

# CRYSTALLINITY AND STRUCTURE OF SHUNGITE-FILLED THERMOPLASTIC COMPOSITES REVEALED BY DSC AND AFM METHODS

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## Introduction

Introduction of a filler into polymer blends offers new advantages for the preparation of electroconducting composites [1–3]. For example, carbon black containing composites based on polyethylene-polypropylene (PE–PP) and poly(oxyethylene)–polystyrene blends show higher electrical dc and ac conductivities at a lower volume filler content than that of the corresponding composites based on individual polymers. This behavior is usually associated with inhomogeneous filler distribution in polymer blends (filler particles are primarily accumulated in one of the polymer phases owing to a higher “chemical affinity” of filler particles for this particular phase or at the interfacial boundary). Similar results have been obtained for shungite-containing composites based on PP and PE [4].

It was found that the order in which components are introduced into the PP–PE–shungite filler (ShF) system has a marked effect on both the percolation threshold and the electrical conductivity of the composites. The order of the incorporation of components into the systems affects the electrical conductivity of composites only using nanodimensional fillers. Such effect was shown for composites based on carbon black with particle size ~30 nm. Otherwise, for composites with graphite with particle size 40–60  $\mu\text{m}$  such effect was not obtained [5].

Electroconducting characteristics of the shungite-containing PP–PE blends are assumed to be controlled not only by the inhomogeneous distribution of ShF particles in the polymer blends but also by the structural rearrangements induced by the introduction of ShF into the PP–PE blends [4]. The purpose of this study is to investigate the effect of ShF on the surface structure and morphology of polymer components in the PP–PE–ShF composites.

## Experimental

PP, high density PE and ShF with a carbon content of 39 mass. % were used. Shungite carbon of ShF is characterized in [6]. Characteristics of ShF used: particle size 0.5–10  $\mu\text{m}$  (containing a fraction ~ 1 % of the total mass of ShF with an average particle size of 10–100 nm); specific surface 40  $\text{m}^2/\text{g}$ ; density 2.26  $\text{g}/\text{cm}^3$ .

Composites were prepared by mixing in melt in a Brabender mixer at 180°C. Double PP-PE and ternary PP-PE-ShF composites with PP : PE volume ratios of 80 : 20 and 50 : 50 (PP80-PE20 and PP50-PE50, respectively) were obtained.

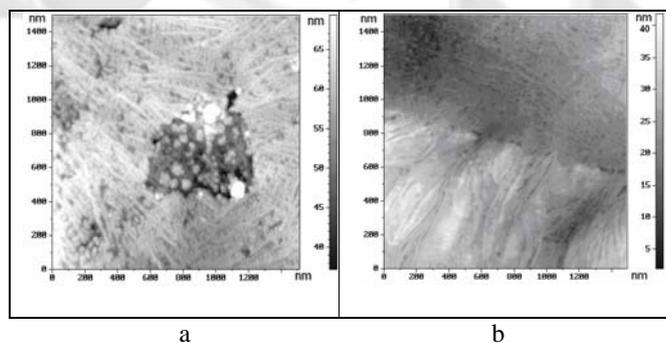
To prepare PP-PE-ShF composites, two methods of the incorporation of components were employed: 1) ShF was incorporated into PP melt and PE was added then (method 1); 2) ShF was incorporated into a mixture of PP and PE (method 2) [4]. The volume concentration of ShF in composites was varied from 5 to 45 vol. %.

In shungite-containing composites, the degrees of crystallinity of PP and PE,  $\alpha_{\text{PP}}$  and  $\alpha_{\text{PE}}$ , were estimated by DSC on a PerkinElmer (model DSC7) scanning thermal analyzer. The AFM observations were performed on a Solver P47 atomic force microscope in the tapping mode. Samples for DSC and AFM-studies were prepared according to the procedure described in [4].

## Results and Discussion

PP and PE are known to be thermodynamically incompatible in mixture, regardless of their ratio, i.e. either one polymer forms a disperse phase in the matrix of the other polymer, or both polymers are present in mixture as two continuous phases. Independently of its content, ShF has no effect on the miscibility of the above polymer components.

However, as evidenced by the AFM observations, the morphology of PP80–PE20 and PP50–PE50 blends is different. Figure 1 presents typical AFM images (not less than 30 for each sample) of the surface fragments with dimensions of 1.5  $\times$  1.5  $\mu\text{m}$  for (a) PP80–PE20 and (b) PP50–PE50 blends. The AFM images show that, in the first case, one can observe PE inclusions (0.1–0.7  $\mu\text{m}$ ) with a lamellar structure incorporated into the ordered lamellar structure of PP. For the PP50–PE50 blend (Fig. 1b), the corresponding AFM images show the continuous disordered regions of crystalline phases of PP and PE, and their structure includes lamellas of different thicknesses.

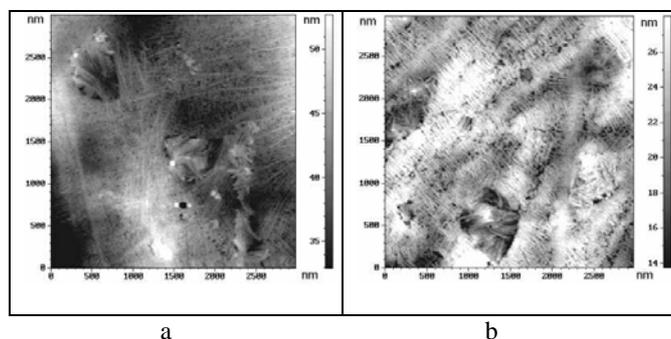


**Fig. 1** AFM images of the surface regions (1.5  $\times$  1.5  $\mu\text{m}$ ) for (a) PP80–PE20 and (b) PP50–PE50 blends (topography regime).

The surface structure of shungite filled PP80–PE20 and PP50–PE50 composites containing up to 20 vol. % shungite filler is similar to that of initial PP–PE blends and is independent of the order of mixing (methods 1 and 2).

However, when the content of ShF exceeds 22 vol %, the surface structure of samples is sensitive to the order of mixing. When ShF is added to PP (method 1), a spherulite structure is formed in PP-phase; when ShF is added to the PP–PE blend

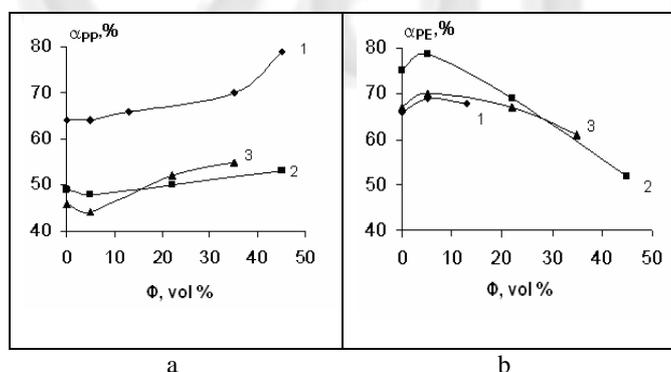
(method 2), PP primarily crystallizes as fibrillar aggregates (Figs. 2a, 2b). In all cases, the structure of PE is composed of randomly distributed lamellas.



**Fig. 2** AFM images of the surface region ( $3 \times 3 \mu\text{m}$ ) of the PP80-PE20-ShF composite containing 22 vol. % ShF (topography regime). The composites prepared by (a) method 1 and (b) method 2.

In the shungite-containing composites, changes in the degree of crystallinity of both polymer components depend on their ratio and on the content of ShF. Figure 3 shows dependences of crystallinity degrees of PP (Fig. 3a) and PE (Fig. 3b) on the concentration of ShF in composites. For comparison, this figure shows dependences for individual shungite-containing polymers.

The effect of ShF on the crystallinity of polymer components in PP-PE-ShF composites is controlled by the ratio between PP and PE, because PP is characterized by its high affinity towards ShF [7].



**Fig. 3** Dependences of crystallinity degrees (a)  $\alpha_{PP}$  and (b)  $\alpha_{PE}$  on the content of shungite filler for various composites: (1) (a) binary PP-ShF and (b) PE-ShF composites; (2) PP80-PE20-ShF composites; (3) PP50-PE50-ShF composites.

Crystallinity of PP and PE in ternary blends depends on the second polymer component and on the filler. In the case of PP, as the content of ShF increases,  $\alpha_{PP}$  should increase (Fig. 3a, curve 1); in the presence of PE,  $\alpha_{PP}$  decreases, because the PE melt is likely to limit the crystallization of PP [8]. In the case of PE, minor amounts of ShF slightly affect  $\alpha_{PE}$ . On the other hand, PP serves as nucleation sites for PE, a

circumstance that is responsible for changes in  $\alpha_{PE}$  for the PP80-PE20 and PP50-PE50 blends at a low content of ShF (Fig. 3b, curves 2, 3). As the filler content increases, the conditions of crystallization of PE become worse because ShF does not show any affinity to PE. This phenomenon is most pronounced for the PP80-PE20 blends where (as evidenced by the AFM data) PE is a disperse phase in the PP matrix.

## Conclusions

The surface structure of PP-PE-ShF composites depends on the order of incorporation of ShF to the polymer blend as revealed by AFM.

Crystallinity of PP and PE in PP-PE-ShF composites depends on the second polymer component as well as on ShF. With an increase of content of ShF, the fraction of the crystalline phase in PP increases due to the high affinity between PP and ShF, although the degree of crystallinity of PE decreases.

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