# Physical-Mechanical and Thermal Properties of Polyethylene Toughened with Submicron $BaSO_4$ Particles

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**Summary:** The mechanical and thermal behaviour and the morphology of High-Density Polyethylene (HDPE), filled with different types of Barium Sulfate ($BaSO_4$) submicron particles have been examined. Composites with a filler content in the range 5-15 vol% were obtained with a twin screw mixer-single screw extruder and then analyzed by means of DSC, SEM and tensile and Charpy impact tests. The effect of different surface treatments of filler particles on the composite properties has been studied. The results indicate that the addition of $BaSO_4$ particles leads to slight increase in Young's modulus and to a decrease in the yield stress independently of surface treatment. The fracture resistance tests demonstrated a strong influence of filler content and surface agents on impact parameters. The use of $BaSO_4$ filler appears to induce a good toughening of HDPE, especially at low volume content, while surface agents reduce particle agglomeration and decrease the adhesion between filler and polymer matrix.

**Keywords:** $BaSO_4$; polyethylene (HDPE); surface agents nanocomposites; thermal properties; toughness

## Introduction

In the last years the large employment of polymer materials in industry, has stimulated research and development of new materials that can be easily and economically synthesised and fabricated. In particular polymers, such as polyethylene and polypropylene, have had a big success because these materials present a good versatility and an amazing ratio between price and performance. In order to improve the chemical, physical and mechanical properties of these materials much research has focused on polyolefin composites filled with different types of

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particles. The main problem is that the introduction of rigid fillers in a polymer matrix increases the stiffness but at the same time decreases the impact resistance. Besides many polymers, as HDPE have ductile behaviour in standard conditions but are brittle under impact loading, in particular at low temperature and in presence of notches or defects. Among the numerous techniques developed to improve toughness of polymers, rubber toughening has been shown to be more versatile[1]. However, the disadvantages of this method consist in obtaining a lower strength material, because of the decrease of Young modulus and yield stress, a lower chemical and solvent resistance, a higher viscosity in the molten state and the opacity of final materials. In order to avoid the reduction of stiffness and resistance typical of rubber toughening method a new promising approach is to utilise rigid fillers. According to Argon and Cohen[2], for toughening to occur in rigid filler composites the particles must debond from the matrix, creating voids around the particles and allowing the interparticle ligaments to deform plastically. Moreover it is very important that the voids should not form immediately upon the application of stress as this may reduce the elastic modulus[2-3]. Argon and Cohen[4-6] have demonstrated that HDPE composites present a notable toughness if the particles are small enough and do not form agglomerates. Therefore, the attention must be focused on the size and the surface coating of the particles. In order to decrease the aggregation tendency of filler particles, a suitable surface agent must be used to modify the surface of the particles making the filler compatible with the polymer matrix. The surface agent must promote also a good dispersion of the filler through the polymer chains.

The aim of the present work is to obtain a physical-mechanical, thermal and morphological characterization of HDPE filled with different types of $BaSO_4$ submicron particles. It can be used to improve such properties as chemical and heat resistance, dimensional stability and mechanical strength, etc. $BaSO_4$ filled polymer composites have high density (useful, for example, in applications where sound deadening is required), low thermal conductivity, and they are also opaque to X-rays[7]. In particular, in this work, the effect of different surface treatment of filler particles on the composite properties has been elucidated.

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## Experimental part

### *Materials and procedures*

The following materials were employed: high-density polyethylene (HDPE), Eltex B4020N1332, ($\rho$ = 0.962 kg/dm$^3$), from Solvay Polyolefins, Rosignano, Italy; different types of experimental Barium Sulfate powders with particle size of 0.25 μm, provided from Solvay Barium and Derivates, Massa, Italy. Some powders were coated with various surface agents, such as a suitable surfactant (1sDA25, 1sDA50, DA25), a fatty acid (1sAS25, 1sAS50) and a salt of a fatty acid (1sST25). Besides uncoated filler particles (1s) were used for comparison. The general code used for identifying the composites was PEXXYY, where XX indicates the type of surface treatment and YY the amount of surface agent (DA, AS or ST) in wt% . $BaSO_4$ powders and HDPE were first mechanically mixed to obtain the required volume percentage. The mixtures were then fed into a two stage processing unit composed by a twin screw non-intermeshing co-rotating mixer (COMACPLAST, Milano) and a MV45 single-screw extruder (COMACPLAST, Milano). The extruded materials were cooled in water at room temperature. A milling device was employed to granulate the resultant composite pellets; tensile and fracture specimens were produced using an OIMA-85 ECO 3080 injection moulding machine.

### *Calorimetry*

Thermal properties have been studied with a Perkin-Elmer DSC-Pyris Diamond calorimeter. Specimens with weight between 5 and 9 mg were heated above their melting temperature with at heating rate of 10°C/min under nitrogen flow. Subsequently the samples were cooled with same rate of 10°C/min to room temperature, and second heating was run with same conditions of the first heating cycle. Temperatures ($T_m$ and $T_c$) and enthalpies of phase transitions were obtained in correspondence to the melting and crystallization peaks respectively, and from the corresponding peak area. The percent of crystallinity for HDPE and its composites has been calculated by the ratio of melting enthalpy ($\Delta H_f$) to enthalpy of 100% crystalline HDPE sample ($\Delta H^0_f = 292\ J/g$), taking into account the effective HDPE content.

### *Tensile tests*

Tensile tests were carried out with an Instron 4302 apparatus, at a crosshead speed of 10 mm/min, which corresponds to a strain rate of 0.4 min$^{-1}$. ASTM D638 Type I dog-bone tensile bars of

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HDPE composites had the following dimensions: nominal gauge length of 50 mm, width of 12.7 mm and thickness of 3.2 mm. At least five samples for each material were tested at room temperature. The Instron tensometer was connected to a computer for data collection and analysis. Longitudinal ($\varepsilon_1$) and transverse strain ($\varepsilon_2$) were measured during deformation using two extensometers, one along the tensile direction (axial) and the other perpendicular to it (lateral). The two lateral strain components were assumed to be equal and the volume strain was computed by using the following equation:

$$\frac{\Delta V}{V_o} = (1+\varepsilon_1)(1+\varepsilon_2)^2 - 1$$

*Impact tests*

Fracture parameters were evaluated by using an instrumented Charpy impact tester from CEAST (Torino, Italy). Data acquisition has been controlled by means of a home developed software, SOFTIMPACT© [8] and analysed according to the ESIS protocol[9] for the determination of linear elastic fracture mechanics (LEFM) parameters[10]. This software displays both the load and the energy versus load-point displacement curve. An impact speed of 0.99 m/s has been used on specimens (SENB) with the following dimensions: length of 25 mm, width of 17.5 mm and thickness of 6.5 mm.

*Microscopy*

Scanning electron microscopy (SEM) has been performed with a JEOL JSM300 microscope operating at voltage of 10-12 kV. All samples were coated with gold-palladium by means of a sputter coater Edwards S150B.

## Results

*Tensile tests*

The engineering stress-engineering strain curves obtained from tensile tests for two types of HDPE composites are shown in Fig. 1a,b.

The stress-strain curves exhibited a maximum at a certain deformation associated with yielding. The Young's modulus for PE1s composites increases quite linearly with increasing the filler volume fraction, while for PE1sAS25 remains practically constant in comparison with the

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Young's modulus of unfilled HDPE. By considering the yield stress values, taken as the maximum stress, it can be noticed that only PE1s composites show an increase in this parameter with filler content. When particles are coated with surface agents an evident decrease of yield stress with increasing particle volume fraction is found, indicating that the debonding phenomenon happened prior to or at the start of plastic deformation.

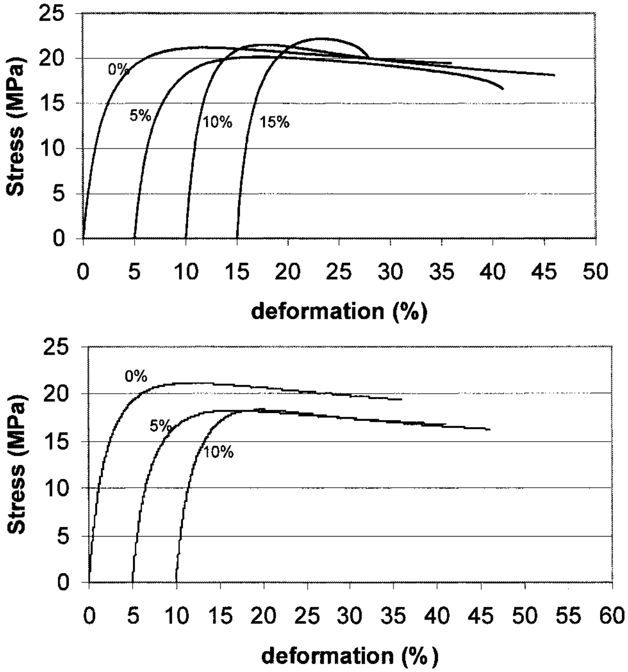

Fig. 1: Engineering stress- engineering strain curves of PE1s (a) and PE1sAS25 (b).

All types of HDPE composites, with the exception of PE1s15, that shows a strong necking effect, deform uniformly along the gauge length up to the maximum elongation measurable with the strain gauge used in this test (40%); in fact at this value of strain the test was stopped. Generally it was found that the introduction of $BaSO_4$ particles in the polymer matrix does not show significant changes. As reported in Fig. 2, all composites present a positive volume deviation ($\Delta V$), especially for PE1sAS25, PE1sAS50 and PE1sST25 composites, which show a quite linear

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behaviour with increasing $BaSO_4$ content. The strain-induced volume dilatation has been attributed to the formation and growth of microvoids following filler-matrix debonding.

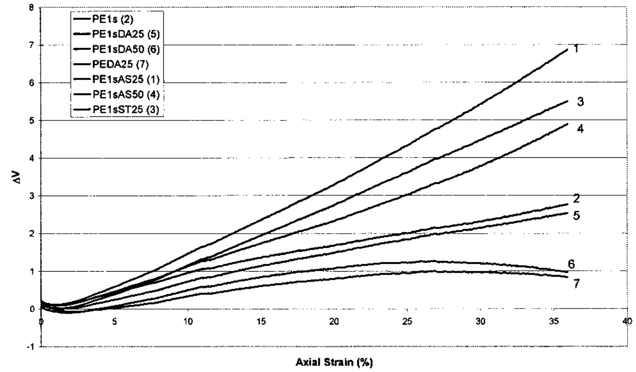

Fig. 2: Variation of volume (*ΔV*) vs. axial strain for all types of composites at 10 vol% $BaSO_4$.

*Impact tests*

In order to analyse the fracture behaviour of HDPE specimens filled with different types of $BaSO_4$ powders, the LEFM method has been applied to measure the $K_{IC}$ and $G_{IC}$ values. The procedure for the determination of linear elastic fracture mechanics (LEFM) parameters has been developed for rigid materials and the following size criteria must be respected:

$$B > 2.5(K_{IC}/\sigma_y)^2$$

In our case, all HDPE composites do not satisfied these criteria, indicating sufficient ductility of these compounds. Nevertheless the results obtained from impact test can be used with some care. In Fig. 3 the fracture toughness ($K_{IC}$) versus filler volume fraction for all types of HDPE composites is shown. The PE1s, PE1sDA25, PE1sDA50 and PEDA25 composites show a slightly decreasing fracture toughness with increasing $BaSO_4$ content, while PE1sAS25, PE1sAS50 and PE1sST25 present a notable increase of $K_{IC}$ in comparison with that of polymer matrix. Besides both PE1sAS25 and PE1sAS50 composites present a better behaviour at 5% volume filler fraction. In comparison the PE1sST25 composite shows a totally different behaviour: its fracture toughness increases almost linearly with increasing $BaSO_4$ content. Macroscopically, all composites present a ductile fracture surface, where significant whitening can be clearly observed.

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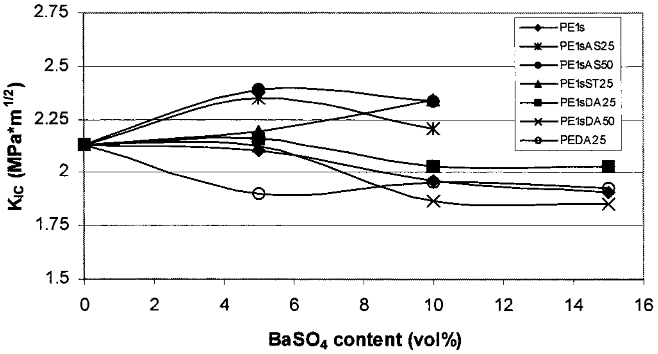

Fig. 3: Trend of $K_{IC}$ vs. volumetric filler content for HDPE composites.

*SEM analysis*

SEM analysis has been conducted on fracture surfaces of Charpy specimens. All composites filled with different types of BaSO4 present a heterogeneous fracture surface. It is possible to identify three different zones: a zone next to the notch, an intermediate brittle-ductile zone and a ductile zone. This last zone is characterised by whitening caused by deformation, where it can be observed evident conic structures with large "seaside" lines (Fig.4). Fracture starts at the center of these structure, where an agglomerate is present and acts as a defect. By using larger magnifications of the various zones we have been able to study the filler dispersion particles in the polymer matrix for all types of composites. The results of this analysis have demonstrated that the debonding phenomenon between filler and matrix occurs already in the intermediate zone, while the last zone was characterised by formation of numerous fibrils oriented perpendicular to the "seaside" lines (Fig. 5). By SEM analysis of different types of composites, we can conclude that a good dispersion of filler particles in the polymer matrix was obtained for PE1sAS25 and PE1sST25 composites and this confirms the results of impact fracture toughness reported above. On the contrary a bad dispersion was found for PE1s, thus explaining its poorer fracture resistance.

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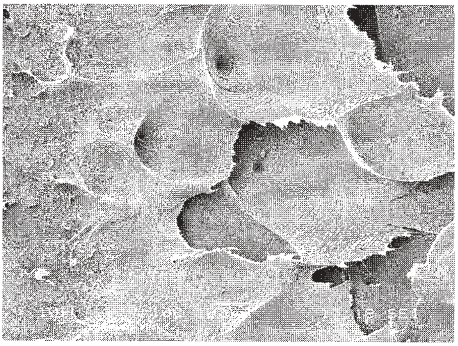

Fig. 4: SEM micrograph taken from fracture surface of PE1sAS50 composite.

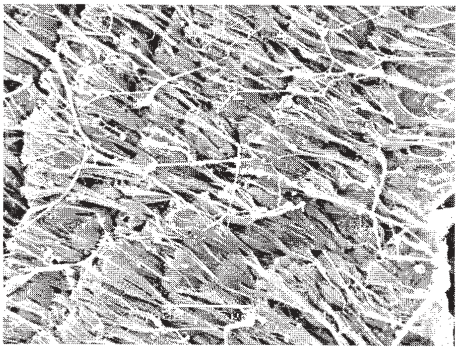

Fig. 5: SEM micrograph of the fracture surface of PE1sAS50 composite.

*Calorimetry*

The thermal behaviour of HDPE composites has been analysed by DSC as a function of $BaSO_4$ content and coating treatment. In order to examine the effect of different surface treatments on the crystallization behaviour and crystallinity of the polyolefin matrix, thermal parameters of HDPE composites with 10 vol% filler content are reported in Table I. As it can be seen the crystallization and melting temperatures are not influenced by any type of surface agent, while a certain increase of enthalpy values are evident in comparison with those of polymer matrix. The values of crystallization temperature ($T_c$) of the various examined system, recorded on the cooling run, indicate that the coating type does not induce nucleating effects: in fact, for these samples the DSC thermograms show a single crystallization peak at almost 116°C.

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Tab. 1: Variation of thermal properties as a function of particle type.

| **Name** | **$T_m$ (°C)** | **$\Delta H_f$ (J/g)** | **$T_c$ (°C)** | **$\Delta H_c$ (J/g)** | **$T_{onset}$-$T_c$** | **$X_c$** |
|---|---|---|---|---|---|---|
| **HDPE** | 132.5 | 171.9 | 116.2 | 172.9 | 3 | 0.58 |
| **PE1s** | 131.6 | 192.4 | 116.7 | 183.7 | 2.4 | 0.66 |
| **PE1sDA25** | 131 | 172 | 116.2 | 173.9 | 2.4 | 0.59 |
| **PE1sDA50** | 131.5 | 196.4 | 116.2 | 183.5 | 2.4 | 0.67 |
| **PEDA25** | 130.7 | 196.3 | 115.7 | 178.7 | 2.5 | 0.67 |
| **PE1sAS25** | 132.9 | 202 | 117.4 | 185.4 | 3 | 0.68 |
| **PE1sAS50** | 132.4 | 196.5 | 116.7 | 193.5 | 2.4 | 0.67 |
| **PE1sST25** | 133.2 | 197.5 | 116.3 | 188.8 | 3 | 0.67 |

Also the melting temperature ($T_m$) is little changing (almost 132°C) for all types of composites: this suggests that the crystal structure of polymer matrix is not affected by the characteristics of filler particles. From the values of melting heat ($\Delta H_f$) for some types of HDPE composites, reported in Tab. 1, it can be observed that an increase of about 10-15% of the enthalpy of melting follows from the introduction of filler particles into the matrix, especially for PE1sAS25, PE1sAS50 and PE1sST25 composites. This means that the addition of Barium Sulfate particles with surface treatment slightly improves the crystallinity of unfilled HDPE: in fact Xc of unfilled HDPE is 0.6 and the maximum value obtained is 0.68 for the PE1sAS25 at 10 vol% of $BaSO_4$.

It is interesting to observe that the two composites with fatty acid coating and that with a fatty acid salt as surface agent show both an increase in $K_{IC}$ and crystallinity. These materials also show a substantial volume increase in tensile tests. On the other hand the composites containing a surfactant, while they show an increase in crystallinity, do not lead to an improvement in toughness. The volume change behaviour indicates a lower volume increase compared to composites with fatty acid coated particles, an indication of a stronger filler-matrix adhesion. This leads us to the hypothesis that both filler debonding and the increase of crystallinity might be responsible for the increased toughness shown by these composites. In fact, crystal phase is believed to play an important role during the drawing of ligaments between neighbouring cavitated particles. Therefore, an increase of crystallinity should have a positive effect on both

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$K_{IC}$ and $G_{IC}$. On the other side, debonding is also necessary for ligament drawing and matrix fibrillation.

## Conclusions

The mechanical, morphological and thermal characterization of composites based on polyethylene filled with different types of submicron Barium Sulfate particles has been carried out. The effect of different surface treatment of filler particles on all characteristics has also been studied. For all HDPE composites, the Barium Sulfate particles lead to a good fracture toughness especially the composites PE1sAS25, PE1sAS50 and PE1sST25. This notable impact resistance has been explained by mechanism of matrix/filler debonding characterised by whitening effect of fracture surface of specimens, in accordance with the results of SEM analysis. Besides the addition of filler particles leads to a slight increase of Young's modulus but does not appear to modify the thermal properties of polymer matrix, although a slight increase in crystallinity has been observed for some composites. The function of all types of surface agent is that to improve the particle dispersion in the matrix and to favor the matrix/filler debonding. This phenomenon has been confirmed by volume measurements during tensile test, which showed a significant increase of volume strain with deformation. In particular the major variation of volume has been obtained for PE1s and PE1sAS25 composites. The PE1s composites present a major adhesion and interactions between filler and matrix, with improved mechanical properties, such Young's modulus and yield stress.

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