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# HIGH DENSITY POLYETHYLENE COMPOSITES CONTAINING ALUMINA-TOUGHENED ZIRCONIA PARTICLES: MECHANICAL AND TRIBOLOGICAL BEHAVIOR

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## 1. Introduction

High Density Polyethylene (HDPE) is one of the most used polymers in commodity markets, as it can be transformed by traditional extrusion, blow and injection molding processes. It is very cheap and shows high performance and service life in many applications, including airplanes and automobile interiors and medical devices. Bio-inertia and biocompatibility have awakened the interest in such a polymer also in the biomedical field as implant for bone analogue replacement [1].

Over the years, HDPE composites have been studied in the effort of improving the inorganic filler dispersion and interfacial adhesion with the polymer matrix, for their applicability as joint/bone replacements. For example, alumina and partially stabilized zirconia (PSZ) have been used as partial replacement of hydroxyapatite (HA) in HDPE/HA composites, showing an improvement of mechanical properties (fracture strength and fretting resistance), meanwhile preserving cell viability. Also graphene oxide, carbon nanotubes (CNTs) and CNTs with boron nitride (BN) nanoplatelets have been used for successfully increasing mechanical properties and wear resistance.

Alumina-toughened zirconia (ATZ) can be considered as a possible reinforcement for HDPE in biomedical applications. As a bulk component, it is one of the most promising material, thanks to its excellent mechanical and tribological properties, together with biocompatibility and bioactivity [2]. In our previous works, the addition of ATZ (up to 20 wt.%) to Ultra High Molecular Weight Polyethylene (UHMWPE) turned out to be a promising way to enhance Young modulus, yield stress and hardness, without compromising the other mechanical parameters [3]. In this light, composites at different concentration of ATZ in HDPE were prepared by melt extrusion technique, aiming at studying the influence of ATZ loading, distribution and dispersion on the mechanical behavior (dynamic-mechanical analysis, tensile and impact tests). Tribological investigation was also performed at 37°C (body temperature) under dry and lubricated conditions (both water and fetal bovine serum -SBF- were employed as lubricants). Hard fillers as alumina, silica and zirconia nanoparticles have demonstrated to increase the wear performance over their homopolymers; in

this context, the use of ATZ may represent a suitable solution also for increasing wear resistance of HDPE. A systematic study about the effect of the incorporation of ATZ particles into HDPE on the mechanical and tribological behavior of the resulting composites has not been reported yet. ATZ/HDPE composites may represent a new class of materials exhibiting peculiar features, suitable for different applications, specifically devoted to the biomedical sector. Besides, the ease of processability of proposed composites may overcome the difficulties encountered when UHMWPE matrices are considered.

## 2. Results and discussion

Figure 1 shows some typical SEM micrographs from cryogenically fractured surfaces of HDPE/ATZ with mixing ratio of 98/2, 95/5, 93/7 and 88/12. All the images show finely and rather uniformly dispersed ATZ particles, considering that the size of the primary particles of ATZ is about 30 nm [3]. The agglomerates (usually below the  $\mu\text{m}$  size) become more evident at higher ATZ concentrations (Figure 1C and 1D, referring to HDPE/ATZ 93/7 and 88/12, respectively). ATZ particles appear detached from the matrix, as indicated by the presence of voids, suggesting a weak filler-polymer interface. The crystallinity values of the composites (Table 1), calculated by XRD analysis, are always higher than that of unfilled HDPE, suggesting that ATZ particles act as a heterogeneous nucleating site for crystallization. Some mechanical parameters obtained by stress-strain curves are resumed in Table 1. The addition of a few amount of ATZ particles (1–3 wt.%) significantly enhances the Young modulus (E) of HDPE, reaching an increase of 22% for HDPE/ATZ 99/1, as compared to the unfilled counterpart. A slight increment is also observed for higher ATZ loadings, although the differences among the mean values are limited. This behaviour could be explained considering that the crystallinity increase observed for all the composites is hindered by the presence of voids and/or agglomerates, prevailing for ATZ loadings ranging between 5 and 12 wt.%. In addition, based on the higher level of crystallinity induced at higher ATZ loadings, it can be supposed that this is not a key parameter for determining the Young modulus enhancement.

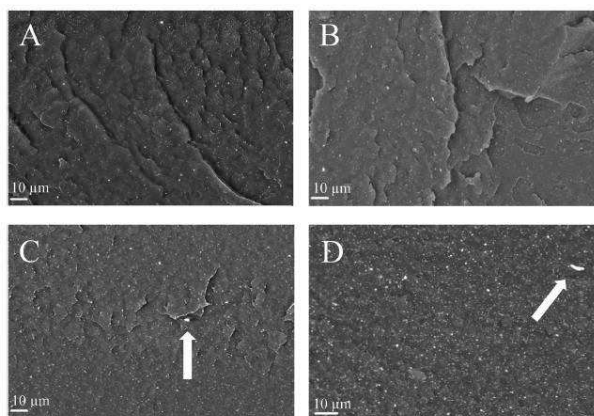


Figure 1: SEM micrographs of fractured surfaces of (A) HDPE/ATZ 98/2; (B) HDPE/ATZ 95/5; (C) HDPE/ATZ 93/7; (D) HDPE/ATZ 88/12 (white arrows indicate some ATZ agglomerates).

The presence of ATZ reduces the yield strength ( $\sigma_y$ ) of HDPE by more than 5%, supporting the detrimental effect induced by the presence of aggregates (and voids), hence limiting the potential benefit of the crystallinity increase.

Table 1: Crystallinity degree ( $\chi_c$ ) and some mechanical parameters of HDPE/ATZ composites.

Sample	$\chi_c$ (%)	$E$ (MPa)	$\sigma_y$ (MPa)
PE	69 $\pm$ 2	969 $\pm$ 17	25 $\pm$ 2
PE/ATZ 99/1	71 $\pm$ 2	1189 $\pm$ 34	24 $\pm$ 1
PE/ATZ 98/2	73 $\pm$ 2	1139 $\pm$ 16	25 $\pm$ 1
PE/ATZ 97/3	74 $\pm$ 2	1125 $\pm$ 48	24 $\pm$ 1
PE/ATZ 95/5	74 $\pm$ 2	1047 $\pm$ 22	24 $\pm$ 1
PE/ATZ 93/7	75 $\pm$ 2	1088 $\pm$ 53	22 $\pm$ 1
PE/ATZ 88/12	75 $\pm$ 2	1001 $\pm$ 47	19 $\pm$ 3

Figure 2 shows the coefficient of friction (COF) as a function of cycles number in dry condition, water and SBF medium for HDPE and HDPE/ ATZ 88/12. After the running-in process, the COF approaches a steady value over all the sliding distances. In air, neat HDPE shows a COF value of 0.13. The COF increases in the presence of ATZ, reaching an almost stable value around 0.21 [4], regardless of ATZ loading. Unfilled HDPE exhibits the lowest wear resistance (estimated as wear rate and average depth), which is in good agreement with the highest hardness and elastic modulus ratio (Table 1) [4]. The tribological behaviour can be interpreted with one of the most accredited wear mechanisms in which, after initial wear cycles, the real tribo-contact is established between polymer surface and a polymeric transfer film. Such three body wear situation results in a low COF value due to weak-bonding forces (hydrogen bonds and van der Waals forces) among the involved surfaces.

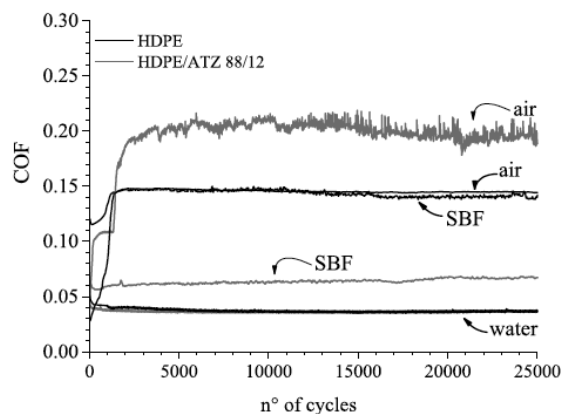


Figure 2: COF as a function of number of cycles in air, water and SBF solution at 37 °C for unfilled HDPE and HDPE/ATZ 88/12.

## Conclusions

In the present work, we have found that the crystallinity increase and formation of voids and agglomerates seem to play an opposite role in determining the stiffness of HDPE/ATZ composites. Composites with few aggregates and voids (low ATZ amount) and limited increase of polymer crystallinity lead to an increased polymer stiffness (in terms of both Young and storage moduli). Stiffness decreases at higher ATZ loadings, probably because of the higher amount of aggregates and voids, in spite of a higher crystallinity induced in the matrix. The wear behavior of HDPE/ATZ composites is significantly affected by the presence and type of lubricant. In dry condition, the effects of the filler on the wear resistance are likely due to the higher surface hardness of the composite and to the contribution of the filler to the transfer film. As result, higher COF and wear rate values are observed in the composites as compared to unfilled HDPE. In water, the effect of the filler is completely annulled; the relevant factors include the decrease of frictional heat, the reduced shear stresses and the debris removal. In SBF medium, some adverse reactions can mask the real wear rates. In this condition, it seems that ATZ exerts a positive effect on the COF decrease. In the light of the mechanical and wear results in lubricant conditions, these composites could be promising candidates for moderate load-bearing orthopedic applications.

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