Chemical and physical modifications of polyethylene containing nanostructures

A.M. Visco[1], V. Brancato[1], P. Primerano[1], M.F. Milazzo[1],
M. Cutroneo[2], C. Scolaro[2], F. Caridi[2] and L. Torrisi[2]

[1]*University of Messina , Dept. of Electronic Engineering, Industrial Chemistry and Engineering, C/da di Dio, vill. S. Agata, 98166 Messina, Italy*
[2]*University of Messina, Department of Physics, V.le D'Alcontres 31, 98166 S. Agata, Messina, Italy*

Abstract

The polyethylene is an interesting polymer with a good mechanical strength, ductility, biocompatibility and chemical inertia. It founds several applications in many fields, such as chemistry, engineering, bio-medicine and micro-electronics.

The polyethylene chemical and physical properties can be modified embedding different nanostructures in its bulk. Carbon nanotubes, metallic oxides, coloured pigments and other species can be inserted at different concentrations in the polymer material during the preparation phase of thin films and sheets.

Mechanical, optical, thermal and chemical properties can be modified significantly depending on the filler concentration. The absorption coefficient at different radiations can be controlled by the amount of doping structure. In the visible region, for example, the high transparency of pure polyethylene can be strongly reduced by low concentrations of carbon nanotubes.

The colour, the mechanical resistance, the wet ability of the polyethylene and other parameters can be changed by the doping species in order to prepare special devices useful for many applications.

Introduction

Academic and industrial researches are interested in the development of multifunctional materials. In the last decades, great attention was directed to the preparation of advanced composites with suitable synthetic polymers and fillers, with the purpose to obtain the best physical and mechanical features.

For example, the use of filler such as the carbon nanotubes (CNTs) in a polymeric matrix has attracted great attention due to their highly interesting properties such as the mechanical or electrical ones [1]. They are widely used in the manufacturing of advanced nanocomposites employed in special applications, from microelectronic to aerospace fields. So, in order to improve the mechanical properties of the polymeric matrix, it is necessary a good dispersion of the CNTs in the matrix as well as a strong interaction among the two components [2]. By this way, the matrix can be well bonded to the filler that controls the resulting mechanical strength of all the nanocomposite.

The modification of some physical properties, such as thermal behavior, optical properties (absorption power of laser light), electrical conductivity and thermal stability, is another interesting aspect of the addition of a filler in a matrix. For example, the use of fillers or pigments can be useful in the plastic welding or to make the polymers (generally high insulating materials) electric conductor [3].

The traditional welding of plastic can be made by thermal contact of two counterparts of the same polymeric material; this anyway, is not a thorough method that induces the loss of the starting geometry of the components.

While, laser welding is an accurate technique that permits the retention of the initial geometry of the plastic components that must be jointed. It is well known that a flexible and multipurpose material, such as polyethylene, is an insulating plastic. It has high transparence toward the laser light and a melting temperature of about 130°C. This last property inhibits its use in special applications at high temperatures and pressures [4].

In this paper we studied an high molecular weight polyethylene (the UHMWPE) mixed with CNTs, iron oxide particles and glass containing a pigment, the methylene blue, with the aim to investigate the mechanical and physical changes induced by the presence of different amounts and type of the colored fillers. Several mechanical and physical test were carried out on UHMWPE pure and embedded with the colored fillers at different load (within the range 0.1 wt%-10 wt%).

In particular, we observed changes of both surface and bulk properties, described in the following.

Materials and methods

The polymeric matrix was the Ultra High Molecular Weight Polyethylene, **UHMWPE**, Ticona, GUR 1020, $M_w \approx 3\times10^6$g/mol and average size of particle powder = 150 micron. The fillers were: multi wall carbon nanotubes (**CNT**) obtained by Chemical Vapor Deposition technique have typical outer diameter d_n of CNTs is of 10 nm and length l_n of 10 µm. The aspect ratio (l_n/d_n) is of 1000 and the purity >95% [7]. Iron oxide (**Fe_2O_3**), supplied by Across Organics with a purity level of 99.999%, particle size of ten nanometer order. A glass matrix of calcium silicate at high porosity (particle size < 75µm and surface area of 70÷100 m^2/g) was employed to stabilize and retain an organic pigment, the methylene blue hydrate (**BM**), Fluka.

The composites were made by mixing in ethanol the UHMWPE with fillers into an ultrasonic bath for two hours and then heating at 80°C the mix under magnetic stirring to evaporate the solvent. The composites were moulded in a hot press at 200°C/20 min, P=20MPa , obtaining sheets of 60mm×60mm and 1mm of thickness colored as blue, black and red, with BM, CNTs and Fe_2O_3 , respectively.

SHORE D hardness mechanical tests were performed by means of a PCE-HT 210, according to the ASTM D 2240 international protocol. The resolution is of 0,1 degrees of hardness and precision of ±1 degrees, in scale range from 0 to 100.

Contact angle(θ) measurements were carried out by a micro-syringe that deposited a 1 µl drop of pure distilled water, at 20°C, on the polymer surfaces [5] .

Tensile stresses were applied to the dog bone samples, cutted by a Ray Ran cutting machine (ASTM D638 M3, geometry: 60 mm x 2.5 mm and 1 mm of thickness) by an universal testing machine LLOYD LR 10K and crosshead speed=10 mm. Generally, 10 specimens were tested in order to give the average value.

The melting temperature was determined by a Differential Scanning Calorimeter (Q100 TA Instruments) from 25 °C up to + 180 °C, with a heating rate of 10°C/min.

The Absorption Percentage of the laser light (Optical Spectroscopy) were carried out on polymeric sheets 90 µm thickness at 240nm, 600 nm and 1080 nm of wavelengths. The absorption percentage was calculated by the following formula:

$$A = 100 - T \qquad (1)$$

where A = absorption percentage, T = I_T/I_0 transmittance percentage, where I_0 = incident laser intensity and I_T= transmitted laser intensity.

The electrical conductivity, σ (S/cm), was determined as 1/ ρ (electrical resistivity, Ω cm). The electrical measurements were performed using a HP3457a multimeter and a voltage supply, at temperature within the range of 350-425 K (four probe method) on samples cylindrically shaped (diameter=12 mm, high of 1 mm, gold layer coated to ensure good contact with the electrodes.

Results

The surface relative hardness is plotted in fig.1 considering the ratio D/D_0, where D is the hardness of each sample with different filler load and D_0 is hardness of pure UHMWPE. The plot shows that the surface hardness improves only when CNTs are added to the polymeric matrix, especially at high percentages. The beginning D/D_0 value (referred to the UHMWPE + 0.3% of CNTs) is 1,007. It improves until 1,035 when the 10 wt % of CNTs is present. In this last case, high loads improve the hardness probably due to the high tendency of the CNTs to agglomerate themselves in bundles.

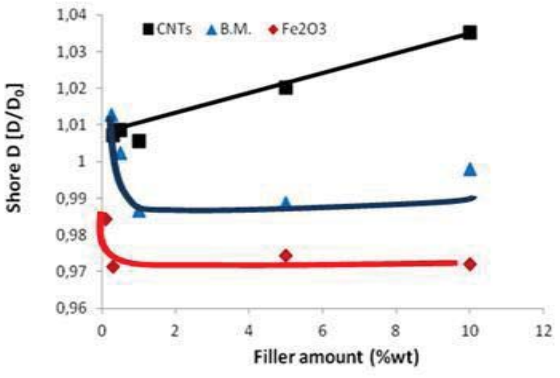

Figure 1 – Relative hardness Shore D of UHMWPE pure and with the three fillers with growing loads.

This effect is highly probable with great concentrations of CNTs. Instead the surface hardness of UHMWPE decreases in presence of the other two fillers: low amounts of BM and Fe_2O_3 are enough to lower the beginning surface hardness of the polyethylene.

The graph of **figure 2** shows the contact angle measurements performed on the UHMWPE pure and embedded with CNTs in growing amount. The contact angle improves after low load additions of CNTs filler (0.1- 1.0 wt %) from the starting value of about 84° to 105°, which represents the maximum value. High CNT loads decrease the contact angle value, that become similar to the pure UHMWPE.

This result shows that the wet ability of UHMWPE decreases with low filler loads but then it re-improves with high CNT contents.

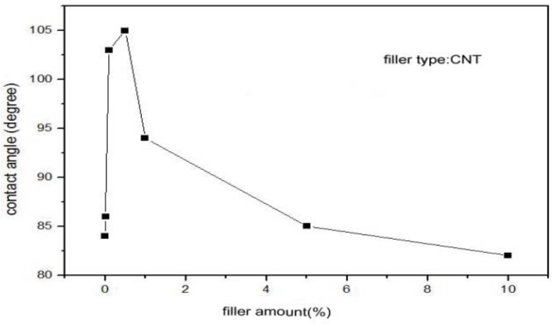

Figure 2 Wet ability of UHMWPE pure and with CNTs with growing loads.

The presence of low amounts of CNTs, well dispersed in the polymeric matrix during the chemical mixing probably, lowers the hydrophilic character of the pure polyethylene. As consequence, the polymer become more hydrophobic. As already discussed, high loads produces bundles of CNTs for their natural tendency to agglomerate. So, the hydrophilic character of the pure polyethylene improves again. The natural tendency of CNTs to agglomerate themselves in bundles was observed in the hardness measurements with high amounts of CNTs, previously discussed: so the wet ability results are in agreement with the hardness ones. The other fillers (Fe_2O_3 and BM) exhibited a behavior similar to the CNTs, although less pronounced due to the lower agglomerating tendency compared to the CNTs.

In order to study the bulk properties change after the addition of filler in growing amount (within the range 0.1-10 wt %), were performed tensile, calorimetric, optical and electrical tests on UHMWPE both pure as filled.

The effect of filler amount on the ductility of UHMWPE is compared in **figure 3**. As shown, the progressive addition of BM decreases not much the material deformability. The material stiffness improves while the elongation at break decreases.

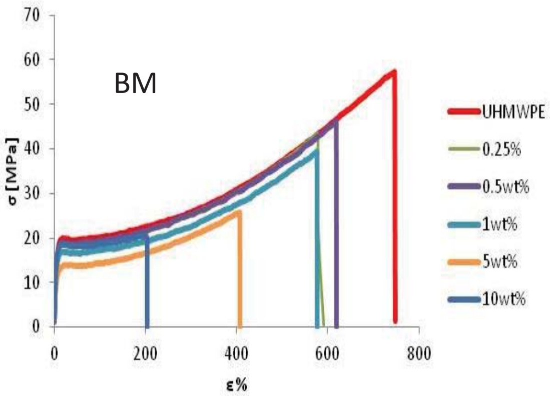

Figure 3 – Average stress-strain curves of UHMWPE pure and with BM as filler at growing loads.

This behavior can be explained considering that the filler presence inhibits the macromolecular chains sliding so they lose their mobility and their characteristic high ductility. This occurs especially in presence of high filler loads. The behavior obtained in presence of BM is representative of the other fillers (Fe_2O_3 and CNTs).

The addition of the filler changes also the polyethylene calorimetric behavior. The T_m/T_{m0} ratio (where T_m is the melting temperature of filled UHMWPE, at the different loads, and T_{m0} is the melting temperature of pure UHMWPE, ≈133°C) *vs* filler amount are plotted in the graphs of **figure 4**. This graph clearly indicates that the addition of BM induces an appreciable enhancement of the T_m/T_{m0} ratio while it decreases in presence of either carbon nanotubes or iron oxide. The result above discussed suggests that only the presence of high percentages of BM enhance the thermal behavior of the polyethylene. Instead the addition of carbon nanotubes or iron oxide worsen it.

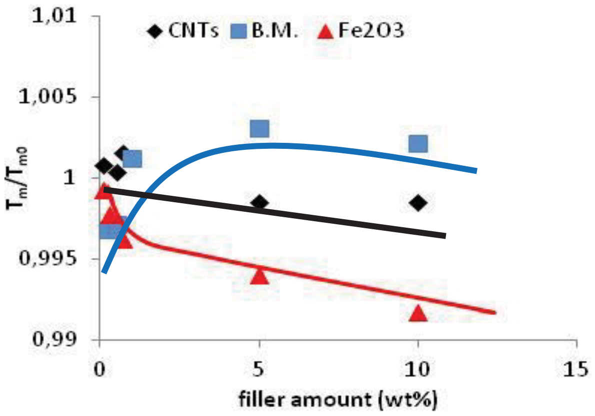

Figure 4 – Change of the melting temperature (T_m/T_{m0} ratio) after the filler addition in different amount.

The light absorption percentage values of five samples (pure PE, PE with 1 wt% of B.M., PE with 5 wt% of B.M., PE with 1 wt% of Fe_2O_3 and PE with 1 wt% of CNTs) are shown in **figure 5**. We investigated three wavelengths in ultraviolet, visible and infrared part of the spectrum. The UHMWPE is transparent to the laser light but it became highly absorbing in presence of CNTs and Fe_2O_3 at all the wavelength investigated. Instead the BM presence makes the material highly absorbent only at the lowest wavelengths, in the UV region, and less in the visible or in IR region. The optical measurement results suggest also that a higher filler load should be preferable to have a greater absorbent material.

The electrical conductivity of the UHMWPE samples containing 0.5 wt% of CNTs at 350K is of 2.7 μS/cm; it decreases with increasing the temperature, changing at 393K due to the melting process of the polymer. The conductivity grows with the CNT load, since with 1.0 wt % it become of 55 μS/cm [6]. This result highlights s that the conductivity is due to the presence of CNTs along the polymeric matrix.

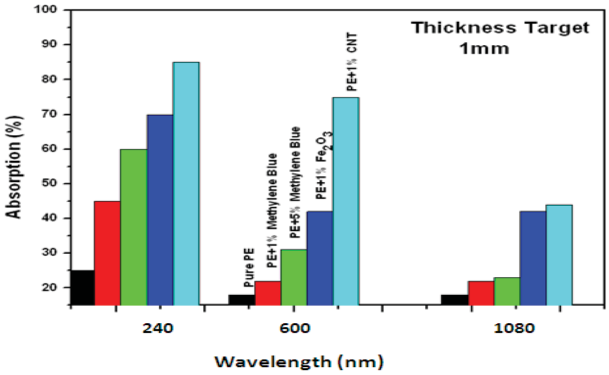

Figure 5 – Optical spectroscopy measurements of UHMWPE pure and with filler at different wavelengths

The melting of UHMWPE favors the mobility of the macromolecular chains where the CNTs are deposed. So they lose their initial network distribution over the polymeric matrix and the conductivity, consequently, falls.

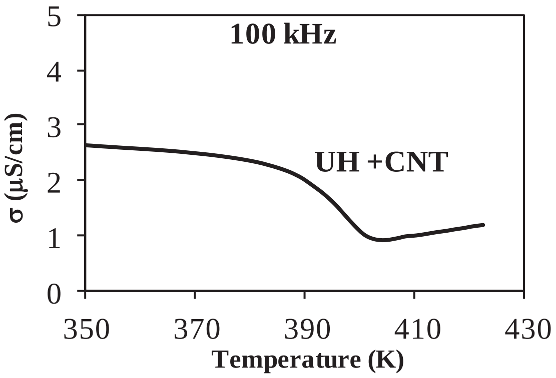

Figure 6 – Electrical conductivity of UHMWPE pure and with the 0.5 wt% CNT at different temperatures

Conclusions

The polyethylene UHMWPE is a multipurpose polymer with high molecular weight, employed for especial uses, like in the biomedical field for its high mechanical performance, or in the chemical industry, for its chemical inertia, or in the electronic field, for its insulating features.

Its main properties are: good deformability, high yielding strength and good stiffness; besides it has also a high transparency, low hardness and low use temperature. The addition of filler changes the polyethylene properties dependently on the filler amount and type. Just regulating these parameters, different physical and mechanical modification can be induced in the material, as above described by the experimental results. In particular, the surface as well as the bulk properties can be changed. Low filler amounts (generally within the range 0.1-1.0 weight percentages) give a different effect compared to the higher (up to 10 wt%).

The high filler loads, if on the one hand improves the plastic material stiffness, the electrical conductivity (with carbon nanotubes filler) and the optical properties, on the other hand change the melting temperature. The surface properties are instead changed by low filler amounts that improve the hydrophobic character of UHMWPE and decrease its hardness. Vice versa with high filler loads. The behavior is strictly depending on the filler type. Among the fillers studied, the BM induces the best thermal stability while CNTs the best optical absorption properties. The UHMWPE embedded with the iron oxide generally exhibits intermediate features between the UHMWPE with BM and UHMWPE with CNTs.

References

[1] Z. Spitalsky, D. Tasis, K. Papagelis, C. Galiotis, Prog. in Polym. Sci,35,357–401, 2010.

[2] Z. Yaping, Z. Aibo, C.Qinghua, Z. Jiaoxia Mat. Sci.& Eng.A 435 – 436(2006)145 - 149

[3] L. Torrisi, F. Caridi, A.M. Visco, N. Campo Appl. Surf. Sci.257 (2011) 2567-2575

[4] L.Dosser, K. Hix, K. Hartke, R. Vaia, M. Li, Photon Processing in Microelectronics and Photonics III. Proceedings of the SPIE,vol. 5339, 465-474 (2004).

[5] L. Torrisi , C.Gentile, A.M. Visco, N.Campo. 2003. Rad. Eff. and Def. in Solids. 158:731-741.

[6] N. Campo, A.M. Visco . Inter.J. of Polym. Anal. and Charac.,15 (7),438 –449, 2010