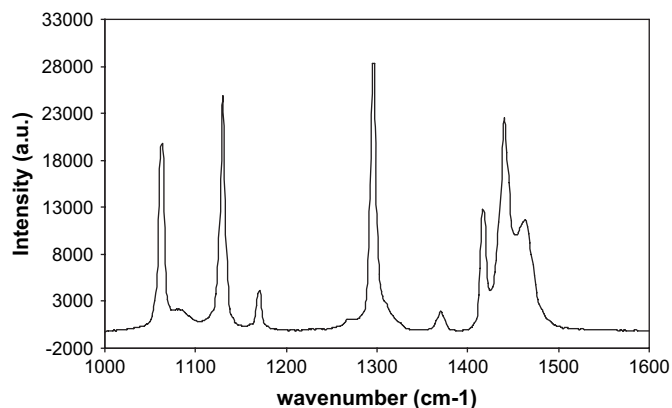
Fig. 4. Raman spectrum for GUR 1020 UHMWPE irradiated and aged for 41 months.

carried out using software developed by the Collaborative Computational Project for Fibre Diffraction and Solution Scattering (CCP13).

Raman spectra were recorded with a Horiba Jobin Yvon spectrometer using a laser light source with a wavelength of 514 nm. The laser power was 20 mW, the slit width was 300 μm, and accumulation time was 30 s collected 5 times. Samples of 1 mm thick were sectioned with a microtome from the centre of the irradiated blocks and placed on glass slides to be examined.

3. Results and discussion

Fig. 2 shows typical DSC plots for a control sample and an irradiated sample, and Table 1 details the DSC results for all of the materials investigated. Figs. 3 and 4 show, as typical examples, the Raman spectra of a control and an irradiated sample, and Figs. 5 and 6 illustrate the derived phase composition of the 10 Mrad series of materials examined. Figs. 7 and 8 show WAX and SAX results for a GUR 1020 control material and an irradiated and aged material. Additional X-ray diffraction results have been presented elsewhere [12].

Considering first the DSC results, these show the anticipated increases in crystallinity with irradiation and a further increase upon ageing, and these observations are consistent with previous experiments on these types of materials. The usual explanations are that immediate chain scission reactions, consequent upon irradiation, give the short term increase in crystallinity through release of
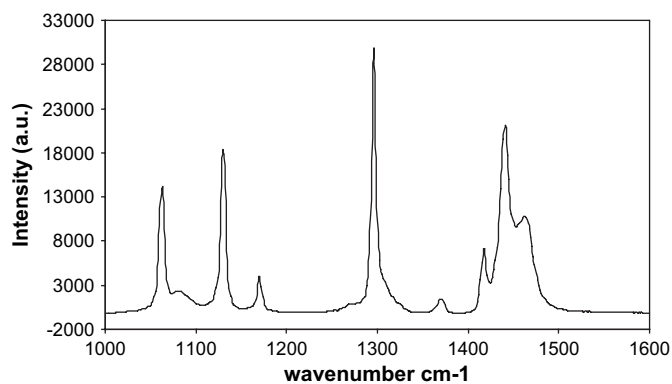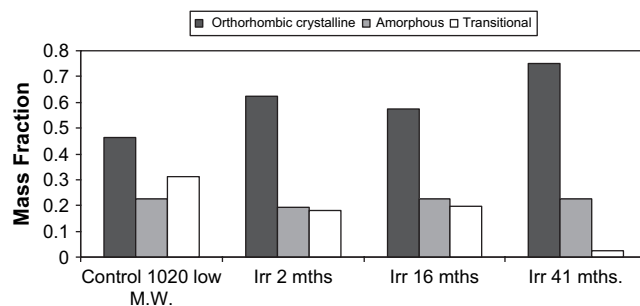

Fig. 5. Phase composition of the GUR 1020. Radiation dose 10 Mrad.

interlamellae tie chains, and over the longer term oxidation and oxidation product rearrangement reactions result in further chain scission allowing continued crystal growth. The lower crystallinity measured with the higher molecular weight polymer is indicative of the considerable hindrance to molecular diffusion in the melt.

Applying Strobl's analysis to the Raman data yields the results shown in Figs. 5 and 6 and allows a more detailed interpretation of the radiation induced crystallinity increase using the three-phase

Table 1
DSC results for materials examined

GUR 1020	Crystallinity (%)	Peak melting temperature (°C)	GUR 1050	Crystallinity (%)	Peak melting temperature (°C)
Control	51.6 (sd 1.7)	143	Control	45.0 (sd 0.9)	142
3.5 Mrad 7 days	53.8 (sd 0.7)	138	3.5 Mrad 7 days	53.6 (sd 0.4)	141
10 Mrad 7 days	57.3 (sd 1.5)	147	10 Mrad 7 days	53.7 (sd 1.2)	146
10 Mrad 25 months	60.3 (sd 1.3)	146	10 Mrad 25 months	51.7 (sd 0.6)	140

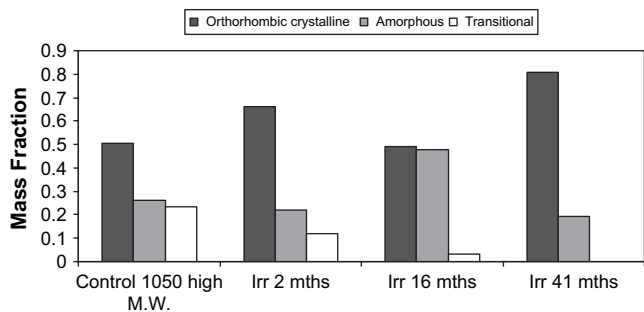Crystallinity values are the averages of at least three measurements.

Fig. 6. Phase compositions of the GUR 1050 materials. Radiation dose 10 Mrad.

model. The same general trends in respect of change in phase mass ratios are apparent with both materials. The most obvious observation is the steady fall with time of the mass fraction of all-*trans* non-crystalline material, whilst the overall crystallinity increases with time. In both cases the 16-month figure is lower than expected and the reasons for this are not understood. The mass fraction of fully amorphous material reduces slightly throughout the observation period, although again one of the 16-month results falls outside this trend. With both materials the overall increase in crystallinity is broadly similar to that observed using DSC, although the time intervals for the DSC work and the Raman work are not the same, providing support for the validity of the method in this application.
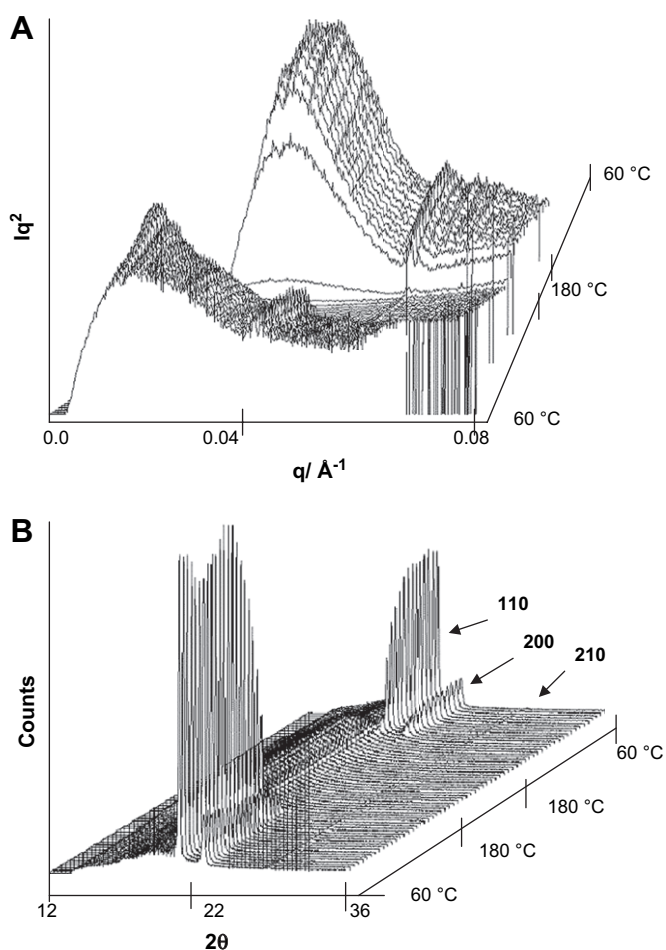

Fig. 7. SAXS and WAXS plots for GUR 1020 control material (un-irradiated) as it is melted and re-crystallised.
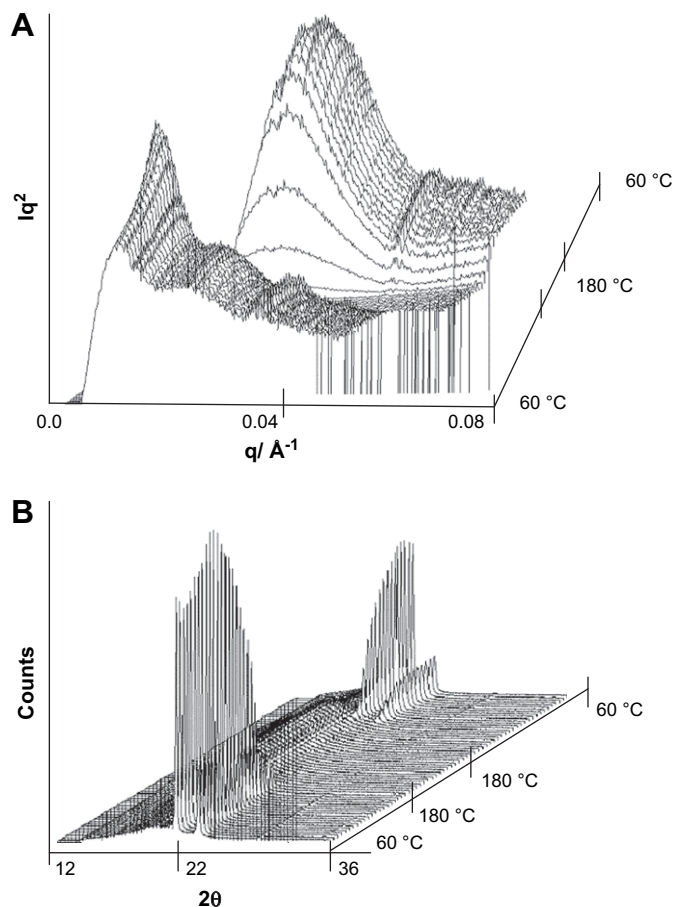

Fig. 8. SAXS and WAXS plots for GUR 1020 10 Mrad aged 21 months as it is melted and re-crystallised.

Indication of the nature of the crystal growth processes can be obtained from examination of the X-ray data, examples of which are shown in Figs. 7 and 8. The peaks evident in the WAX patterns (110, 200 and 210 planes) have been indexed and according to the literature [21] are those of the orthorhombic crystal structure, as found in lower molecular weight fractions of polyethylene; and there is no change in these peaks with dose or time. The SAX results, shown in Figures 7 and 8, suggest that as well as some refinement of the original lamellae, evident as a sharpening of the main peak, growth of a second population of crystals occurs at a q value of approximately 0.03 Å^{-1}. (It is thought that the small sharp peaks at higher q values are artefacts, but their origin is not known.) Comparison of diffraction data for the lower and higher molecular weight materials before irradiation shows little qualitative difference, but after irradiation the development of the second SAX peak is more evident in the GUR 1020, indicating a continuing dependence of crystallisation on chain mobility. With all materials re-crystallisation from the melt occurs after significant super-cooling and results in a single SAX peak, indicating now a homogeneous crystal population. This suggests that any crosslinking reactions, coincident with the scission processes, have not locked in the previous structure. Earlier work [22] has identified a minor re-crystallisation event occurring after the main peak in aged irradiated materials, but the SAX data shows no evidence of this.

Measurement of the overall lamella thickness of the original lower molecular weight material gives a result of 182 Å, indicating approximately 118 repeat units per fold length and the higher molecular weight material is slightly less than this at about 135 Å indicating about 88 repeat units per fold length. Re-crystallisation always leads to thinner lamellae and this is probably a cooling rate

effect as the original materials were taken from large compression moulded blocks and therefore subjected to much slower cooling rates than 10 °C/min used in the synchrotron re-crystallisation experiments. Taken overall there is little change in maximum lamellae thickness with dose or with ageing, indicating that the system is close to the optimum fold width for the particular cooling conditions.

It is considered that the spectroscopy and SAX results provide convincing evidence for a three-phase model of polyethylene in general and UHMWPE in particular. The fully crystalline orthorhombic material is present in the usual chain folded lamellae structures; a significant amount of material is present in the all-*trans* form and the balance is fully amorphous. It is possible that the all-*trans* material is located on or near the lamellae surfaces and chain scission within or close to this region releases chains for further crystallisation.

In its original state UHMWPE contains three phases, fully crystalline orthorhombic, fully amorphous and an intermediate all-*trans* ordered phase. It is likely that this latter phase is associated with the surface of the crystallites and involves re-entrant loops and other interfacial material. On irradiation, scission within or close to this interfacial material, allows a "cleaning up" of the surface of the original lamellae leading to the observed sharpening of the main SAX peak and the formation of a second population of small crystallites, responsible for the emerging small peak in the SAX plots. Premanth et al. [8] have also suggested that irradiation and ageing leads to the formation of thin crystallites within the amorphous region. With time, further chain scission contributes to both crystallisation processes at the expense of the total mass fraction of all-*trans* or interfacial material, progressively moving the material closer to a two phase structure.

Given the interest in understanding the nature of the photo-initiated oxidation and scission reactions in these materials the question arises as to whether the nature of the phase pre-disposes it towards certain types of rearrangement consequent upon irradiation. The general presumption is that reactions do not occur within the crystal core and are limited to the amorphous regions, but it may be possible that certain types of rearrangement are more favoured within the all-*trans* phase than in the random fully amorphous.

4. Conclusions

UHMWPE is best regarded as a three-phase material which contains in addition to the fully crystalline and fully amorphous phases a significant interfacial all-*trans* phase. On irradiation and ageing this interfacial phase provides the feedstock for further crystallisation resulting in refinement of the original lamellae and creation of new small crystallites. Melting and re-crystallisation of irradiated and aged material reverts the structure to a single crystal population.

It is likely that all of the current procedures, designed to produce more stable grades of UHMWPE for implant applications, depend upon aspects and combinations of the aforementioned processes

for their success. As part of this investigation a number of proprietary "stabilized" materials were examined using the techniques described above, and although the procedures used to stabilize them could not be ascertained, again because of commercial sensitivity, no observations falsified the above ideas.

The mass fractions of all-*trans* or interfacial material recorded in this work is quite high, but such an observation is consistent with comments by Glotin and Mandelkern [16] that the interfacial content becomes significant for molecular weights greater than about 1×10^5 for linear polyethylene fractions. Strobl and Hagedorn [14] have also noted that the interfacial fraction is reduced through heat treatment, and so it is likely that some of the stabilization methods, now in industrial use, are simultaneously affecting several material parameters.

References

[1] Kobayashi A, Freeman MA, Bonfield W, Kadoya Y, Yamac T, Al-Saffar N, et al. J Bone Joint Surg Br 1997;79(5):844–8.
[2] Kadoya Y, Revell PA, Kobayashi A, Al-Saffar N, Scott G, Freeman MA. Clin Orthop 1997;340:118–29.
[3] O'Neill P, Birkinshaw C, Leahy JJ, Barkley R. Polym Degrad Stab 1999;63(1): 31–9.
[4] O'Neill P, Birkinshaw C, Leahy JJ, Buggy M, Ashida T. Polym Degrad Stab 1995; 49(2):239–44.
[5] Nusbaum HJ, Rose RM. J Biomed Mater Res 1979;13:557–76.
[6] Bhateja SK, Andrews EH, Young RJ. J Polym Sci Polym Phys Ed 1983;21:523–36.
[7] Birkinshaw C, Buggy M, Daly S, O'Neill M. J Appl Polym Sci 1989;38:1967–73.
[8] Prenmath V, Bellare A, Merrill EW, Jasty M, Harris WH. Polymer 1999;40: 2215–29.
[9] Shibata N, Kurtz SM, Tomita N. J Biomech Sci Eng 2006;1:107–23.
[10] Wang A, Zeng H, Yau S-S, Essner A, Manely M, Dumbleton J. J Phys D Appl Phys 2006;39:3213–9.
[11] Dumbleton JH, D'Antonio JA, Manley MT, Capello WN, Wang A. Clin Orthop Relat Res 2006;453:265–71.
[12] Barron D, Collins MN, Flannery MJ, Leahy JJ, Birkinshaw C. J Mater Sci Mater Med 2008;19:2293–9.
[13] Mutter R, Stille W, Strobl G. J Polym Sci Part B Polym Phys 1993;31:99–105.
[14] Strobl GR, Hagedorn W. J Polym Sci Polym Phys Ed 1978;16:1181–93.
[15] Lin W, Cossar M, Dang V, The J. Polym Test 2007;26(6):814–21.
[16] Glotin M, Mandelkern L. Colloid Polym Sci 1982;260(2):182–92.
[17] Fallia M, Alamo RG, Mandelkern L. Polym Test 1992;11:151–9.
[18] Barron, D. The morphology of irradiated ultra high molecular weight polyethylenes. Ph.D. thesis, University of Limerick, 2007.
[19] Bras W, Derbyshire G, Ryan A, Mant G, Lewis R, Felton A, et al. X-ray optics and microanalysis. Proceedings of the thirteenth international congress. Manchester, UK: IOP, Bristol, UK; 1992. p. 635–8. Sponsor: Royal Soc.; IOP; Royal Microscopical Soc.; ICI; BP; Weir Mater.; Unilever.
[20] Cernik RJ, Barnes P, Bushnell-Wye G, Dent AJ, Diakun GP, Flaherty JV, et al. J Synchrotron Radiat Part 2 2004;11:163–70.
[21] Balta-Calleja FJ, Vonk CG. X-ray scattering of synthetic polymers. New York: Elsevier; 1989.
[22] Barron D, Birkinshaw C. Polymer 2005;46(23):9523–8.