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Influence of Vitamin C on Morphological and Thermal Behaviour of Biomedical UHMWPE

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Summary: Biomedical Ultra-High-Molecular-Weight Polyethylene (B-UHMWPE) is widely used in orthopaedics as a biomaterial because of its mechanical properties and biocompatibility. However the adding of vitamin antioxidants can influence the inflammatory process. Thus, the objective of this study is to evaluate the influence of adding ascorbic acid (vitamin C) at different concentrations to the B-UHMWPE matrix, using for this purpose the Scanning Electron Microscopy (SEM) and Differential Scanning Calorimetry (DSC) analyses. The vitamin C was mixed with B-UHMWPE in concentrations of 0.5, 1.0 and 2.0%wt and the molding was performed with a 10MPa load at 160 °C for 6min.The fracture surface of cross-sectional area of B-UHMWPE modified with vitamin C showed that the vitamin is present in the polymer matrix in the form of small agglomerates, being an indication that there was no fusion of the vitamin C during the processing step. Using the technique of differential scanning calorimetry it was observed that the melting temperature remained constant as well as the crystallisation temperature, but there was a small variation in crystallinity with the addition of vitamin C. From this study, we conclude that the presence of vitamin C (ascorbic acid) did not alter the thermal properties of crystallisation and melting of B-UHMWPE.

Keywords: biomedical UHMWPE; compression molding; scanning electron microscopy, thermal properties; vitamin C

Introduction

Ultra-high-molecular-weight polyethylene (UHMWPE) is a bio compatible polymer with good chemical resistance, excellent toughness, high resistance to physical abrasion, low friction coefficient and good mechanical properties.[1] Biomedical UHMWPE is widely used in orthopaedic implants such as the acetabular component of the hip and knee, with satisfactory clinical results. In these applications an important problem is associated with the wear of UHMWPE. One method of improving the wear resistance of UHMWPE is by radiation crosslinking and a subsequent thermal treatment in order to diminish or eliminate residual free radicals created during the previous irradiation. However a disadvantage in this melting procedure is the decrease in crystallinity of the irradiated polymer, therefore, reducing some of its mechanical properties.[2–6]

It is well established in the literature that the irradiated UHMWPE improves both mechanical properties and oxidative response when the vitamin E (antioxidant) is added into it. There are two methods of incorporating vitamin E into UHMWPE. One is to blend vitamin E with UHMWPE powder before the consolidation of them and the radiation crosslinking. Although the polymer oxidation is protected by the vitamin E, the efficiency of crosslinking is reduced and consequently the UHMWPE resistance to wear, gained without adding the vitamin, is partly lost. Another method is the diffusion of vitamin E into the UHMWPE after the consolidation and

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radiation processes. In this case, the cross-linking of the polymer is not affected by the vitamin addition, but the diffusion leads to a concentration profile of the vitamin along the interior of vitamin E-UHMWPE blended system.[7,8] Tomita *et al.*[9] reported that the presence of vitamin E results in a reduced of hardness at grain boundaries of UHMWPE, implying in crack propagation reduction. They pointed out that the reason of this reduction is not clear, suggesting that the vitamin may be distributed at grain boundaries of the polymer. Other authors[10–13] suggest that vitamin E improves the oxidative stability of the UHMWPE after the irradiation process because of its ability to react with peroxy radicals on the polymer chains, hindering the oxidation reaction.

Consolidation of the polymer is carried out at high pressures and temperatures of at least 180 °C, so any additive of the UHMWPE must have good thermostability, which is the case of vitamin E.[14] In order to make sure the additive has the desire features, evaluation tests of the consolidation process with the substance must be performed. Thus, vitamin C has potential use in this application because it is one of the most important natural antioxidant, its melting point near to 180 °C and it's also a water soluble antioxidant.[15,16]

When a biomaterial is implanted in bone structure a local tissue injury occurs. In the early hours of the implant this injury is characterised by the appearance of an acute inflammatory response and the formation of hematomas.[17] As part of the inflammatory response there is a formation of free radicals. Therefore, several aspects of acute and chronic inflammatory processes are triggered by the release of oxidants through phagocytosis. One way to combat the severity of an inflammatory process and damage caused by free radicals is using antioxidants.[18] The intake of vitamins with antioxidant properties seems to have an additional beneficial effect on oxidative stress and inflammatory state.[19] Recently Rocha *et al.*[20] showed that vitamin C (ascorbic acid) has proven to be rather effective on reducing the oxidation of UHMWPE and modifying the kinetics of the first stage slowing down there action. New studies[21,22] reported the diffusion mechanism of vitamin E into the UHMWPE matrix. Using a Fickian model (no-erosion/degradation model), several authors were able to describe the diffusion behaviour and predict vitamin E concentration profiles for vitamin E-doped samples. Also, recent papers indicate that ascorbic acid therapy inhibit pro-inflammatory cytokine release in a human cell model.[23] Mikirova *et al.*[24] found that vitamin C treatments may reduce inflammation in cancer patients.

Then, in this paper the effects of vitamin C on the thermal property and morphological feature of the consolidated compounds of biomedical UHMWPE/vitamin C are discussed based on DSC analyses, thermogravimetry and scanning electron microscopy.

Experimental Part

Biomedical ultra-high-molecular-weight polyethylene (B-UHMWPE) was kindly donated by Baumer S.A, Brazil, and the vitamin C (ascorbic acid) was obtained from Galena Chemicals & Pharmaceuticals Brazil, with 98.3% purity. Both components were solid blendedin different ratios (0.5, 1.0 and 2.0% wt mass of vitamin C) given the powder mixtures of B-UHMWPE/vitamin C.The structural formula of vitamin C is shown in Figure 1.

Compression Molding

Pure B–UHMWPE and B-UHMWPE/vitamin C mixtures were pressed under 10MPa and 160 °C for 6 min in a Manual Hydraulic Press (Marconi, Brazil).The film samples

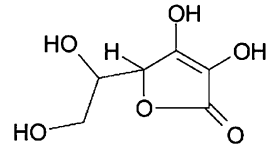

Figure 1.
The schematic representation of the vitamin C molecule.[25]

obtained were between 0.31and 0.35mm thick.

Thermal Characterisation

DSC analyses were performed on a Shimadzu Differential Scanning Calorimeter (DSC-60) in order to investigate the degree of crystallinity and melting behaviour of the pure and modified B-UHMWPE samples. Previously there were cut into small pieces and uptake samples of approximately 6.000 mg. For each sample, two heating cycles were performed to determine the crystallisation temperature (Tc) and the melting temperature. In the first heating cycle the samples were heated from room temperature to 150 °C with a heat rate of 10 °C/min under argon atmosphere and hold for 3min to eliminate the influence of the previous thermal history. Then the samples were cooled to room temperature at a rate of 10 °C/min and hold it for 3min.The cooling was recorded and the crystallisation temperatures (Tc) were determined from these profiles. Following, the second heating cycle was launched and recorded from room temperature to 300 °C to determine the samples melting temperatures. This upper temperature was chosen because the melting temperature of vitamin C was at this temperature range. From these profiles the fusion enthalpy(heat of fusion) was determined by integrating the endothermic peak area from about 103 °C to 146 °C.Then the degree of crystallinity was calculated from the following equation:

$$\%X_c = (\Delta H_m / \Delta H_m^\circ) \times 100$$

Where ΔH_m is the heat of fusion of the sample, and ΔH_m° is the heat of fusion for 100% crystallinity UHMWPE taken as 291 J/g according to the literature.[26]

The TG analysis was performed on a DTG-60H Shimadzu Thermogravimetry apparatus to study the thermal degradation of the pure and modified polymer. Approximately 6.0 mg of samples were loaded and heated from 100 to 700 °C with a heat rate of 15 °C/min under argon atmosphere.

Morphological Characterisation

Analysis was performed in a Scanning Electron Microscope (SEM), Leo 1430 Zeiss. All samples were evaluated after cryogenic fracture in liquid nitrogen and their cross-sectional area were analysed. The sample surface was sputter coated with gold to avoid charging.

Results and Discussion

Figure 2 depicts the TG curves of pure and modified samples. It can be observed an initial loss weight at 190.21 °C, assigned to the degradation of vitamin C, implying the absence of thermal degradation in the compression molding process (for pure and B-UHMWPE/vitamin C),because the consolidation temperature of these samples are 160 °C. Jigyan *et al.*[27] has been suggested three stage of decomposition process to vitamin C: the first associated with loss of molecular H_2O and molecular CO_2, the second equivalent to the apparent molecular weight and third due to slow weight loss of ascorbic acid. In Figure 2-e it can be observed this decomposition behaviour of vitamin C. There, the first stage take place between 190–250 °C with a weight loss percentage of 40%, the second stage at 274–519 °C with a weight loss of 33% and the third stage occurred at 510–700 °C.The upper temperature limit of 700 °C was

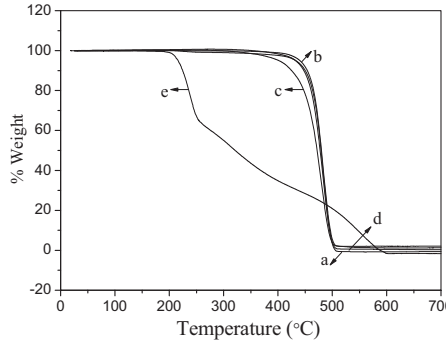

Figure 2.
TG curves of pure and modified polymers. a) pure B-UHMWPE; b) 0.5%wt Vitamin C; c) 1.0%wt Vitamin C; d) 2%wt Vitamin C and e) pure Vitamin C.

chosen taking into account the thermal decomposition of the B-UHMWPE matrix. The pure polymer presented only one stage of decomposition with initial and final degradation temperatures equal to 331.77 °C and to 445.87 °C, respectively. The modified polymers showed a similar thermal behaviour to the B- UHMWPE matrix.

Figure 3 shows the DSC curves for the first and second heating cycles for the pure and modified polymer(0.5, 1.0 and 2.0%wt of vitamin C), pointing out their crystallization temperature under argon atmosphere (Figure 3-a). The calculation of crystallinity was performed for the pure and modified B-UHMWPE with the vitamin C. For these calculations the melting enthalpy were obtained from the DSC melting curves, as described above, and the melting enthalpy of a crystal of pure B-UHMWPE reported in the literature.[14] It should be noted that there were no significant change in crystallinity of B-UHWMPE after the addition of small concentrations of vitamin C in the polymer matrix. The melting temperature (T_m) and the crystallisation temperature (Tc) of the pure and modified B-UHMWPE remained unchanged at about 134 °C and 115 °C, respectively (Figure 3b and c). These results show that the presence of vitamin C did not affect the thermal behaviour of pure B-UHMWPE. On the other hand, all samples presented a peak at about 193 °C, assigned to melting of Vitamin C. These results suggest that adding of vitamin C does not alter the thermal properties of the polymer or its crystallinity. This fact indicates that the properties that depend on the crystallinity will remain unchanged.

Table 1 shows the values of the melting and crystallisation temperatures and crystallisation enthalpy for the first and second heating as well as the crystallinity achieved by means of eq. 1.These results are in agreement with those reported by Liu *et al.*[14], as they also observed that thermal properties of biomedical UHMWPE were not altered to the addition of a low concentration of estradiol.

Figure 4 shows the fracture surfaces of cross-sectional area of pure and modified B-UHMWPE. And in these micrographs, the arrows indicate the presence of vitamin

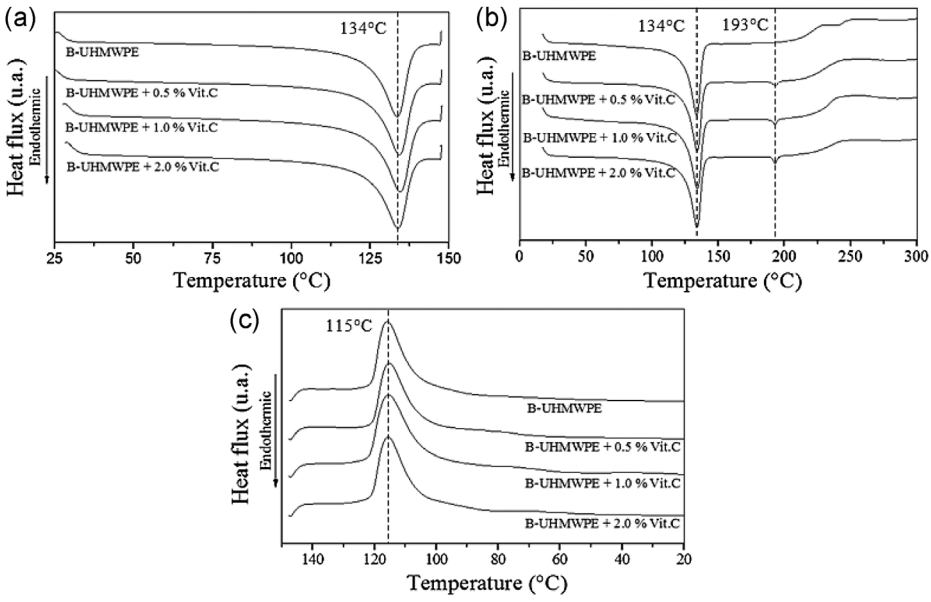

Figure 3.
DSC curves of pure and modified polymers: a) Melt temperature in first heating b) Crystallisation temperature and c) Melt temperature in second heating.

Table 1.
Melting Temperature (Tm), Crystallization Temperature (Tc), melting enthalpy(ΔH_m), cristallisation enthalpy(ΔH_c) and Crystallinity (X) of pure and modified B-UHMWPE obtained after second heating.

	1st Heating (a)			T_c	ΔH_c	2nd Heating (b)				
	T_m	ΔH_m	X			T_m	ΔH_m	X	T_m^*	ΔH_m^*
	°C	J/mol	%	°C	J/mol	°C	J/mol	%	°C	J/mol
Pure B - UHMWPE	134	110	36	115	109	133	116	40	–	–
Pure Vitamin C	196	211	–	–	–	–	–	–	–	–
0.5% Vitamin C	134	114	40	115	97	134	117	41	193	2.8
1.0% Vitamin C	134	119	41	115	117	134	115	42	193	3.8
2.0% Vitamin C	134	108	37	115	113	134	114	40	193	4.3

* Tm and $^*\Delta H_m$ to Vitamin C.

C in the B-UHMWPE matrix. It can be seen that vitamin C is not solubilised in the polymer matrix after the molding process conditions. The increase of vitamin C in the loading resulted in its agglomerates on the B-UHMWPE. These can be observed in all modified B-UHMWPE samples in Figure 4b-d, showing that the Vitamin C remained intact in the polymer. In all compositions, the Vitamin C exhibited a poor adherence to polymer. These results suggest that there is a weak interaction between vitamin C and B-UHMWPE.

To the best of the Authors' knowledge, there is a lack of works on UHMWPE/ Vitamin C compounds, so important questions are still unclear. For example, their potential applications to orthopaedics.

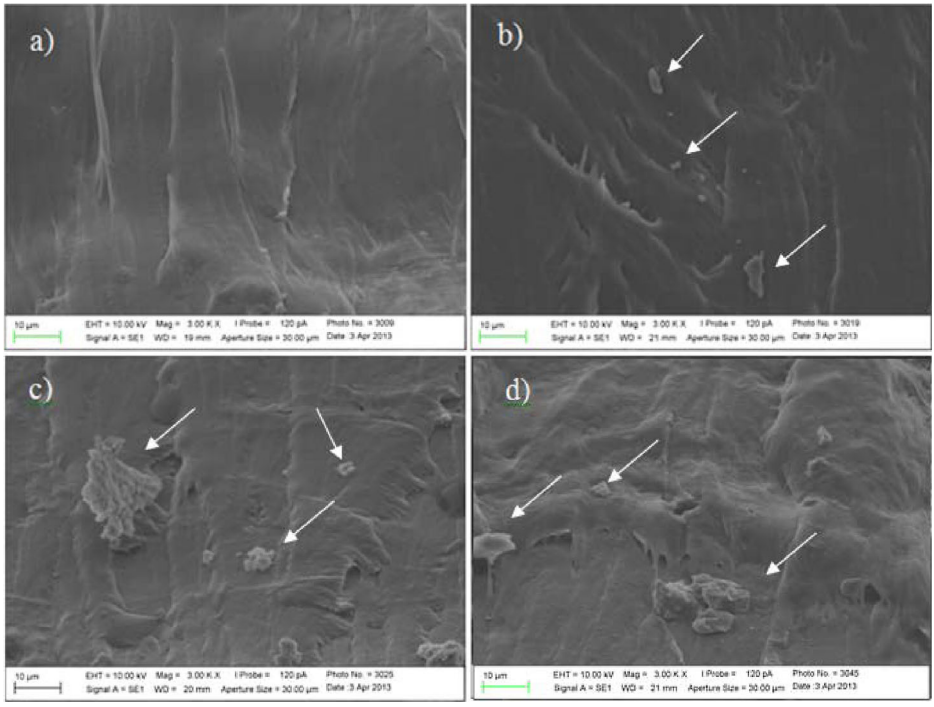

Figure 4.
Images obtained by scanning electron microscopy. a) B-UHMWPE, b) 0.5wt% of vitamin C, c) 1.0wt% of vitamin C and d) 2.0wt% of vitamin C.

Therefore, complementary studies are required in order to acquire proper explanations for this issue.

Conclusion

From this study, the results suggest that it was possible to incorporate vitamin C in B-UHMWPE without its degradation in processing temperature. The vitamin C altered neither melting nor crystallization temperatures of B-UHMWPE and it was not solubilised in this polymer, remaining intact. However, further studies are required to examine the influence of vitamin C in the other material properties.

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