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Polymer Blends Filled with Carbon Black: Structure and Electrical Properties

Yevgen Mamunya

Institute of Macromolecular Chemistry, National Academy of Sciences of Ukraine, Kharkovskoe shausse, 48, Kiev, 02160, Ukraine

Summary: Morphology and electrical conductivity of polymer blends based on polypropylene, polyethylene, polyoxymethylene, polyamide 12, copolymer ABS filled with carbon black (CB) were studied. When filler is introduced in polymer blend, three cases of filler spatial distribution can be obtained. CB can be distributed randomly within polymer matrix, can be situated in one of the polymer components or can be localized on the boundary of the polymer components. The existence of different cases of filled blends structure is defined by following reasons: thermodynamic factors (relationship between interface surface tensions of polymer-filler γ_{pf} and polymer-polymer surface tension γ_{pp}); kinetic factors (relationship between viscosities of polymer components); processing factors (methods of the filler introduction in the complex polymer matrix, which can enhance or depress the influence of thermodynamic and kinetic factors).

Introduction

The electrical characteristics of the carbon black (CB) filled composites are the main object of many investigations because of a number of the technical appliances[1,2]. Such composites can be used as antistatic materials, flexible heaters, contact materials for computing machinery, sheath of cables, shielding materials. Two main factors influence the values of the electrical conductivity of CB filled composites: content of carbon black in a polymer matrix and spatial distribution of the CB particles. If carbon black forms a highly branched structure, the conductivity appears at lower CB content than in case of a more random distribution[3,4]. The first papers appeared more than 15 years ago indicating that the binary blends used as polymer matrix enable to effectively regulate the CB spatial distribution in the volume composite and result in the ordered CB distribution instead of the random one[5,6]. This provided an opportunity to control the structure of conductive phase and electrical properties of composites, that resulted in a large interest to such systems and highly increased number of papers devoted to the carbon black filled polymer blends[7-13]. The aim of this work is to study the effect of a structure on conductivity of the polymer blends containing carbon black.

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Experimental

The structure and electrical conductivity were studied by using the following materials : polypropylene (PP), polyethylene (PE), polyoxymethylene (POM), polyamide 12 (PA-12), co-polymer ABS (ABS) and the blends PP/PE, PE/POM ABS/PA containing carbon black (type P-245, surface area 108 m^2/g, produced in Russia according to the standard GOST 7885-86). Composites were prepared by mixing the polymers with filler in an extruder at 200 ^{0}C. In general, filled blends can be prepared by the following five methods (note only the methods A-D were used in this work):

method A - first the CB is introduced to the polymer 1, then the concentrate of filler in the polymer 1 is diluted by polymer 2;

method B - on the contrary, the concentrate of CB in the polymer 2 is prepared and then is diluted by polymer 1;

method C – all three components are charged to extruder and mixed at the same time;

method D – the filler is mixed with the previously prepared polymer blend;

method E - CB is introduced both in the polymer 1 and polymer 2, which is followed by mixing of the filled polymer components.

The high conductivity values were measured by the 4-electrode method on direct current. The measurements in the low conductivity range were carried out by using an E 6-13A teraohmmeter (direct current, voltage on electrodes 100 V). The composite microstructure was studied by transmission electron microscopy by using the method of replication was used.

Structure

Binary polymer blend of the incompatible polymers forms a heterogeneous structure. When the filler is introduced to the polymer blend, three cases of the filler spatial distribution can be obtained. Filler can be distributed randomly within the polymer matrix, can be contained in one of the polymer components or can be localized on the boundary of the polymer components. The existence of different morphologies is given by the following factors:

- *thermodynamic factor* (relationship between interface surface tension polymer 1 - filler γ_{pf1}, polymer 2 - filler γ_{pf2}, and polymer-polymer γ_{pp});
- *kinetic factor* (relationship between viscosities of the polymer components η_{p1} and η_{p2} at the temperature of processing);

- *processing factor* (methods of the filler introduction to the complex polymer matrix, which can either enhance or depress influence of thermodynamic and kinetic factors).

Influence of the thermodynamic factor. Behavior of the filler particle at the boundary of two polymer melts is defined by the following conditions (if the melt viscosities of polymer components are identical and do not depend on the filler distribution)[12]:

a	$\gamma_{pf1} > \gamma_{pf2} + \gamma_{pp}$	the particle is completely wetted by polymer 2 and is completely immersed in it
b	$\gamma_{pf2} > \gamma_{pf1} + \gamma_{pp}$	the particle is completely immersed in polymer 1
c	$\gamma_{pf1} < \gamma_{pf2} + \gamma_{pp}$ $\gamma_{pf2} < \gamma_{pf1} + \gamma_{pp}$	the particle is located on the boundary polymer 1 - polymer 2,

The values γ_{pf} were calculated from the Fowkes equation: $\gamma_{pf} = \gamma_p + \gamma_f - 2(\gamma_p \cdot \gamma_f)^{0.5}$, values γ_{pp} were taken from the literature[14-16], and values γ_p and γ_f are given in papers[3,10,12]. Parameters for calculation of these relationships are listed in the Table 1.

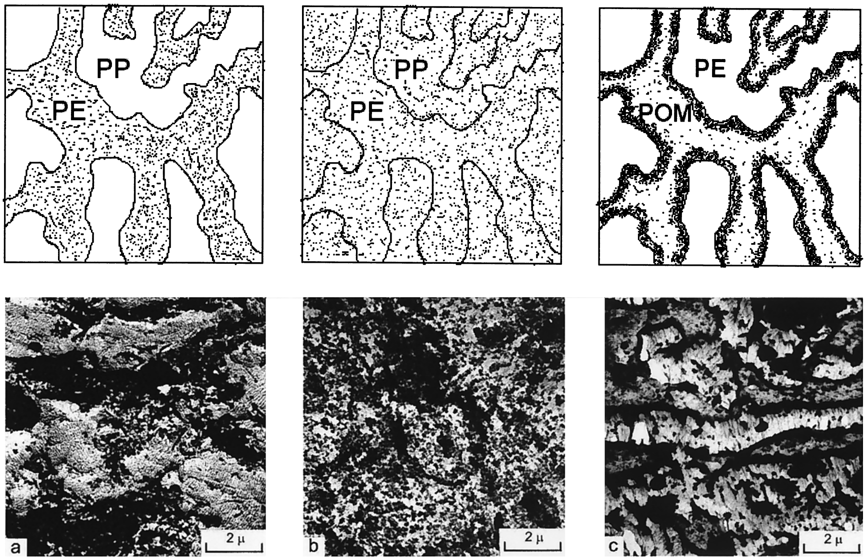
Table 1. Surface and interface tensions of components of the polymer composites.

Filled polymers and blends	Parameters (at 140 ^{0}C)			γ_f, mJ/m^2
	γ_p, mJ/m^2	γ_{pf}, mJ/m^2	γ_{pp}, mJ/m^2	
PP+CB	23.1	3.90	--	55*
PE+CB	27.3	2.43	--	
POM+CB	28.2	2.17	--	46$^{12)}$
PP/PE-CB (method **A**)	--	--	1.1	
PP/PE-CB (method **B**)	--	--	1.1	42,2**
PE/POM-CB (method **A**)	--	--	6.5	

* at 20 °C $^{3)}$, ** at 160 °C $^{10)}$

If the values γ_{pf} and γ_{pp} fulfil the conditions ***a-c***, then condition ***b*** is achieved for blend PP/PE and condition ***c*** for PE/POM. Hence, the filler particles are located within polymer 1 (PE) in blend PP/PE and on the boundary of the polymer components in blend PE/POM. A structure model of filler distribution in blends PP/PE and PE/POM is shown in Fig.1. It displays how the filler can be distributed in a polymer blend depending on conditions ***a-c*** and the filling methods.

Influence of the processing factor. When the filled polymer blend is prepared from the concentrate PE+CB (method A), the carbon black initially introduced in PE remains in it when the concentrate PE+CB is diluted by PP. Consequently, the filler is localized only within the PE phase of the blend PP/PE-CB and the framework structure is formed by PE containing CB.



a
Filled blend
PP/PE-CB
method A

b
Filled blend
PP/PE-CB
method B

c
Filled blend
PE/POM-CB
method A

Fig. 1. Structure model and morphology of the real polymer blends filled with carbon black.

In this case, the processing factors enhance the influence of the thermodynamic factors (Fig. 1a). In another case (method B), when the filled polymer blend was prepared from the concentrate PP+CB, the carbon black initially introduced in PP tends to move to PE from PP during mixing of melted composite and its distribution in both polymer phases becomes uniform (Fig. 1b). Consequently, the processing factors depress influence of the thermodynamic factors.

In accordance to condition ***c***, the filler is localized on the polymer-polymer boundary in the blend of PE/POM (Fig. 1 c). When method A is used, CB moves from POM to the boundary PE-PMO during preparation of the composite in an extruder. The pictures of morphologies of composites based on PP/PE and PE/POM blends agree with the structure model.

Influence of kinetic and processing factors. When the polymer components exhibit different melt viscosities ($\eta_{p1} >> \eta_{p2}$), the kinetic factor should be considered. During processing the filler is localized in the polymer component with the lower viscosity [17]. Since the melt viscosities of ABS and PA are very different (η_p of PA-12 is $2.3 \cdot 10^2$ and η_p of ABS is $5.6 \cdot 10^4$ Pa·s respectively), the filler is located in the PA phase during formation of the filled system in extruder.

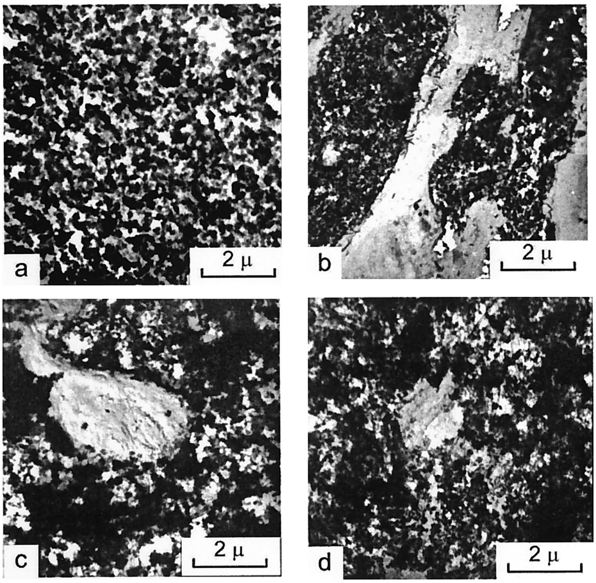


Fig. 2. Structure of filled PA (a) and filled blend ABS/PA-CB by method A (b), method C (c) and method D (d).

Fig. 2a shows a spatial distribution of carbon black in polyamide where CB aggregates are randomly distributed in the polymer matrix. When the method A of filling was used (e.g. concentrate PA+CB is diluted by ABS), the carbon black initially introduced in PA remains in the polymer component with low viscosity (PA) (Fig. 2b). Consequently, the kinetic and processing factors act synergistically. This case corresponds to structure **a** of the structure model (Fig. 1a). Using the filling method C (mixing in extruder of two polymer components and filler together) results in the filler spatial distribution, which is intermediate between random and ordered cases (Fig. 2c). Apparently CB partially enters the polymer component with high viscosity and spatial distribution of filler becomes more random. Method D gives the filler distribution close to that obtained by method C (Fig. 2d). In this case, the processing factor slightly depresses the influence of the kinetic factor.

Electrical conductivity

Dependencies of conductivity σ on the filler volume content φ shown in Fig.3 and 4 for various systems exhibit the percolation behavior. The experimental values of conductivity were compared with the calculated ones by using the following equation[18]:

$$\sigma = \sigma_c + (\sigma_m - \sigma_c)\left(\frac{\varphi - \varphi_c}{F - \varphi_c}\right)^t, \qquad \varphi > \varphi_c \qquad (1)$$

where σ_c, σ_m are values of conductivity at $\varphi = \varphi_c$ and $\varphi = F$, respectively. F is packing-factor equal to limited amount of the filler in the polymer system[4], t is critical exponent.

The use of method A shows that the same conductivity in the filled blends can be reached at the lower filler content than in the filled individual polymers (Figs. 3a, 3c and Fig. 4, line 5). Methods C and D provide less effective decrease of the filler content (Fig. 4, lines 3, 4) whereas method B slightly increases of φ_c value (Fig. 3b). The values of the percolation threshold φ_c of filled polymers and polymer blends for different methods used to prepare the polymer composites are given in Table 2.

Data in Table 2 show that φ_c values increase progressively from PP < PE < POM < ABS < PA. This suggests that the filler phase structure of filled PP or PE is more branched than that of ABS or PA. Hence, the conductivity develops at the lower value of the filler content. An unusual percolation behavior of the filled blends PP/PE-CB, PE/POM-CB and ABS/PA-CB is seen. The φ_c value for blends is much lower than in case of CB-filled individual polymers (except for the method B). The largest decrease in

φ_c is provided by method A because this one promotes the effect of both kinetic and thermodynamic factors.

Table 2. Values of percolation thresholds of polymer systems filled with carbon black.

Composite	filling method of polymer systems				
	polymer+filler	method A	method B	method C	method D
PP+CB	0.05	-	-	-	-
PE+CB	0.08	-	-	-	-
POM+CB	0.12	-	-	-	-
ABS+CB	0.15	-	-	-	-
PA+CB	0.21	-	-	-	-
PP/PE-CB	-	0.04	0.06	-	-
PE/POM-CB	-	0.03	-	-	-
ABS/PA-CB	-	0.06	-	0.09	0.10

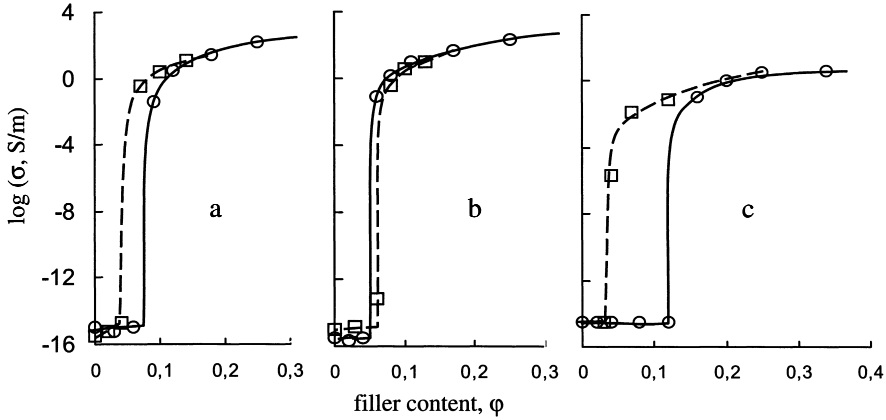


Fig. 3. Dependence of conductivity versus filler volume content of filled polymer blends PE-CB and PP/PE-CB, method A (a), PP-CB and PP/PE-CB, method B (b), POM-CB and PE/POM-CB, method A (c). Experimental values (points), calculated values in accordance of eq.1 (lines) for both binary (solid lines) and ternary mixtures (dashed lines).

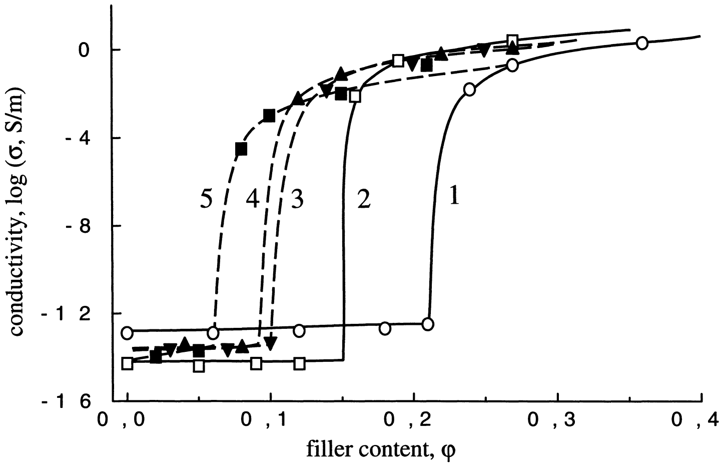


Fig. 4. Dependence of conductivity versus filler content of filled polymers PA+CB (1), ABS+CB (2) (solid lines) and filled blends ABS/PA-CB obtained by methods D (3), C (4) and A (5) (dashed lines). Calculated values were by using eq.1 (lines), experimental values are shown by points.

These results can be explained by formation of a special structure of polymer blends which is considered above. Filler is distributed into one of polymer component or localized on the polymer-polymer boundary in blend and creates branched structure. Thus, the filler spatial distribution in the volume of polymer blends becomes ordered and differs from the random one obtained in case of the individual polymers.

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