Introduction The phenomenon of carbon black (CB) particles gathering at the interface in binary heterogeneous polymer blends is not only of fundamental interest, but has a practical aspect as a method for improving the electric conductivity of composite polymer materials [1-12] and the mechanical properties of polymer blends with a low interfacial adhesion [13-15]. The works examining the causes of this phenomenon are few in number. Most of authors only note that some part of the filler tends to accumulate at the interface. Contradictory assumptions of the conditions necessary for such localization are made. Some workers [1-2] argue that a necessary condition for such localization is the essential difference between the energies of interactions of polymer components with a surface of powder particles. The others [5-8], in contrast, suppose that this phenomenon takes place only when the polymeric components of a blend have low and approximately equal energies of the interaction with the filler surface. Some authors [3] hold that a filler is driven out to the interface due to the crystallization of polymer components of a mixture. Sumita et al. [9] reason, that the causes of filler localizing at the interface reduce to the well-known thermodynamic conditions for solid particles to reside at the interface between two non-miscible liquids. Experimental The polymers used are characterized in Table 1. Table 1 - The characteristic of used polymers Polymer Density g/cm3 Viscosity,Pa·s (413 K, 15 s-1) Molecular weight, ´10-3 Comments High Pressure Polyethylene (PE) 0.922 2900 37 (h) MFI =2.1 g/10 min (at 463 K; 2.16 kg) Polypropylene (PP) 0.91 2500 (at 463 K) - MFI =3.2 /10 min (at 503 K; 2.16 kg) Polyurethane (PU)* 1.21 3500 - OH : NCO =1.01 Polyisobutylene (PIB) 0.91 11300 118 (h) cis-1,4-Polybutadiene (PBD) 0.92 - 104 (h) Mooney - 48 (373 K) Polystyrene (PS) 1.05 9800 (433 K) 190 (w) Polymethylmethacrylate (PMMA) 1.19 11200 (at 433 K) 150 (h) Copolymer of Ethylene and Vinylacetate (EVA): 0.950 980 15.5 (w) Containing 28.9 wt.% Vinyl-acetate Copolymer of Butadiene and Acrylonitrile (BNR) 0.986 Moony - 54 (at 373 K) 220 (w) Containing 40 wt.% Acrylonitrile Polyvinylacetate (PVA) 1.19 - 140 (h) Polydimethylsiloxane (PDMS) 0.98 - 560 (h) Polychloroprene (PCP) 1.22 - 170 (h) Mooney - 62 (373 K) MFI is the melt-flow index, h is the viscosity-average molecular mass, w is the weight-average molecular mass. *PU was prepared on the basis of polyoxytetraethylene glycol, 4,4 - diphenylmethane diisozyanat and 1,4 - buthane diol High-pressure polyethylenes (PE) with different values of the melt-flow index (MFI) also were used. The viscosity values of PE are given in Fig. 1. Poly(methyl methacrylate) (PMMA) of various viscosity was prepared by fractionating the initial polymer by molecular weight. The fractionation was carried out by stepwise polymer sedimentation from a chloroform solution using hexane. The viscosity values of the obtained PMMA samples are given in Fig. 1. Fig. 1 - r of the (PE+CB) +PMMA (1) and (PS+CB) +PE (2) systems versus the effective viscosity of PMMA and PE correspondingly. Concentration of CB: 5.4 vol. % in the PE phase (1), 9.3 vol. % in the PS phase (2) Carbon black under study (No.254) had specific surface area 250 m2/g, average size and density of primary aggregates 28 nm and 1.8 g/cm3, correspondingly, and specific volume electric resistance 1.5×10-3 Ohm×cm (with a density of 0.5 g/cm3). Low-molecular weight liquids were purified and distilled. The values of heat of carbon black wetting by liquids {DH} were measured by means of a DAK1-1A calorimeter at 298 K. Polymers were mixed with carbon black in melt at 433±5K (for PP at 453 K) using laboratory rolls. The mixing was carried out in two stages. At the first stage the whole portion of CB was mixed with one of polymers, and then the second polymer was added. The mixing time at each stage was five minutes. Polymer samples for measurements of the specific volume electric resistance (r) were prepared by moulding using a hydraulic press at 443 ±3 K (for PP at 463 K) under a pressure of 30 MPa for 300 ±5 seconds. If r was less than 1×106 Ohm×cm, it was measured potentiometrically at 293 K (ISO 1853-75) using stripes 100 mm long, 10 mm wide and 1.2 mm thick. The potential difference was recorded for a 20 mm site so that contact resistance was eliminated. The results scattering between parallel experiments was ±18 %. For the electric resistance exceeding 1×106 Ohm×cm r was measured according to the ISO 2878-78 procedure on plates 1.2 mm thick with an area of 16 cm2. In this case stainless steel electrodes were pressed over the whole surface to both sides of a plate. The measurements were made using an E6-13 teraohmmeter with a 10 V potential difference between the electrodes. The scattering in r values between parallel experiments was ±31 %. The carbon black distribution in polymer blends was examined by means of optical microscopy in transmitted light on thin (1 to 5 mm thick) sample slices according to the procedure described in [11]. The bond strength between a filler and polymer was assessed by the exfoliation force (F) of the polymer under study from filler particles fixed in a matrix of another polymer, polypropylene [14]. In this order carbon black was stirred into molten PP, and a plate was moulded from this composition. The surface of the plate was treated with an abrasive to remove a polymer layer and expose the carbon black surface. Then the plate was coated from solution by a layer of the polymer under study. After removing a solvent the force of the coating polymer exfoliation from the plate surface was measured. Results and discussion It is known that carbon-black filled polymers conduct electric current only with the concentration of carbon black exceeding the threshold of percolation (jp). In heterogeneous polymer blends carbon black is distributed non-uniformly between polymer phases. If the concentrations of carbon black in both phases of a blend are lower than jp, the blend can conduct electric current only subject to the condition that the part of carbon black is localized at the interface and its concentration here reaches the percolation threshold [12]. So if the concentration of carbon black in both phases of a blend is only slightly lower than jp, even a minor accumulation of carbon black at the interface confer conductivity on the polymer blend. This enables the extent of carbon black aggregation at the interface to be judged by the conductivity value. A variety of blends (Table 2) was analyzed under the condition that the carbon black is localized in a single polymer phase and its concentration in this phase is slightly below jp. To confine carbon black within one of the phases of a blend, the sequence of carbon black mixing with polymers was altered. Carbon black was first introduced into one of polymer components of a blend, and only then another component was added. A filler is known to retain almost entirely in that phase of a heterogeneous blend where it was introduced initially [1, 2, 10, 11, 12]. The localization of carbon black at the interface takes place not in all of the blends (Table 2). For most of blends the presence or absence of this phenomenon depends on the sequence of components mixing. All the blends in Table 2 may be divided into three groups based on the presence of the superadditive electrical conductivity and the effect of blending sequence on electric conductivity. The first group consists of blends where the effect of superadditive electric conductivity is observed only with a certain sequence of components blending. The second group involves blends where a lowered r value is observed only with preliminary carbon black introduction into either of two polymer components, but the sequence of components mixing strongly affects the degree of r lowering. Table 2 - Electrical conductivity of the (P1+CB) +P2 systems Phase P1 (50 vol. %) Phase P2 (50 vol. %) jp CB for a phase P1, vol. % The contents CB in a phase P1, vol. % r of a phase P1, Ohm·cm r of a phase P2, Ohm·cm r of a blend, Ohm·cm Blends in which CB localization at the interface takes place only from one of two phases. PE+CB PU 6.8 5,3 >1·1012 3·1010 1.3·104 PU+CB PE 10 8,5 7·107 >1·1012 9·108 PE+CB BNR 6.8 5,3 >1·1012 3·109 5.9·104 BNR+CB PE 16.5 15,5 4·107 >1·1012 2·109 PE+CB PCP 6.8 5,3 >1·1012 3·1010 2·104 PCP+CB PE 18 16 3·108 >1·1012 1·1011 PE+CB PMMA 6.8 5,3 >1·1012 >1·1012 2·104 PMMA+CB PE 15.5 14 >7·1011 >1·1012 >1·1012 PS+CB PMMA 11.5 9,3 >1·1012 >1·1012 3.2·103 PMMA+CB PS 15.5 14 >1·1012 >1·1012 >1·1012 EVA+CB PS 5 2,7 1,5·1011 >1·1012 >1·1012 PS+CB EVA 11.5 9,3 >1·1012 7·1011 7.2·102 PE+CB PDMS 6.8 5,3 >1·1012 >1·1012 3·104 PDMS+CB PE 4 3 >1·1012 >1·1012 >1·1012 PS+CB PDMS 11.5 9,3 >1·1012 >1·1012 2.2·103 PDMS+CB PS 4 3 >1·1012 >1·1012 >1·1012 PIB+CB PDMS 8.6 6,5 >1·1012 >1·1012 2·107 PDMS+CB PIB 4 3 >1·1012 >1·1012 >1·1012 Blends in which CB localization at the interface takes place from both phases. PE+CB PS 6.8 5,3 >1·1012 >1·1012 6·109 PS+CB PE 11.5 9,3 >1·1012 >1·1012 4·104 PP+CB PS 5.3 4,2 >1·1012 >1·1012 6.3·108 PS+CB PP 4.2 3,6 >1·1012 >1·1012 6.9·103 PE+CB EVA 6.8 5,3 >1·1012 8·1011 1·107 EVA+CB PE 5 2,7 1,5·1011 >1·1012 5·108 Blends in which CB localization at the interface is very small. PE+CB PIB 6.8 5,3 >1·1012 >1·1012 >1·1012 PIB+CB PE 8.6 6,5 >1·1012 >1·1012 >1·1012 PE+CB PP 5.9 4,8 >1·1012 >1·1012 >1·1012 PP+CB PE 5.3 4,2 >1·1012 >1·1012 >1·1012 PE+CB PBD 6.8 5,3 >1·1012 >1·1012 >1·1012 PBD+CB PE 9 8 >1·1012 >1·1012 >1·1012 The blends which do not conduct electric current with any sequence of components blending constitute the third group. The study of the compositions by optical microscopy shows that increased electric conductivity takes place only for those blends and mixing procedures for which the carbon black localization at the interface is observed (Fig. 2). It is reasonable to propose that the process of filler localization at the interface between polymeric phases as well as between low-molecular weight phases is fully controlled by the thermodynamics of the competitive wetting of a solid particle by these phases, which is consistent with Sumita [9]. The phenomenon of solid particles aggregation at the interface between low-molecular weight liquid phases has been much studied, e. g., for emulsion stabilized by high-dispersity powders or for powder flotation [16]. The thermodynamic condition of localization of solid high-dispersity particles between Fig. 2 - Distribution of CB in the blends: (PE+CB)+PU (a); (PU+CB)+PE (b), (PS+CB)+PE (c), (PE+CB)+PDMS (d) filled with 2.5 vol. % CB (Optical micrograph). The ratio of polymers is 1:1. Taking the components in brackets means their premixing. Magnification: 1100 low-molecular weight liquid phases stems from the Young law [16]: (1) where s13 is the interfacial tension between the first liquid and the particle surface, s23 is the interfacial tension between the second liquid and the particle surface, and s12 is the interfacial tension between the liquids. Such a localization is thermodynamically efficient and will take place with any angle of solid surface wetting by liquid phases except for the angle equal to zero. With the unsatisfied condition (1), the particles of a filler would be fully wetted by one of the liquid phases (the phenomenon of spreading) and could not gather at the interface. The validity of the last proposal is supported by the fact that carbon black localization at the interface is most pronounced for polymer blends with a high surface tension between polymers, i.e. in those polymer pairs where thermodynamic gain of particle transfer to the interface is essential [17]. The applicability of the condition (1) for polymer blends is difficult to test because of lacking data on interfacial tension between a filler and polymer. Nevertheless, there is an experimental observation contradictory to the condition above. This is dependence of carbon black localization at the interface on the sequence of components mixing. Indeed, the satisfied condition (1) inevitably results in the satisfied thermodynamic conditions of the transfer of particles to the interface both from the first phase (s13>s23-s12), and from the second phase (s23>s13-s12) [16]. Therefore, from the thermodynamic viewpoint, with the unsatisfied condition (1) the aggregation of solid particles at the interface must be observed for any sequence of components mixing. So, for example, the localization of carbon black at the interface of two low-molecular weight liquids does not depend on the sequence of components mixing. Altering the sequence of components mixing can affect only the thermodynamic efficiency of process of filler redistribution from the bulk to the interface, but not the parameters in (1). It should be noted that in most of publications cited above carbon black was introduced into the blend of polymers, and the problem of the influence of components blending sequence on the localization of carbon black at the interface was not considered [2, 4, 5-10]. To reveal the causes and conditions necessary for carbon black to localize at the interface there was a need in evaluating the energy of adsorption interaction of polymers with the filler surface. However, now there is no simple and reliable method to assess the efficiency of interaction of polymers with a surface of high-dispersity powders. At the same time it is well understood that the energy of adsorption interaction of low-molecular weight analogs of polymers with a solid surface which depends on the surface energy of a solid body and the chemical nature of an adsorbent is comparable with such interaction for polymers [18, 19]. This makes it possible to judge qualitatively the relative energy efficiency of adsorption interaction of corresponding polymers with the carbon black surface by the interaction energies of low-molecular weight analogs. The efficiency of the interaction of liquid low-molecular weight analogs of polymers with the carbon black surface was estimated by the value of wetting heat (DH) (Fig. 3). Fig. 3 - The heat of CB No. 254 wetting by liquids versus the polarity of a liquid. Carbon tetrachloride (1), n-hexane (2), 2,2,4 - trimethylpentane (3), ethylbenzene (4), toluene (5), 1 - chlorbutane (6), MMA (7), tetrahydrofuran (8), ethylacetate (9), hexanol - 1 (10), dimethylformamide (11), acetonitrile (12), ethanol (13), ethylene glycol (14), glycerin (15), water (16) The studies show (Fig. 3) that DH of CB is in a certain manner dependent on the polarity x. The polarity of polymers and liquids was calculated as follows: x = (dp2 + dh2) / d (2) where: dp and dh are polar and hydrogenous components of the solubility parameter of a liquid, d is the solubility parameter of a liquid [20, 21]. With increasing x the wetting heat of CB No.254 passed a maximum at x = 0.33. This value is consistent with the magnitudes of surface polarity for two other types of CB calculated on the basis of Hansen’s three-dimensional solubility parameter. So, for two different types of CB x was equal to 0.43 and 0.38 [20, 21]. The DH increase up to a certain x value is due to the formation of not only dispersion bonds but hydrogen and polar bonds with oxygen- containing groups on the CB surface as well. The further fall in DH is obviously connected with the decreasing energy of dispersion interaction between liquids. The fact that the dependence of interaction of organic liquids with the surface of some metal oxides on the polarity of a liquid passes an extremum was noticed by the researchers [22] (the interaction was assessed by the impregnation of powders by liquids). The data obtained indicate that the increase in the polarity of polymers up to x = 0.33 - 0.35 must result in rising energy of their adsorption interaction with CB. Besides, the relative efficiency of the interaction between polymer and a filler was judged indirectly by the specific force of exfoliation (F) of polymer from a filler [14]. The permissibility and reliability of such estimation for elastic polymers is evidenced by the fact that F of these polymers rises linearly with the increasing CB volume fraction in PP [14]. The F values show that with increasing polarity of polymer (Table 3) its adhesion to a filler rises. This correlates well on a qualitative level with the estimates of their interaction with CB from the wetting heat data (Table 3). According to the results of these measurements, PE, PIB, PBD, PP, PS, and PDMS have the lowest and closest magnitudes of the energy of adsorption interaction with the CB and aerosil surface. The rest of polymers, judging by wetting heat and exfoliation force (Table 3), arrange in the following series according to the increasing efficiency of their interaction with CB and aerosil: EVA BNR PCP PU PVA. Table 3 - The characteristics of the interaction of polymers and their low-molecular weight analogs with CB №254 Polymer Low-molecular weight analog Notation x [17, 20, 21, 23] DF, * kN/m Name x [20, 21, 23] DH, mJ/m2 PE 0 0.025 n - hexane 0 170 PIB 0 0.02 2,2,4-trimethylpentane 0 175 PS 0.012 0.015 Ethylbenzene 0.0076 205 PBD 0.003 0.15 Hexene-1 - 180 PDMS 0.04** 0.03 Cyclic tetramer of dimethylsiloxane 0.04 200 EVA - 0.3 - - - BNR - 0.46 - - - PCP 0.11** 0.65 1-chlorobutane 0.11 270 PU - 1.17 - - - PVA 0.33 2 Ethylacetate 0.33 365 * DF is F gain for the CB content increase in the substratum (PP) from 0 to 42 vol. % ** calculated from the ratio of polar and dispersion components of surface tension [17]. The analysis shows that when an essential difference in adhesion of polymer components of a blend to CB takes place (PE+PU, PE+BNR, PE+PMMA, PE+PCP, PS+PMMA), CB moves to the interface only from the phase characterized by lower adhesion to CB. However, this rule is invalid for explaining the effect of the sequence of components blending on CB localization at the interface in the blends of polymers having close energies of adhesion to a filler, such as PE+PDMS, PS+PDMS, PIB+PDMS, PE+PS, PS+PP. The results obtained show that in these blends the removal of a filler from the bulk to the interface occurs from the phase of polymer characterized by higher value of cohesion energy (Table 4) (from PS to the interface with PO and PDMS, from PO to the interface with PDMS). As for the phase with low cohesion energy, such redistribution here either is absent (from PDMS to the interface with PE, PS, PIB) or is insignificant if the cohesion energy difference for polymer components is small (from PE or PP to the interface with PS). Table 4 - The characteristics of cohesion energy of polymers at 433 K [17, 23] Polymer s, mN/m Polymer s, mN/m PDMS 13.0 EVA 26.2 PP 20* PVA 26.3 PU 23 ** PS 29.9 PIB 24.8 PMMA 30.5 PE 25.1 PCP 31.5 PE 24.0* * at 463 K ** given for the low-energy block of copolymer. It is known [16] that the wetting force of liquids increases with increase in their adhesion to the surface as well as with decrease in their cohesion energy. Taking into account Dupre’s equation, inequality (1) may be written in the following form: (3) where: s1 and s2 are the surface tension values of the first and the second liquids at the interface with air, correspondingly; wa1 и wa2 are the adhesion energies of the first and the second liquids to the surface of a particle. The liquid with greater adhesion to a surface and lower surface tension has a preference in wetting this surface. When the energies of polymer-surface interaction are close, the polymer with lower surface tension (smaller cohesion) exhibits better wetting force. [16]. This suggests that the migration of carbon black towards the interface in most of blends proceeds effectively from the polymer phase with lower capability of wetting the carbon black surface. The redistribution of carbon black from the phase of polymer with higher wetting force to the interface takes place only for a small difference in wetting force of polymer components and is less pronounced. This conclusion determines the conditions necessary for a filler to localize at the interface, but cannot explain the causes of such strong influence of the sequence of components mixing on a process, and hence, does not reveal the essence of a phenomenon. It is impossible to understand the effect of blending sequence on filler localization at the interface from the single viewpoint of thermodynamics of particle wetting by two liquids. It is due to the fact that in polymer mixtures, for well-known reasons, the most energetically efficient distribution of a filler described by (1) is not achieved. The study of a filler redistribution towards the interface shows that this process for all blends is completed after 2-3 minutes of mixing and does not depend on the sequence of components adding (Fig. 4). The increasing time of mixing to 30 minutes does not lead to the filler localization at the interface in those cases, where it has not taken place within 3 minutes after the start of mixing. To the contrary, where the mixing was prolonged to 10 minutes, r for many blends slightly rises. The essential difference in electrical conductivity values for blends of identical formula but different sequence of preparation, and the stability of conductivity during the mixing process suggest that the concentration of a filler at the interface is governed by the equilibrium between the number of particles arriving at the interface and those removed back to the phase. Indeed, taking into account that, although the redistribution of a filler from a phase to the interface gives no energy gain and is associated with overcoming a high activation barrier of macromolecule desorption, it does occur. So, according to the statistics, the concentration of filler particles at the interface must rise in time, but it remains constant (Fig. 4). Fig. 4 - r of polymer blends versus time of mixing. The CB content: 5 vol. % in the PE phase, 8.5 vol. % in the PU phase, 9.3 vol. % in the PS phase. The ratio of polymers is 1:1 A great difference in electrical conductivity of blends prepared by two different mixing procedures indicates that in a blend with low conductivity there exists a potential for greater number of filler particles to be localized at the interface than it is observed. However, this possibility is not realized. This can be explained only by the equilibrium existing between the number of particles arriving at the interface and those leaving the interface for a phase. Let us analyze this equilibrium in more detail. Firstly specify that the localization of a dispersed particle at the interface means that the macromolecules of both polymers are adsorbed on this particle. The velocity of particle transfer from a phase to the interface is determined by the number of their successful collisions dependent on the filler concentration in a phase. The collision is said to be successful when a part of macromolecules of the preliminarily filled polymer previously adsorbed on a filler is substituted by the macromolecules of another polymer component. The replacement of a very small number of macromolecules may be treated as a transfer of a filler particle to the interface. The replacement is associated with overcoming an energy barrier of the desorption of macromolecules from a solid surface, which can be rather high for some macromolecules [24]. However, at the surface of a filler there always exists some part of macromolecules having a relatively low adsorption energy (small number of contacts with a surface). These macromolecules can be with relative ease substituted after a collision of particles for macromolecules of another polymer. High shear stress acting during mixing promote a macromolecule to overcome the activation barrier of desorption. Obviously, the average activation energy of desorption is higher for macromolecules of the polymer having the higher wetting force. Consequently, the rate of filler particles migration to the interface must be lower from a phase with higher wetting force than from a phase with lower wetting force. However, with a satisfied condition (1), after a long period of mixing the interface would be filled with particles without regard to the phase which they left. Nevertheless, the experimental data are contradictory to this concept (Fig. 4). Therefore, the essential role in establishing the equilibrium concentration at the interface is played by the rate of filler particles leaving the interface and arriving at a phase. Consider the factors controlling the rate of particles leaving the interface for a phase. The removal of a particle from the interface is a result of the shear stress exerted on the particle by the polymer environment and is described by the Stokes law [25]. The shear stress affecting a particle is in direct proportion to its size, the viscosity of a polymer medium, and the shear rate. In certain situations this shear can abstract a particle from the interface and return it to one of polymer phases. The adhesion of a particle (Wa) to the unfilled polymer phase counteracts its removal from the interface. Only those particles stay at the interface for which the force of binding to the opposite phase exceeds the force of their separation from this phase. The ratio of these forces will determine the equilibrium concentration of a filler at the interface. Let us estimate these forces. In both phases of a heterogenous polymer blend the shear stress is the same, so the same is the force of particle removal from the interface. Hence, the local equilibrium concentration of particles at the interface will be determined by their adhesion to a phase. In this case it is important to specify to what of two polymer phases the adhesion is considered. It is known [1] that the transfer of filler particles from one phase of polymer blend to another is observed very rarely. Therefore, in most cases the particles of the filler after abstraction from the interface return back in that phase from which they came to the interface. Otherwise a fast transfer of the filler would be observed from a phase of lower wetting force to opposite polymer phase. So the force holding particles at the interface is a result of their adhesion to the unfilled polymer phase. Besides, this suggests that dispersed particles at the interface occupy non-equilibrium positions and are confined predominantly in the preliminarily filled phase. The energy of particle adhesion to a phase is determined by the following expressions [16]: $Wa31 = s23 - s13 + s12$ (4) $Wa32 = s13 - s23 + s12$ (5) where:Wa31 is the work of particle adhesion to the phase 1; Wa32 is the work of particle adhesion to the phase 2. The adhesion of filler particles to the phase of polymer with the greater wetting force is higher than to the phase with smaller wetting force. Analyzing the ratio between the rates of particles arriving at and leaving the interface, it may be concluded that the smaller is the wetting force of a polymer phase where particles are located, the greater is their concentration at the interface. This is consistent with experimental observations (Table 2, Fig. 4). However, the proposed mechanism of establishing the equilibrium concentration of carbon black at the interface between polymers does not explain why carbon black does not migrate to the interface from one of two phases whereas such transfer occurs from another phase. Indeed, if the condition (1) is satisfied, the transfer of carbon black from either of two phases to the interface is thermodynamically efficient. Even with a low adhesion of a filler to the interface the local concentration of a filler at the interface would slightly exceed its concentration in phase. However, such an excess is not observed for a number of polymer pairs attributed to the first group according to the data in Table 2. A broad spectrum of the energies of adsorption of macromolecules on a solid surface suggests that under certain conditions the localization of a filler at the interface is feasible even if the condition (1) is not fulfilled. This may take place if the location of the whole of a filler within a phase of one of polymers and not at the interface is thermodynamically efficient (s13>s12+s23 or s23>s12+s13) and a filler was introduced initially into a phase of another polymer. In this case the transfer of CB from one phase to another is thermodynamically favourable. It is necessary for a filler particle to transfer from one phase to another that the macromolecules of polymer previously adsorbed on its surface should be fully replaced by the macromolecules of the second polymer. However, such a replacement is unlikely because of a very high adsorption energy of some part of macromolecules. The experimental data confirm that such replacement is very rare to occur [1,10,11]. The partial replacement of macromolecules is more probable since there is a portion of macromolecules with low adsorption energy [24]. Such partial replacement just implies the localization of a filler at the interface. Since the interfacial tension between polymers is minor [17] and the adhesion of polymers to a filler differs essentially (Table 3), it may be supposed that the filler localizing between polymer phases by the latter mechanism is most probable. The filler localization at the interface in all blends assigned to the first group according to Table 2 is likely to follow the last mentioned scheme. In those blends the local concentration of a filler at the interface is also governed by the equilibrium between the number of particles arriving at the interface and leaving it for a phase. From the above discussion it follows that with increasing difference in wetting forces of polymers the equilibrium concentration of CB at the interface must rise when a filler transfers to the interface from the phase of a lesser wetting force and must fall when it comes here from the phase of higher wetting force. Besides, the rise of interfacial tension between polymers must promote the increase in local concentration of CB at the interface when it is redistributed from any phase. Taken together the experimental observations (Table 2) confirm the validity of the latter conclusion. Thus, dependence of the interfacial filler concentration on the sequence of components mixing is due to the peculiarities of macromolecule adsorption on a solid surface. Because of a high activation energy of desorption from a solid surface for a major part of macromolecules [24], the redistribution of dispersed particles from one polymer phase to another practically does not occur and those cannot occupy equilibrium position at the interface. Under these circumstances when a difference in wetting forces of phases takes place, the sequence of blending has a determining effect on the possibility and extent of the localization of dispersed particles at the interface. Let us consider the blends assigned to the third group according to Table 2. In the PE+PIB, PE+PP, PE+PBD blends the polymer components have close values of cohesion energy and similar interaction intensity with the carbon black surface and hence, close wetting force. Besides, these pairs exhibit very low interfacial energy [17]. Consequently, even though the condition (1) is fulfilled, the equilibrium CB concentration at the interface in these polymer blends will only slightly exceed the concentration in phase. The experimental data are fully consistent with this assumption. So, if CB is confined only in a single polymer component and its concentration here is 1.5 volume % below jp, the concentration of CB at the interface does not reach the percolation threshold (Table 2). However, when the concentration of CB in phase is 0.3 % below jp , the PE+PP and PE+PIB blends conduct electric current and have r equal to 8·103 and 2·104 Ohm·cm correspondingly. Because of close wetting forces of the polymers in these blends, the migration of a filler to the interface is possible from both phases. Owing to this fact, when CB is preliminarily introduced into both polymer components and CB migrates to the interface from both phases, the fall in electric resistance of these blends below the ‘additive’ values is observed even if the CB concentration in both phases is 1.5 % below the percolation threshold. The essential role played by shear stress in the process of filler localizing at the interface suggests that the process is strongly affected by the viscosity of polymer components. Particular attention was given to the systems (PE+CB) +PMMA and (PS+CB) +PE, a case of the most interest since a filler is here redistributed from a phase of polymer with lesser wetting force. In these systems the viscosity of PMMA and of PE correspondingly was varied (Fig. 1). The variation of viscosity within 300 to 1500-1700 Pa·s range for PMMA and from 250 up to 1500 Pa·s for PE only moderately increases r of the (PS+CB) +PE blend (Fig. 1, the viscosity is given for the conditions close to those of mixing: shear rate is 100 s -1). When PMMA and PE viscosity exceeds the above limits, r of blends rises essentially. Such viscosity effect can be understood from the viewpoint of kinetics. The wetting of a filler by high-viscosity polymers occurs predominantly under the action of external forces straining polymer and indenting the filler particles into polymer bulk. When the polymers differ greatly in viscosity, the rate of strain will be far less for a high-viscosity polymer phase than for that of low-viscosity. So the high-viscosity component has no time to wet the filler particles surrounded by the low viscosity, easy to deform polymer. As a result, the CB localization at the interface is not observed. Besides, the rise of the viscosity of either of two polymer components increases viscosity of the system as a whole, and in the blending conditions this causes the shear stress and the force of particle break-off from the interface to rise. As a result, the equilibrium concentration of particles at the interface decreases. The ratio of polymer viscosity values, under which a substantial drop in local interfacial CB concentration is observed, differs for various polymer pairs. The greater is the difference in wetting forces of polymers, the more times the viscosity of the second (having higher wetting force) polymer, can exceed the viscosity of the preliminarily filled polymer. So, this ratio is about 4 for the PE+PMMA blend, and about 2 for the PS+PE blend. The best conditions for particles to localize at the interface are provided when viscosity of the second polymer is slightly lower than that of a preliminarily filled polymer component. Conclusions 1. The possibility of dispersed particles to be redistributed from a polymer phase to the interface between two polymers and the extent to which this event proceeds is substantially determined by the relative capacity of polymer components to wet the surface of filler particles and by the sequence of blending the components. When a difference in the wetting force of polymers increases, the concentration of dispersed particles at the interface rises in the event that they have preliminarily been introduced into the phase of polymer with a lesser wetting force, and reduces where they have preliminarily been introduced into the phase of polymer with a higher wetting force. 2. The localization of a filler at the interface in polymer blends is also possible in the case when the residence of particles at the interface is thermodynamically inefficient, but when their transfer from a filled polymer phase to unfilled one gives energy gain. 3. The local concentration of a filler at the interface is determined by the equilibrium established in the process of blending between the number of filler particles arriving to the interface from a polymer phase and those moving in the opposite direction under the action of external mechanical forces. This concentration rises with increasing energy of particle adhesion to the phase of unfilled polymer and with decreasing shear stress experienced by a particle.