

THERMAL AND MECHANICAL CHARACTERIZATION OF POLYETHYLENE AND POLYPROPYLENE COPOLYMER TOUGHENED WITH SUBMICRON BaSO₄ PARTICLES

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Introduction

Many amorphous polymers, as Polystyrene and PMMA, present a brittle behaviour and many ductile semi crystalline polymers, as high-density Polyethylene (HDPE), nylon and isotactic Polypropylene (iPP), are known to be brittle under impact loading, in particular at low temperatures and in presence of notches.

To increase toughness of these polymers several techniques have been developed: copolymerization, addition of plasticizers and rubber toughening. The last method for polymer toughening has been elucidated by Lazzeri and Bucknall [1]. They showed that the main role of rubber particles is that of developing microvoids and to activate dilatational yielding in the deformed zone close to the fracture surface [1]. The disadvantages of this method consist in obtaining a lower strength material because of the decrease in Young's modulus and yield stress etc. It has been recognized that the incorporation of rigid inorganic fillers in commodity and engineering plastics is beneficial to their mechanical properties and particularly stiffness and yield stress. So the general knowledge is that toughness can be increased only at the expenses of rigidity and tensile strength. Despite this general trend, however, there are some major exceptions as in the case of polypropylene and polyethylene where certain types of fillers can give significant increases in fracture toughness.

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 [2]. This shows that uniform dispersion is a more critical factor than just interparticle distance which is reduced when increasing filler content. For the toughening mechanism it is important that the voids should not form immediately upon the application of stress because this may reduce the elastic modulus. Therefore microvoids must form during the deformation process and for this reason the filler should present a low adhesion to the matrix. Besides, in order to limit void coalescence, submicron particles are to be used and the attention must be focused on the size and the surface coverage of the particles. Therefore a suitable surface agent must be used to modify the surface of the particles making the filler compatible with the polymer matrix. This work aimed at studying the morphology and the thermal and mechanical behaviour of Polyolefins, filled with different types of Barium Sulfate (BaSO₄) submicron particles. These polymer composites have low density, high temperature insulation, and low thermal conductivity, and they are also opaque to X-rays.

Experimental Data

The following materials have been used: High Density Polyethylene (HDPE), propylene-ethylene copolymer (PP), containing 4.5 wt.% ethylene, from Solvay Polyolefins and different types of experimental BaSO₄ powders from Solvay Barium and Derivates. The filler particles (0.25µm) were coated with the different surface agents labelled in this work as (A), (B), (C) and (D).

Composites with a filler content in the range 5-15 vol.% were obtained with a MV45 single-screw extruder; tensile and fracture specimens were produced using an OIMA-85 ECO308 injection moulding machine.

The properties of the various composites have been then analysed by means of DSC analysis, scanning electron microscopy (SEM) and tensile and Charpy impact tests.

Results

The thermal behaviour of HDPE and PP copolymer composites has been analysed by DSC as a function of BaSO₄ content and coating treatment.

The values of crystallization temperatures (T_c) of the various examined systems, recorded on cooling from the melt at 10°C/min, are reported in Fig. 1. For composites with HDPE matrix the crystallization (and melting) parameters result to be slightly affected by the particle content and coating type, while for composites with PP copolymer a marked increase of T_c is observed with respect to the pure polyolefin. The maximum shift of T_c (from 97 to 117°C) is found in the concentration range 5-10 vol.% BaSO₄ for the samples with (B) as surface agent. For these samples the DSC thermograms display a double crystallization peak of the copolymer suggesting the occurrence of fractionated crystallization process, which is influenced by the amount of surface agent. For composites with particles coated by surface agent (A) a significant increase of T_c (from 97 to 109°C) is likewise observed supporting a nucleating effect of the coating.

The analysis of melting behaviour for PP copolymer composites showed that both crystal structure and crystallinity are significantly influenced by the type and content of surface agent. In particular, it was found a large increase of the crystallinity fraction for the sample with a filler content of 5 % in the presence of (B) agent. With increasing the BaSO₄ content the effect of surface agent on the phase behaviour becomes less important likely owing to a decreased dispersion of particles in the polymer matrix, which affects the number density and growth process of the crystals.

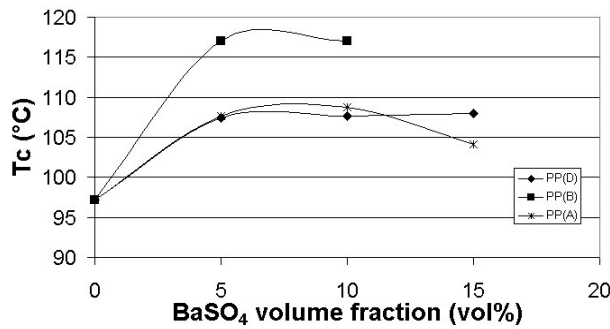


Fig. 1: Crystallization temperature vs. BaSO₄ content for HDPE and PP copolymer composites.

Charpy impact tests have demonstrated that the addition of filler particles with surface treatment improves the fracture resistance of HDPE and PP copolymer, as it can be seen in Fig. 2.

The major improvement of toughness has been obtained using (B) and (C), as surface agents.

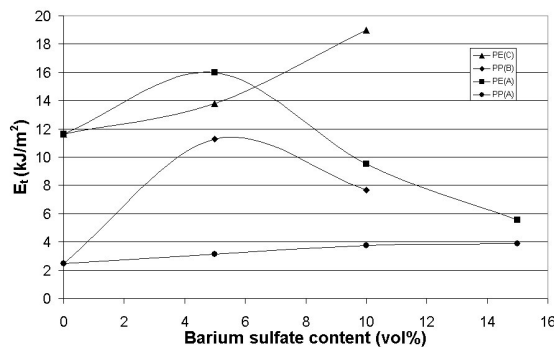


Fig. 2: Total fracture energy (E_t) vs. BaSO₄ content for HDPE and PP copolymer composites.

Tensile tests and SEM analysis indicated that the effect of (D) surface agent on BaSO₄ particles is to increase the adhesion and the interaction between filler and matrix, while the surface agents - especially (B) for PP copolymer composites and (C) for HDPE composites - improve the particle dispersion in the matrix. Besides the debonding phenomenon appears evident only in HDPE composites, which show a fracture surface characterised by whitening effect. The presence of microvoids in PP copolymer matrix composites has been observed only in the samples with (B) treatment. This type of surface agent appears to decrease the adhesion filler-matrix, as it is confirmed by tensile results, shown in Fig. 3.

Therefore the presence of surface agent in the composites leads to a general improvement of all properties; in particular we observed that HDPE and PP copolymer composites with a low surface agent content presented a better mechanical behaviour.

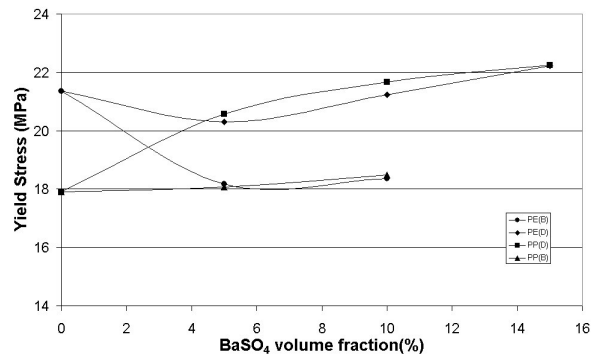


Fig. 3: Yield Stress vs. BaSO₄ content for HDPE and PP copolymer composites.

Conclusions

The main results of this work show an important improvement in stiffness while retaining the impact resistance for all types of composites examined up to 10 vol.% BaSO₄. The presence of a suitable surface agent is a critical variable in preventing the formation of large agglomerates and improves fracture toughness, especially at low BaSO₄ content. The use of (B) and (C) treatment on the particles caused a better dispersion in the polymer matrix and favoured debonding effect.

Moreover a good balance of mechanical properties is obtained for the composites, especially for those based on PP copolymer. A marked effect of particle surface and concentration on the crystallization behaviour and crystallinity of the polyolefin matrix has also been found.

References

- [1] A. Lazzeri, C.B. Bucknall, *J. Mater. Sci.*, **28** 6799 (1993).
- [2] G. Levita, A. Marchetti, A. Lazzeri, *Polym. Compos.*, **10**, 39 (1989).