

The study of conductive shungit-containing polyethylene-polypropylene blends by atomic force microscopy

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Atomic force microscopy (AFM) can be effectively used to obtain the information about surface structure of polymeric systems and structural changes occurred in those systems during its modification.

In this paper AFM method was used to analyze the structural changes of the surface polyethylene - polypropylene (PE:PP) blends and its conductive compositions with carbon containing mineral filler – shungit (Sh). The basic components of shungits (complex mineral from Karelia region, Russia), are noncrystalline carbon and silicon dioxide. Shungits also contain several metal oxides. The content of carbon in shungits varies from 2 to 98 wt %. A special feature of the SF is its compatibility with polar and nonpolar polymers, which provides a means of producing compositions with high filler contents. Recently we have shown that grinded shungit was a promising filler for conducting materials with $\sigma_{dc} = 10^{-6} - 10^{-3} \Omega^{-1} \text{ cm}^{-1}$, because the conducting properties of shungit-containing compositions were easier to reproduce than those of systems with traditional carbon fillers (carbon black and graphite).

Polymeric compositions were prepared by mixing melts in a Brabender-type mixer. The temperature of mixing was 180°C. Polypropylene–polyethylene (PP–PE) and PP–PE–Sh triple compositions were prepared. Sh was introduced in PP(after that PE was added), or PP–PE mixture (method I and method II). We used atomic force microscope (Solver P47, NT-MDT Russia) in the tapping mode (in height image and phase contrast method) with NSG 11 cantilevers with a hardness of 40 N/m and a resonance frequency of ~160 kHz. The samples for the AFM studies were processed as films prepared via free crystallization from the melts of the composites placed between the mica plates.

It is known that PP and PE are incompatible at all mixture ratios; one of the polymers forms a disperse phase in the matrix of the other or both are present in the mixture as two continuous phases. Because of the incompatibility of the polymers, their mixtures are heterogeneous, and their morphology depends on the mixture ratio. AFM image of sample surface of the composition consisting of 80 vol. % and 20 vol. % PE (PP80–PE20), part obtained in phase contrast regime are shown in Fig. 1. We observe spherical (0.2–2 μm) inclusions of PE lamellar in structure and the background of the ordered lamellar structure of PP. For the PP80–PE20 compositions containing 22 vol. % Sh and prepared by methods 1 and 2, AFM images of 6x6 μm^2 sample surface parts obtained in the topography regime are presented in Figs. 2a and 2b, respectively. A comparison of Figs. 2a and 2b shows that the order of the introduction of the components has a noticeable effect on the morphology of the PP80–PE20–Sh composition. We see that the preliminary introduction of the Sh into PP (method I) favors the crystallization of PP in the form of spherulites. When the Sh is introduced into polymeric blends method II, PP crystallizes to form fibrillary structures. PE inclusions structure in blends (Figs. 1, 2), are lamellar in the all cases and don't depend of the introduction method of the Sh. Such dependence of the surface structure of compositions on

the order of mixing, we could see when the content of shungit filler exceeds 22 vol %, when the Sh-containing systems have σ_{dc} . Besides that it was shown that the σ_{dc} of such systems was depend on the order of mixing. The σ_{dc} systems preparing by the method II was more than 1000 times σ_{dc} , prepared by the method I. Furthermore, it is possible that σ_{dc} depends on the structure of PP in the composition.

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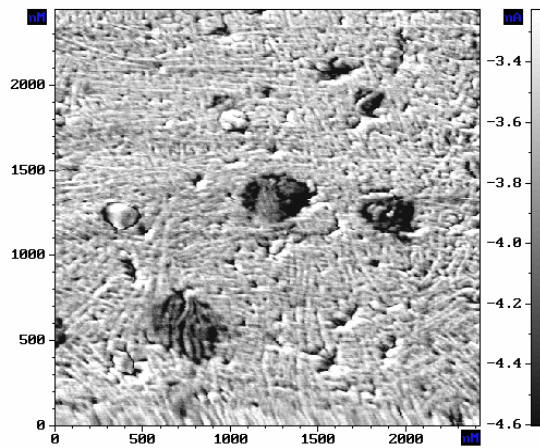


Figure 1. AFM image of the surface part ($3 \times 3 \mu\text{m}^2$) of a PP80–PE20 composition recorded in the phase contrast regime.

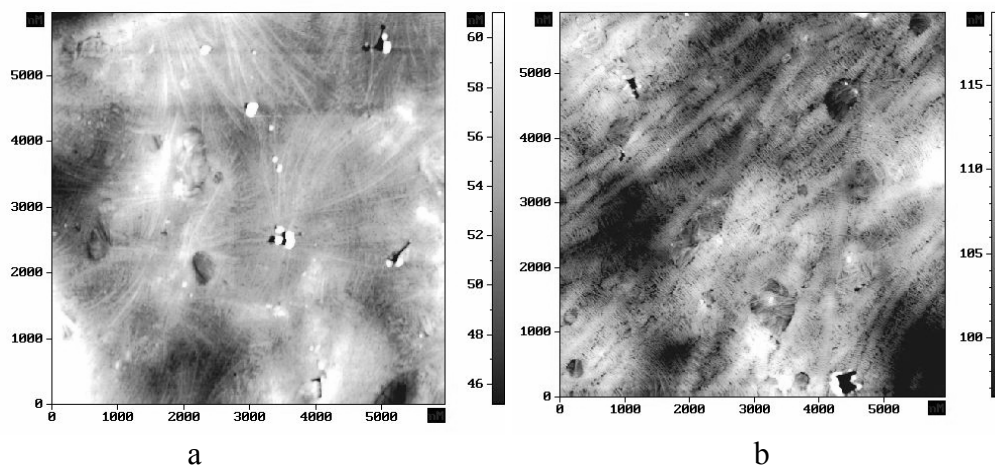


Fig. 2. AFM images (topography regime) of parts ($6 \times 6 \mu\text{m}^2$) of the surface of PP80–PE20 compositions containing 22 vol % Sh introduced by methods (a) 1 (SF was introduced into PP) and (b) 2 (SF was introduced into the PP–PE blend).