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EFFECT OF ADDITION OF A QUASICRYSTAL FILLER ON THERMAL AND DYNAMIC MECHANICAL BEHAVIOR OF COMMERCIAL ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE

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Abstract. The use of filler reinforcement in polymer composite manufacturing processes has been received special attention by both industrial and academic researchers. For example, recent encouraging results suggest that if convenient quasicrystals were used as filler reinforcement, some properties of biomedical UHMWPE (Ultra High Molecular Weight Polyethylene) could be improved. This work discuss some aspects of thermal and dynamic mechanical behavior of commercial UHMWPE reinforced by quasicrystal $Al_{59,2}Cu_{25,5}Fe_{12,3}B_3$ *in a hot indirect extrusion process. Composite characterizations were done by techniques such as: Thermal Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM) e Dynamic Mechanical Analysis (DMA). The results suggest quasicrystal filler increases stiffness, thermal stability, and cristalinity degree of UHMWPE. In addition, quasicristal filler in reinforced polymer matrix is well-dispersed and plays as a nucleant agent, contributing to both better force distribution and mechanical properties.*

Keywords: *UHMWPE, Quasicrystal, Composite*

Introduction

Many times conventional materials (such as polymers, ceramics and metallic alloys) are unable to support the modern technologies with their individual properties alone. However if they are combined conveniently uncommon properties can be obtained and potentially produced using composite manufacturing technologies. The composite matrices can be made of polymeric, ceramic and metallic materials. One of the most attractive factors in polymer composite materials is their high mechanical performance for stiffness and strength/weight ratio, justifying their high demands in many engineering applications such as land vehicles, constructions, marine and aerospace industries. In addition, the techniques of manufacturing of polymer composites are usually much cheaper than ceramic and metallic composites (Callister Jr and Soares 2008; Chawla, 2009).

Polymer matrices can be classified as thermoplastic and thermoset materials. The UHMWPE is an important thermoplastic matrix due to its relevant properties such as low friction ratio, high wear strength and high impact strength. Many kinds of particles can be used as reinforcement in polymer thermoplastic composite due to their availability and simplicity of production in powder form. The incorporation of these reinforcement's leads to many improvements for matrix performance (mainly mechanical stiffness and strength) which are important factors required in industrial applications. The main particle reinforcements are clay, mica, talc and wollastonite because of their high ratios (length to thickness or length to width) ((Padilha 1997; Mallick and Newman, 1990).

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Metallic quasicrystalline particle (quasicrystal) is a recent kind of reinforcement with excellent stiffness, but its fragility limits major applications in engineering problems. A successful case of quasicrystal application is certain problems of coating. For example, they have better performance than teflon in coating pans due to superior wear strength, producing a longer durability of coating. Some quasicrystals are produced in the world in present time, for example, AlCoNi, AlCuCr, AlCuFe and AlCuFeB, which the last two are more studied mainly due to their easy process and good properties (Mourisco 1995; Dubois 2005). Lima et al. (2012) studied a case of small addition of bore in quasicrystal AlCuFe and observed change in its crystalline structure and improvement in its fracture toughness. Some researchers suggested that the good characteristics of quasicrystals can be aggregated to polymer matrix in composites materials (Dubois, 2005; Schwartz et al., 2007; Kenzari et al., 2012; Bloom et al. 2000). Bloom et al. (2002) observed that the addition of quasicrystal into UHMWPE increased its mechanical properties and wear strength.

This work investigates potential changes of thermal and dynamic mechanical properties of composites made by different compositions of quasicrystal particle reinforcement $Al_{59,2}Cu_{25,5}Fe_{12,3}B_3$ in UHMWPE. The concentration of quasicrystal particle in composites was 4, 2, 8,1 and 18,5 wt %. The analyses were done by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) dynamic mechanical thermal analyses (DMA) scanning electron microscopy (SEM).

Experimental

Materials and Methods

The UHMWPE investigated in this study was supplied by Braskem with Mw= 6 x 106 gmol-1 and was used as received. The quasycristal $Al_{59,2}Cu_{25}Fe_{12}$ B_3 was produced in Solidificação Rápida Laboratory(LSR). The UHMWPE/quasycristal composites were prepared at quasycristal concentrations of 4,2, 8,1 and 18,5 wt.%.

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Preparation of Quasicrystal

Aluminum (99.97% purity), electrolytic copper (99.98% purity), iron (99.98% purity) and bore (99.99%) were used to prepare an Al59,2Cu25,5Fe12,3B3 alloy, which was melted in an induction furnace under argon atmosphere. After melting, the alloy ingot was heat treated under vacuum at 750°C for 12 hours. This ingot was milled in a planetary ball with a ball to powder ratio of 10:1, during 20min, in order to obtain quasicrystal particles. The phase quasicrystalline Ψ-icosaedral was verified by X-ray Diffraction(XRD).

Preparation of UHMWPE/Quasicrystal Composites

The powders of UHMWPE and quasicrystal were mixtured by 10min at ambient temperature to obtain homogeneous composites. In beginning, the composites were molded in a hot indirect extrusion process in a cylindrical mold with volume of 21,54 cm^3, at a pressure of 2ton and temperature of 200 ^oC and after 30min the composites were transformed in power by milling. In following, the samples of composites in powder were molded using compression molded in rectangular plates at 180 ^oC, during 20min, at a pressure of 12 ton.

Characterizations

Differential Scanning Calorimetry (DSC)

The differential scanning calorimetry DSC measurements were carried out using a DSC-60 Shimadzu. Sample weights were varied between 3 and 5mg and placed in sealed aluminium pans. A heating/cooling rate of 10^{o}C/min was applied and upper temperature range of 25-200 ^{o}C was selected. The UHMWPE and its composites were tested in argon as an inert gas, with a flow rate of 50,0 ml.min^{-1}.

Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (TGA) were carried out using a DTG-60H Shimadzu. Sample weights were varied between 3 and 5 mg. A heating rate of 10^{o}C/min was applied and upper temperature range of 25-1000 ^{o}C was selected. The UHMWPE and its composites were tested in argon as an inert gas, with a flow rate of 50,0 ml.min^{-1}.

Dynamic Mechanical Thermal Analyses(DMA)

Dynamic Mechanical Thermal Analyses(DMA) of the UHMWPE and its composites were performed using a DMA Q800 V7.1 Build 116 instrument. Measurements of a storage modulus (E´), loss modulus(E´´) and tan δ were recorded as a function of temperature in the range from 25 ^{o}C to 100 ^{o}C at a ramp rate of 5 ^{o}C/min and a frequency of 1.0 Hz. Rectangular plates(50x11,55x3,13mm) were used to perform the tests.

Scanning Electron Microscopy(SEM)

Scanning electron microscopy (SEM) of cryogenically fractured surfaces of UHMWPE/quasicrystal composites were carried out on a LEO 1430 Zeiss instrument. The SEM samples were gold-sputtered prior to observation.

Results and Discussion

Preparation of Quasicrystal

Figure 1a shows the diffractogram of X-ray analysis of the alloy after fusion quasicristalina and figure 1b the diffraction after heat treatment in the heating oven.

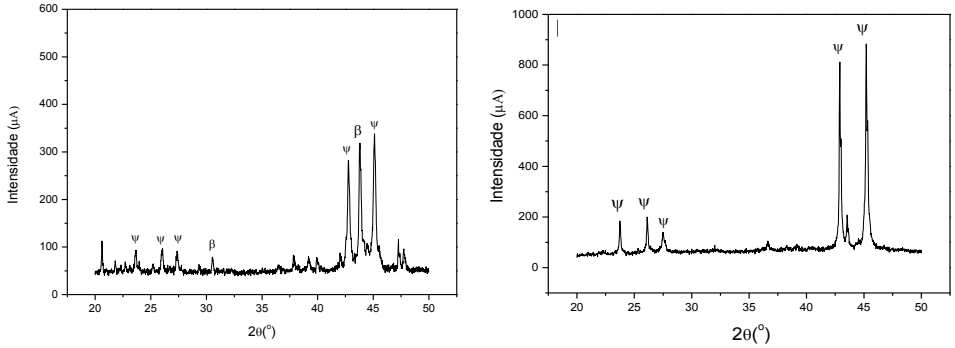

Figure 1. a) XRD of alloy after fusion quasicristalina; b) diffraction after heat treatment for 12 hours.

Figure 1a shows the XRD crude quasicrystalline alloy obtained by casting prior to heat treatment. It can be observed the β crystalline phase and the quasicrystalline Ψ icosahedral phase structure, the β phase is not required in this type of alloys, when it appears mixed with the quasicrystal phase, even at low concentrations, may affect the material properties of quasicrystal. Figure 1b shows the XRD quasicrystalline alloy after the heat treatment, which phase observed is practically Ψ.

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Thermal Analyses

Differential Scanning Calorimetry (DSC)

The thermal properties of UHMWPE and its composites were investigated. The degree of crystallinity(X_c) was calculated using the following equation:

$$X_c(\%) = \frac{\Delta H_m}{(1-W_f).\Delta H_{100\%}} \quad (1)$$

Where: ΔHm is the melting enthalpy of UHMWPE and $\Delta H_{100\%}$ is the standard melting enthalpy of polyethylenes, it´s taken to be in the range of 276,15 -292,88 J/g and the value used in this work was 291 $J.g^{-1}$ [Canevarolo, 2007]; Wf is the weight of quasicrystal in a composite.

The temperatures and enthalpies of melting are shown in Table 1 and Figure 2. Slight differences were observed in the melting temperatures(T_m) of UHMWPE matrix for different composites studied. Moreover, the enthalpies of the phase transitions (degree of crystallinity correspondingly) of UHMWPE/quasicrystal composites were higher than those of neat UHMWPE. The addition of quasicrystal filler until 8,1wt% caused considerable increase in the degree of crystallinity of UHMWPE. This behavior suggests that the quasicrystal filler is an agent nucleant to UHMWPE, so that a potentially increasing of composite stiffness is expected.

Table 1. DSC data of thermal properties of UHMWPE and its composites.

Sample	**ΔH_m(J\g)**	**X_c (%)**	**T_m (ºC)**
UHMWPE/0	87,13	29,9	134,18
95,8/4,2	108,94	37,8	134,74
91,9/8,1	127,21	44,0	134,75
81,5/18,5	49,89	18,00	138,61

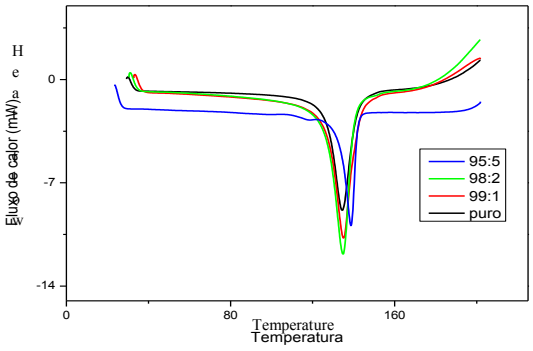

Figure 2. DSC graph of the pure polymer and composite

Thermogravimetric Analysis (TGA)

In figure 3 can be seen that the pure UHMWPE and its composites showed degradation curves in one step, with a temperature of onset of weight loss ($T_{initial}$) above 330 ºC, see the data in Table 2.
The thermal behavior of degradation of the UHMWPE was changed with the addition quasicrystalline filler. It can be seen in Table 2 an increase in the initial temperature ($T_{initial}$) of UHMWPE with increasing concentration of quasicrystal. This means that the percentage of weight loss decreased with the addition of quasicrystal. This same trend was also observed in degradation temperature (T_{onset}), ie, the thermal stability of UHMWPE was increased with the addition of quasycristal and the final temperature of degradation (Tendset) was little changed with the addition of the quasycristal UHMWPE. In temperature

around 500 °C it can be observed a increase in remaining weight when concentration of quasicrystal was increased because in this temperature the quasicrystal has thermal stability.

Table 2. TGA characterization of UHMWPE and its composites.

Sample	**$T_{inicial}$ (°C)**	**T_{max} (°C)**	**T_{onset} (°C)**	**Remaining weight (%)**
UHMWPE/0	332,52	471,58	435,32	0,111
95,8/4,2	370,87	475,09	436,00	0,072
91,9/8,1	406,35	495,27	457,00	0,208
81,5/18,5	414,88	501,01	460,01	0,701

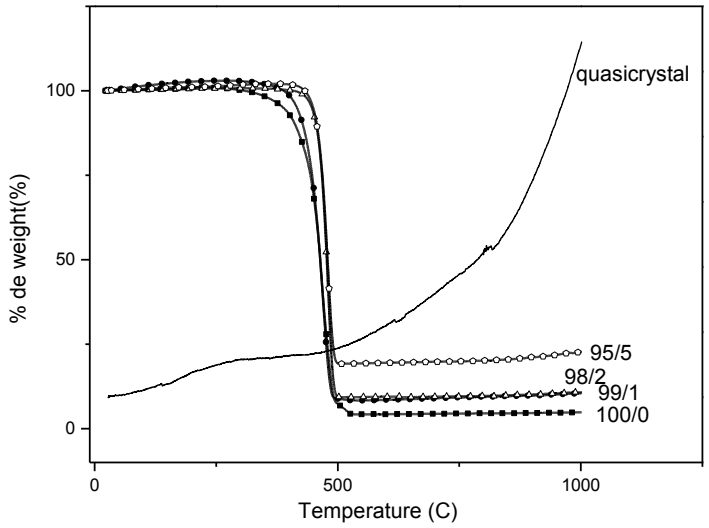

Figure 3. TGA thermograms of UHMWPE and its composites.

As it can be seen in Table 2, the values of T_i and T_{max} of composites are higher than value of the UHMWPE matrix. This behavior suggests that the addition of the quasicrystal filler increases the thermal stability of the UHMWPE. The remaining weight percent was higher in the composite UHMWPE/quasicrystal, 81,5/18,5 due to higher concentration of quasicrystal filler in this composite.

DMA Analyses

Figure 4 shows storage modulus curves of UHMWPE and its composites, the higher the quasicrystal concentration, the higher the modulus in the investigated temperature range compared to UHMWPE. The storage modulus curves of the samples have two regions: the glassy and the glass transition. For the 60-90 °C range can be observed a sharp drop in modulus in the glass transition region of UHMWPE. Fu et al(2008) suggested that stiffness of polymer matrices much increased with the incorporation of micro rigid inorganic particles. In present work was observed that metallic particles also increase the stiffness of UHMWPE matrix.

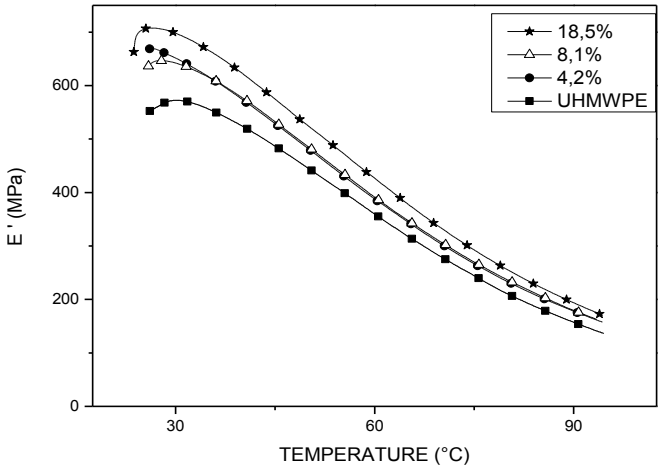

Figure 4- Storage Modulus curves of UHMWPE and its composites.

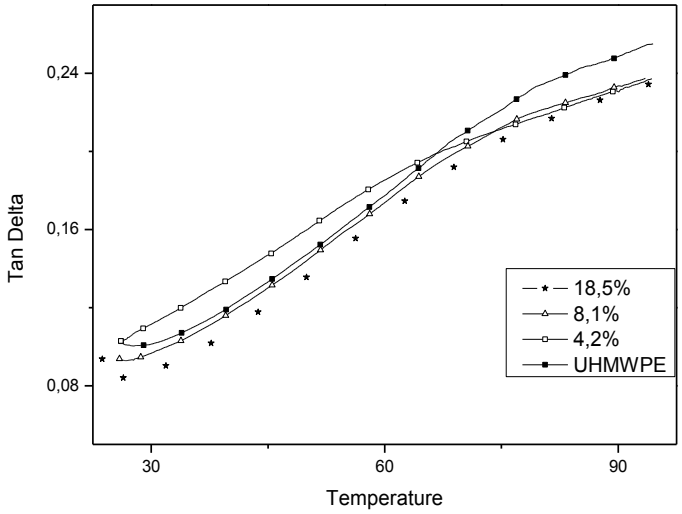

Figure 5. Tan δ curves of UHMWPE and its composites.

The Figure 5 shows the tan δ of UHMWPE and its composites. The results show that tan δ decreased with increasing quasicrystal concentration and increased with increasing temperature, in contrast with storage modulus as shown in Figure 4. Tan δ is given by the ratio E´´/E´ and is an indication of the fractional energy lost in a system due to deformation. The addition of quasicrystal powder caused a reduction in the energy loss of UHMWPE. Chiu et al(1998) pointed out a transition temperature at 70,87 ^{o}C and attributed it to energy absorption for the molecular motions of defective molecular chains that form the crystalline phase in UHMWPE fibers. In present work any transitions on temperature range 70 and 75 ^{0}C can be clearly observed in Figure 5.

Scanning Electron Microscopy(SEM)

The surface morphology of composites is shown in Figures 6-8. All composites studied show a good dispersion of quasicrystal powder in the UHMWPE matrix. However, there is a formation of voids around the quasicrystal powder, resulting in a poor adhesion among the constituents of composite. Moreover, there are a large distribution of size of quasicrystalline particles and the presence of its agglomeration into matrix. Mechanical properties are being evaluated and will be published in future work to confirm if the mixture and adhesion of the quasicrystalline particles were effective in UHMWPE matrix.

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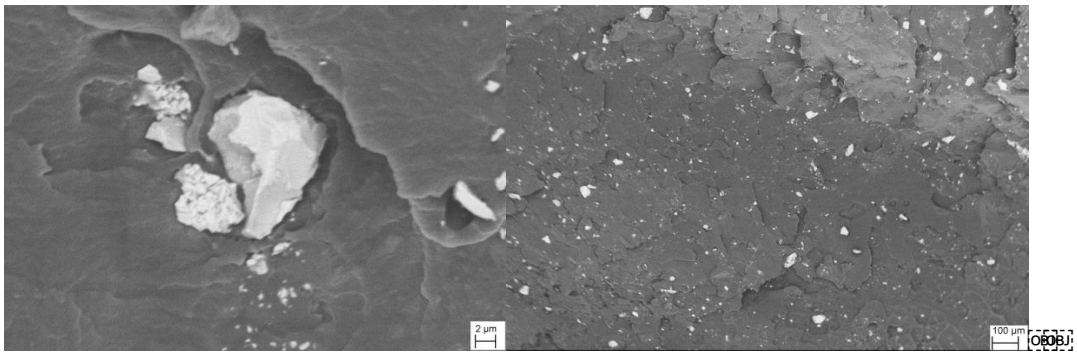
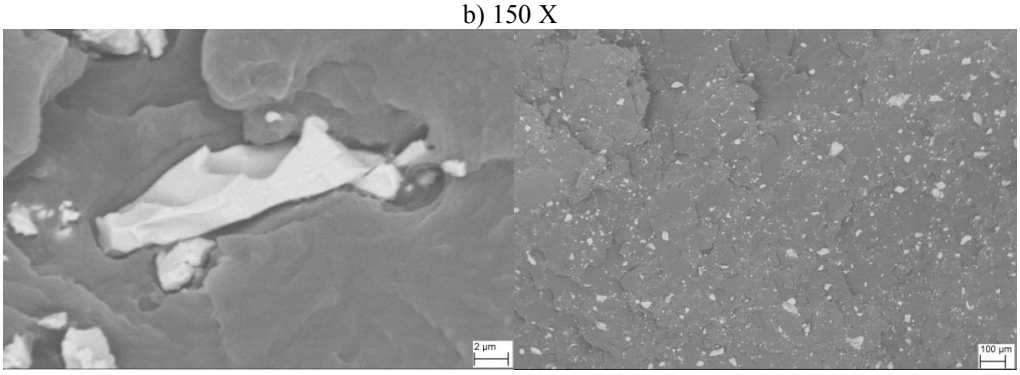


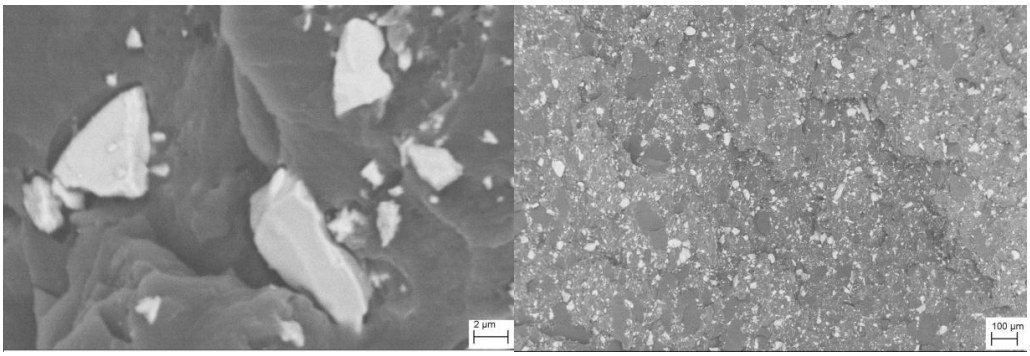
a) b)

Figure 6. SEM fracture images for UHMWPE/quasicrystal composites (95,8/ 4,2): a) 6000 X and b) 150 X



a) b)

Figure 7. SEM fracture images for UHMWPE/quasicrystal composites (91,9/8,1): a) 6000 X and b) 150 X



a) b)

Figure 8. SEM fracture images for UHMWPE/quasicrystal composites (81,5/18,5): a) 6000 X and b) 150 X

Conclusions

1. An increase in quasicrystal concentration until 8,1wt% in the composites produced an increase of the degree of cristallinity and slight differences were observed in the melting temperatures of UHMWPE matrix.
2. An increase in quasicrystal concentration in the composites yielded to an increase of the thermal stability of UHMWPE, mainly at higher concentration of quasicrystal.
3. An increase in quasicrystal concentration in the composites produced an increased of the storage modulus at all temperatures while an increase in temperature reduced the storage modulus values for all concentrations.

4. The surface morphology of composites showed a good dispersion of quasicrystal powder in UHMWPE, poor adhesion among constituents and agglomeration of quasicrystal powders.

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