Journal of Materials Physics and Chemistry, 2017, Vol. 5, No. 1, 39-42
Available online at http://pubs.sciepub.com/jmpc/5/1/5

DOI:10.12691/jmpc-5-1-5

Thermal stability of Ultra High Molecular Weight Polyethylene Nano Composites with $Mg_{0.15}$ $Ni_{0.15}$ $Zn_{0.70}Fe_2O_3$

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Abstract Ultra high molecular weight polyethylene has been commonly used as a biomaterial for total joint replacements. This article concerns with the characterization of nano composites of ultra high molecular weight polyethylene (UHMWPE) with $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$ using analytic techniques such as differential scanning calorimetry (DSC), and thermo gravimetric analysis (TGA). UHMWPE purchased from Sigma Aldrich was used for studies and preparation of nano composites with 1wt% and 2wt% $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$ using the ball milling method. The thermal stability of composites with 1 % of $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$ contents were less stable compared to pure UHMWPE and UHMWPE composites with 2wt% of nano scale $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$. The degree of crystallinity obtained from DSC data was 41%, 40%, and 43% for UHMWPE, UHMWPE+1% of $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$, and UHMWPE+2% of $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$, respectively. The results of current study are useful while considering the nano composites of UHMWPE with $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$ in order to enhance the mechanical strength of UHWMPE for industrial as well as medical applications such as orthopedic implants and bullet proof jackets etc.

Keywords: *crystallinity, UHMWPE, TGA, DSC*

Cite This Article: Asad Muhammad Azam, and Malik Sajjad Mehmood, "Thermal stability of Ultra High Molecular Weight Polyethylene Nano Composites with $Mg_{0.15}$ $Ni_{0.15}$ $Zn_{0.70}Fe_2O_3$." *Journal of Materials Physics and Chemistry*, vol. 5, no. 1 (2017): 39-42. doi: 10.12691/jmpc-5-1-5.

1. Introduction

Ultra high molecular weight polyethylene (UHMWPE) is a conducting polymer used in engineering applications as well as in biomedical implants such as total hip or knee replacement cases. UHMWPE was introduced as biomaterial for total joint applications after the failure of Poly-Tetra-Fluoro-Ethylene (PTFE) in 1962 by Sir John Charnley. Due to high mechanical and chemical properties, UHMWPE has been considered for various industrial applications which include bullet proof jackets and goods for the sports, guide rails etc [1,2]. Implants made of UHMWPE are supposed to have service life around 15-20 years because interaction between UHMWPE with metallic or ceramic parts and surrounding tissues cause complex reactions which tend to reduce service life of implants. However, due to its higher molecular weight, strong chain and crystalline lamellae, it does not flow beyond its melting temperature (Tm). Hence, conventional processes like screw extrusion and insertion molding are considered impracticable to process UHMWPE [3]. Many scientists have tried to explain the oxidation mechanism but a comprehensive and true picture is missing to the best of our knowledge. However, efforts have been made to stabilize or eliminate these radicals by different means e.g. post irradiation, thermal treatments (melting or annealing) and by adding a natural antioxidant such as vitamin E. In addition to this, UHMWPE has been modified by incorporation of micro/nano particles to enhance the structural and thermal stability. Reinforced composites showed poor result of tensile strength because of fiber breakage under injection molding, which was observed by Sclippa and Piekarski. Partial particle fusion and polymer molding problems were reported by others. According to Wright et al, carbon fibers have been found to play a role in preventing firm locking of polyethylene particles prepared from a matrix of poly II knee substitution components when compared to clinical results from retrieved components. Therefore, reinforcement or crosslinking of UHMWPE is requisite to improve its stability. Nano composites with carbon nano-tubes can show much improved properties, e.g. optical properties, thermal, mechanical behavior as well as electrical conductivities [4]. The nano materials reported in powder form may be employed as additives in order to improve UHMWPE for industrial as well as for biomedical applications. Surface free energy is an important factor of biocompatible polymers which has great influence on surface properties like adhesion, wetting as well as biocompatibility [5]. The effect of temperature and heat

flow on structural and physicochemical properties of the ultra high molecular weight polyethylene nano composites with $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$ was studied.

2. Experimental

The appropriate concentrations (1.0% & 2.0 %) of nano-scale $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe2O3$ (which is called as Zn-nano Ferrite) were dispersed in acetone (100 mL) for approximately 45 to 50 min. The blends of UHMWPE and dispersed Zn-nano ferrite (in acetone) were prepared by shaking the admixture. The acetone was then evaporated from the slurry by heating the mixture at 60-70 °C for overnight in an oven. Afterward, ball milling of samples were performed for 2 hours at 200 rpm using the ball milling facility. Subsequently, the homogenized UHMWPE/ Zn-nano ferrite composites were pressed by using hot press (Gibitre Instrument srl or Gibitre Instruments Laboratory Press) and molded into sheets of micron size. After the preparation of UHMPWE/Zn-nano ferrite composite sheets, all the samples were labeled with various codes for their identification as far as concentration of Zn-nano ferrites was concerned. The samples with codes are given in Table 1.

Table 1. Sample codes for identification

Sample Code	Samples	Zn-Ferrites Concentration
P-0	Pure UHMWPE	Nill
PF_1-0	UHMWPE/Zn-nano Ferrites	1.0 %
PF_2-0	UHMWPE/Zn-nano Ferrite	2.0%

3. Characterization Techniques

3.1. TGA

Thermal decomposition is studied using Thermo Gravimetric Analysis (TGA). The sample (~ mg in weight) under examination is immediately brought to the desired temperature non-isothermally during TGA analysis. The weight loss as a function of temperature is counted at a constant heating rate. The results obtained during TGA tests depend upon sample weight, size, heating rate, dimensions and nitrogen flow or purge rate etc. In this particular study we have done the TGA in an open air environment. Thermo Gravimetric Analyzer from Mettler Toledo (Model: TGA/STDA 851^e, Schwerzenbaclz, Switzerland) has been used to investigate thermal stabilities of samples in the present study. The samples (~10 mg) were prepared in an alumina crucible. For all samples, heating process run from 50°C to 600°C at a rate 20°C/min. Temperature versus % loss in sample mass is plotted.

3.2. DSC

Differential scanning calorimeter (DSC) is a largely used characterization technique in thermal analysis of polymeric materials. It has the ability of estimating the degree of crystallinity (Xc), peak melting temperature and re-crystallization temperature. The peak melting temperature and width of the endothermic peak give detail about size distribution and crystal perfection.DSC experimental analysis reported here are taken from TA Instruments (DSC Q100) in an inert atmosphere. The non-isothermal experiments were performed in an inert atmosphere with the rate of 20°C/min of heating from 25°C to 180°C. Firstly, all the samples were heated then cooled to 50°C. The percentage degree of crystallinity was calculated by using equation:

$$X_c(\%) = \Delta H^0{}_m / \Delta H_m \times 100.$$

Here, $\Delta H^0 m$ and ΔHm represent the enthalpy of sample and enthalpy of melting of perfect crystalline polyethylene (290 Jg^{-1}) respectively. Heat of fusion was calculated from endothermic peaks.

4. Results and Discussion

4.1. TGA results

Figure 1 shows the thermo-grams of P-0, PF_1-0, and PF_2-0, respectively with the values of temperature corresponding to the beginning of degradation and mass loss labeled in the figure. All the samples display single step mass loss corresponding to the degradation of polyethylene backbone. Depending on the amount of mass loss with temperature, the trend for each hybrid is divided into four steps: a slight increase in the PE mass loss with maximum value at temperature T_A=313-325°C; an abrupt linear mass loss started at temperature T_B=400°C; a sudden mass gain with maximum value at temperature T_C=450-460°C and the complete volatilization of UHMWPE with onset temperature at T_D=530-537°C. The observed changes in the thermo grams of the hybrids might be explained on the basis of the different processes involved in the decomposition and volatilization of UHMWPE which are: oxygen uptake, oxidation cycle as well as pure thermal degradation. The initial increase in the mass loss of the hybrids is due to the uptake of diffuse oxygen in the amorphous phase of UHMWPE. It can be seen from onset of Figure 1 that the temperature corresponding to the start of thermal degradation (Temperature onset) of pure UHMWPE is 400°C, which is 5°C higher in PF_2-0 and 5 °C lower for PF_1-0 sample. The higher thermal stability of the composites as compared with the pure one is attributed to the formation of a cross-linked network upon chain scission and improved compactness of the PE [6,7]. On the other hand, the influence is found to decrease at 1 wt% of ferrites. The decreased value of crosslink density and increased value of oxidation degradation might be the reason for this because it has been reported that saturation in crosslink density results in improved thermal stability of UHMWPE [8,9]. Finally, the incorporation of $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$ appears to have no significant effect on the volatilization stage of UHMWPE.

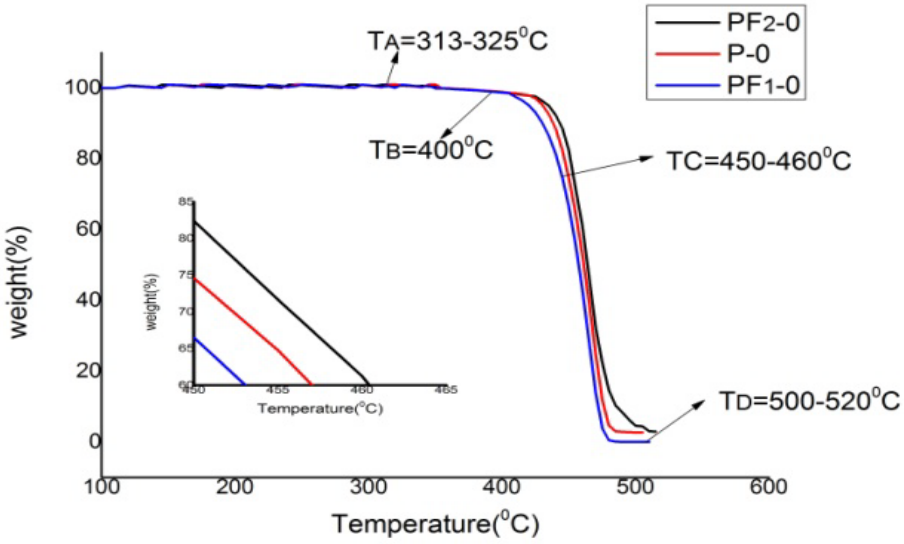

Figure 1. TGA plot of Pure, 1 and 2 wt% $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$ UHMWPE nano composite

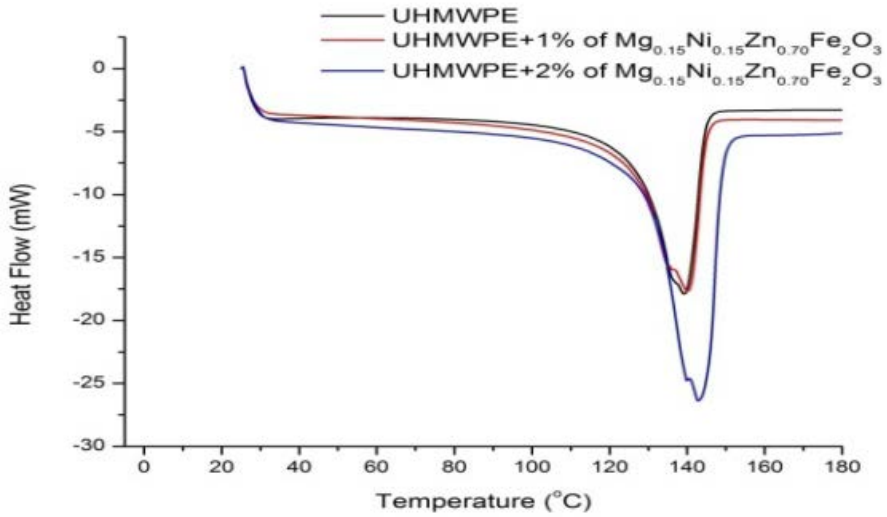

Figure 2. DSC curves of pure UHMWPE and UHMWPE + 1 wt% and 2 wt % of $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$

4.2. DSC Results

For further investigation of the thermal characteristics of UHMWPE/Zn-Nano Ferrites, DSC has been performed and the results of the first heating run are shown in Figure 2. All samples show a characteristic endothermic melting peak with melting temperatures at 138.20°C, 140.56°C, and 143.56°C, respectively. These values are comparable to already reported values in the literature i.e. 137-140°C for UHMWPE. The values of % crystallinity are 41.80 %, 40.82 % and 43.39 %, respectively. The peak melting temperature (Tm), heat of fusion (ΔH^0m), and degree of crystallinity are listed in Table 2 below.

Table 2. Peak Melting Temperature (Tm), Heat of Fusion (ΔH^0m) and (%) Crystallinity of UHMWPE/Zn-Nano Ferrites

Sample code	Tm (°C)	ΔH^0m (J/g)	Crystallinity (%)
P-0	138.20	121.24	41.80%
PF_1-0	140.56	118.37	40.82 %
PF_2-0	143.11	125.83	43.39%

A slight decrease in the heat of fusion (which is calculated while using the area under the endothermic peak) with the incorporation of 1 % $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$ is found while the results for 2 % of $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$ are comparable with the control one i.e. P-0. The possible explanation for this behavior is the chain scissions close to crystalline lamella [10] on incorporation of 1% $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$ is higher as compared to 2 % $Mg_{0.15}Ni_{0.15}$ $Zn_{0.70}Fe_2O_3$.

Further studies are in progress to have in-depth investigation, however, these initial results reveals that adding lower contents of $Mg_{0.15}Ni_{0.15}$ $Zn_{0.70}Fe_2O_3$ causes structural alterations within the UHMWPE matrix. The decrease of heat of fusion for 1 % $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$ also reveals that degree of crystallinity of UHMWPE also decreased for this particular sample.

5. Conclusion

As far as thermal stability is concerned, a composite with 1 % of $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$ contents showed lower

stability than pure UHMWPE and UHMWPE composite with 2 % contents of nano scale $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$. The values for the degree of crystallinity obtained from DSC data were 41.80 %, 40.82 % and 43.39 % for UHMWPE, UHMWPE+1% $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$, and UHMWPE+2% $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$, respectively. Therefore, on the basis of aforementioned results, one can conclude that incorporating $Mg_{0.15}Ni_{0.15}Zn_{0.70}Fe_2O_3$ in $\leq$1% is not beneficial in order to achieve further improvement in UHMWPE properties.

Acknowledgements

The author paticularly Asad Muhammad Azam would like to thank Dr Malik Sajjad Mehmood, University of Engineering and Technology, Taxilla, Pakistan for providing some samples/grades of UHMWPE for this research.

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