ELECTROMASS TRANSFER OF DISPERSE ELECTRICALLY CONDUCTING POLYMER COMPOSITIONS

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We have investigated the change in the morphology and in the characteristics of a layer of soot-filled polyethylene electrodeposited on a substrate as a function of the original composition of the material and the regime of the process.

Electrostatic methods of producing composition materials and coatings represent one of the most effective and ecologically sound technological processes of handling disperse polymer materials. We have on hand considerable research, generalized in monograph [1], in which the various aspects of electrical mass transfer of disperse polymers out of pseudoliquefied systems is studied, including the unique features involved in the charging of polymer particles, the motion of these particles in an electrostatic field, and the deposition and retention of these particles on the substrates being treated. We are dealing here primarily with polymers that have not been completely filled. At the same time, the introduction of even small quantities of disperse modified additives can significantly alter (due to the change in the donor-acceptor interactions of the components) the distribution of the particles in terms of magnitude and charge sign within the pseudoliquefied layer [2], which is reflected in the parameters of the technological process. We should expect even greater changes for extensively filled polymer compositions; however, we have no studies on hand into the nature and unique features of the electrical mass transfer of filled polymers.

In this regard, of considerable interest is a study of the electrical mass transfer of electrically conducting composition materials. On the one hand, this is brought about by the need to seek out efficient technological processes for the fabrication of materials that conduct electricity, said materials based on disperse components. On the other hand, the components of the electrically conducting compositions differ significantly in terms of their electrophysical properties, thus leading to a variety of mechanisms for the charging of these materials in the pseudoliquefaction and discharge in the electrodeposited layer on the substrate.

We have selected soot-filled polyethylene compositions as the object of our study (the characteristics of the original components can be found in Table 1). The majority of the experiments were carried out with a mixture containing 55 mass % of soot, which gave us a low specific electrical resistance for the chosen material (less than 1 Ω·cm) and it offered great potentials for its engineering applications. The compositions were prepared by dry mixing of the components in a bladed mixer. The application of the layer of electrocharged particles of the mixture onto the substrate was accomplished in a manner described in detail in [3], in an electrostatic field which was generated between a high-voltage electrode situated in the pseudoliquefaction chamber of the material and a grounded substrate positioned above that chamber. The coating was formed by melting a layer of the composition onto the substrate at a temperature of 453 K within 0.3 sec under a pressure of 5 MPa. Plates of magnesium-based anodic alloys were used as the substrate to serve as chemical current sources.

The electrical transfer of the mass of a disperse material is characterized by an internal charge and the mass of the material layer electrodeposited on the substrate, with various parameters for the electrostatic field. The charge of the particle layer is evaluated in two ways, the primary one involving a Faraday cylinder method. In the first case, the particle layer is shaken off the substrate into the cylinder and the charge is fixed [3],

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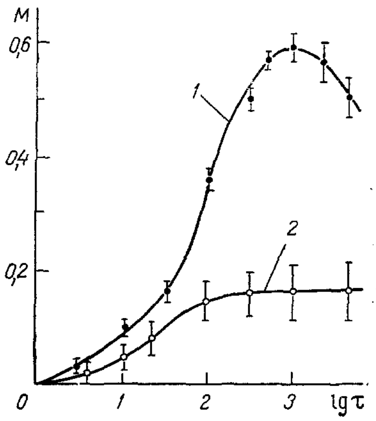

Fig. 1

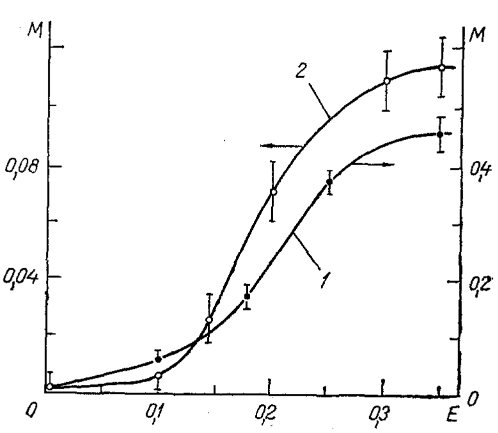

Fig. 2

Fig. 1. Kinetics of electrodepositions of disperse HDPE (1) and of its composition, containing 55 mass % of soot (2), with an electrostatic field strength of 0.25 MV/m. M, kg/m², τ, sec.

Fig. 2. Mass of the electrodeposited HDPE layer (1) and its composition, containing 55 mass % of soot (2), as functions of the electrostatic field strength (duration of electrodeposition τ = 17 sec). E, MV/m.

TABLE 1. Some Characteristics of the Initial Components

Component	Dimension, μm		Density, kg/m³		Specific volumetric resistance ρ_v, Ω·m
	particles	agglomerate	of the saturated layer	of the block	
High density polyethylene, brand 20906-040 (GOST 16338-77)	2—5	20—200	264	940	10^{15}
Industrial grade carbon black, brand P805-E (TU 38 11543-75)	0,12—0,15 [8]	0,4—0,6 [8]	149	—	$\frac{3\cdot10^{-3}}{3\cdot10^{-4}}$ *

*The numerator shows the values of ρ_v for the powder at a pressure of 0.1 MPa, while the denominator shows these values at a pressure of 1 MPa.

using the V7-30 voltmeter as the recording device; in the second case, the charge of the layer is evaluated directly on the substrate [4]. We studied the morphology of the electrodeposited layer by means of an NU-2 universal optical microscope. The content of the soot in the deposite layer was estimated on the basis of the specific intermediate resistance R_i [5] of the coating after the melting of the layer, and this quantity was determined by means of an attached probe (a brass cylinder 30 mm in diameter), with the polished end pressed against the coating under a force of 2 N. The values of R_i were determined from the drop in the voltage U between the probe and the substrate at a current density of 0.3 A/cm² and was calculated in accordance with the formula $R_i = (U/I)(S/d)$. The voltage was recorded by means of the V7-30 voltmeter and the current was recorded with a M2007 milliammeter.

The introduction of soot into the HDPE exerts decisive influence on the kinetics of electrodeposition (Fig. 1), and on the relationship between the mass (Fig. 2) and the integral charge (Fig. 3) of the electrodeposited layer and the strength of the external electrostatic field.

On the one hand, this is brought about by the relatively high electrical conductivity of the soot and it is associated with the formation in the electrodeposited layer of the composition being utilized here of conducting three-dimensional structures which penetrate the layer down to the substrate. This kind of relationship is made evident by the absence of a charge in the electrodeposited layer of the composition as it is recorded directly at the substrate. This effect blocks the appearance of a "reverse crown" in the layer, which is

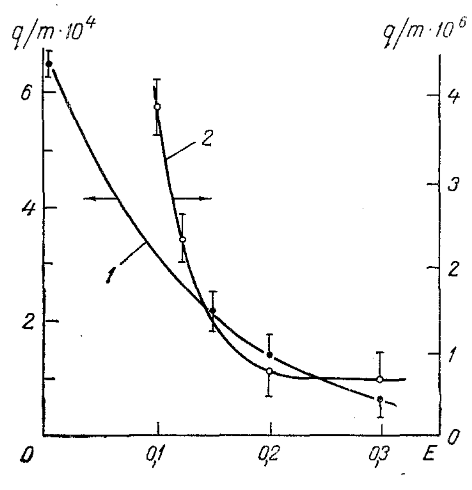

Fig. 3

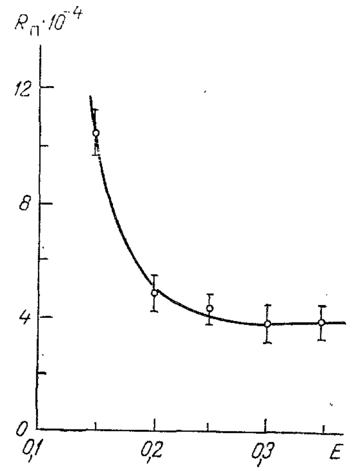

Fig. 4

Fig. 3. Effect of electrostatic field strength on the magnitude of the integral charge of the electrodeposited HDPE layers (1) and its composition, containing 55 mass % of soot (2). q/m, C/kg.

Fig. 4. Specific intermediate resistance of coatings made out of HDPE compositions, containing 55 mass % of soot as a function of the electrostatic field strength. R_o, $\Omega \cdot mm^2/mm$.

TABLE 2. Specific Intermediate Resistance (R_i) of the Electrodeposited Coatings as a Function of the Original Soot Concentration (C) in the Pseudoliquefied Layer

C, mass %	30	35	40	45	50	55
$R \cdot 10^{-4}$, Ohm·mm²/mm *	$\frac{129}{21}$	$\frac{105}{13}$	$\frac{76}{10}$	$\frac{34}{6}$	$\frac{22}{4}$	$\frac{10}{3}$

*The denominator shows the values of R_i for the original composition.

the reason for the existence of an extremum in the kinetic relationship of the mass of the unfilled HDPE layer (Fig. 1, curve 1), and to a significant extent defines its nature within the layer of the soot-filled composition (curve 2). If we compare these curves, we can note the following. First of all, the introduction of the soot reduces the limit masses of the layer (by a factor of more than three). Secondly, the process of electrodeposition of the composition proceeds in an extremely unstable manner, which is borne by the considerable scattering of the mass characteristics of the layer over the entire studied time interval (curve 2). Let us note that for an unfilled polymer low stability occurs only on the descending branch of the kinetic relationship (curve 1), where this "reverse crown" appears.

On the other hand, the specifics involved in the formation of the deposited layer are associated with the changes of its structural state. In the pseudoliquefied layer of an unfilled HDPE its particles combine into agglomerates whose dimensions range from 20 to 200 μm. In an external field of constant direction agglomerates are deposited on the substrate out of this layer, with an excess charge of specific sign (negative polarity in this case). At the same time, this excess charge characterizes the difference between the charges of different signs, since each HDPE particle, because of the nonuniformity of the surface and the bipolar nature of the charge, in the case of pseudoliquefaction exhibits a different local charge polarity at the surface. The location of the agglomerate in the deposited layer, associated primarily with its orientation in the external field during the transfer, is caused by the distribution of the charges at the particle surfaces, where these particles form to combine the given agglomerates, as well as at the surfaces of those agglomerates earlier deposited on the substrate. The dimensions of the agglomerates in the layer on the substrate depend on the parameters of the external field. In particular, with an increase in the original strength of 0.05 to 0.2 MV/m the dimensions of the HDPE agglomerates change from 20-60 to 180-200 μm, thus achieving a significant increase in the layer mass (see Fig. 2).

When carbon black is introduced into the HDPE the dimensions of the agglomerates becomes stabilized. This is because of the following circumstances. During the course of the HDPE pseudoliquefaction process the old agglomerates are constantly broken up and new ones are formed. As the old agglomerates are destroyed the repulsed fragments are enveloped by more mobile particles of soot, on which a charge is induced that is opposite in sign to the corresponding region of the polymer particle surface. As a result, the polymer agglomerate, breaking apart down to minimum size (under the conditions of the experiment), change into agglomerates of the composition material and exhibit dimensions of 20-40 μm. A portion of the carbon black in the pseudoliquefied state remains unbound from the HDPE particles (the "free" soot) and forms soot agglomerates whose dimensions are 0.3-0.5 μm (Table 1).

When a high-voltage potential of negative polarity is applied to the electrodes the carbon black component acquires an excess charge of negative sign in all of the above-enumerated agglomerates, which facilitates their transfer to the substrate. On contact with the substrate it gives up its excess charge, as a result of which only the original charge of the HDPE components remains within the agglomerates of the composition, and also the mirror reflected charge in the carbon black shell. Based on these considerations, the boundary layer of the precipitate may consist only of the composition agglomerates, but not of the agglomerates of the "free" carbon black, which give up their charge on contact with the substrate.

The data presented in Table 2 and in Fig. 4 bear out that the relationship between the agglomerates of the material making up the composition and the "free" carbon black in the electrodeposited layer is not constant and depends on the initial concentration of the carbon black in the pseudoliquefied layer of the composition and the parameters of the external field. With an increase in the original concentration of the soot and with a rise in the field strength we have a reduction in the resistance R_i and a corresponding increase in the amount of contained soot in the layer electrodeposited on the substrate, which may be associated with the increased probability of charging of the soot agglomerates on contact with the high-voltage electrode. In particular, if in the case of low field-strength values the difference in the amount of soot contained in the original composition and in the electrodeposited layer on the substrate amounts to approximately 20 mass %, then as the strength increases to 0.35 MV/m it drops down to 5 mass %.

It should be noted that the reduction in R_i that occurs with the increase in the field strength may be associated not only with the increase in the concentration of the soot, but also with an intensification of the effect of soot-particle orientation in the electrostatic field and in the formation of a more ordered electrically conducting three-dimensional structure within the deposition layer.

The mass characteristics of the composition layer are smaller than the mass of the unfilled polymer over the entire range of external-field parameters (see Fig. 2). At the same time, the introduction of the soot exerts considerably less influence on the mass characteristics of the layer than on the charged state of the layer (Fig. 3). An evaluation of the charged density for the electrodeposited layer shows that with a field strength of 0.25 MV/m for the HDPE it amounts to $1.7 \cdot 10^{-4}$ C/m^2, while for the soot-filled composition it amounts only to $6.7 \cdot 10^{-6}$ C/m^2. The low value for the charge density in the case of the composition provides a basis for the hypothesis that the electrostatic interaction of the layer and the substrate is not the solitary cause for the retention of a rather substantial mass of the composition on the substrate.

The principal role in the retention of the electrodeposited layer of charged particles on the electrically conducting substrate is played by the adhesion interaction of the layer with the substrate, which is achieved fundamentally by Coulomb forces (the forces of mirror reflection between the integral charges of the layer and those induced on the substrate, but of opposite sign), as well as by the molecular forces associated with the properties of the materials in contact with each other. The contribution of these components to the adhesion interaction can be ascribed to numerous factors, of which the most important is particle size [6].

Based on the data of [6], with a reduction in particle and agglomerate size the contribution of the molecular component of the adhesion interaction increases and with dimensions smaller than 1-10 μm exceeds the contribution of the electrical (including Coulomb) forces. Therefore, for an unfilled polymer with particles and agglomerates of rather large size the principal role in the retention of the layer can be assigned to the Coulomb forces, which is a consequence of the high level of the charged state of the electrodeposited layer. For a composition which contains soot whose particles and agglomerates are considerably smaller in size than the HDPE particles, the main contributions to the retention of the electrodeposited layer on the substrate is made by molecular forces.

The role of the molecular component is particularly noticeable in analyzing the influence of the field parameters on the characteristics of the electrodeposited layer (Figs. 2-4). As was noted earlier, the relationships between resistance and field strength (Fig. 4) demonstrates the increase in the soot content within the layer. At the same time, with an increase in field strength we have a substantial reduction in the magnitude of the integral charge of the layer (after it has been shaken off the substrate into a Faraday cylinder) (Fig. 3), which can be explained in the case of an unfilled HDPE by the participation in the transfer of an ever larger number of agglomerates with a low excess charge. However, despite the indicated changes (the increase in the soot content in the layer and the reduction of the layer's integral charge), leading to a reduction in the Coulomb forces of the adhesion interaction of the electrodeposited composition layer relative to the substrate, its mass characteristics perceptibly increase as the field strength increases. Apparently, this is brought about by a strengthening of the molecular forces because of an increase in the density of particle contact in the layer at the boundary with the substrate, and this is associated with the increase in the strength of the field. The data from [7] also points to the possibility of intensifying the molecular interaction of the contact materials in transfer and in the electrodeposition of the layer of charged particles.

In conclusion, let us note that the data presented here demonstrate the possibility of controlling the electrical conductivity of the electrodeposited composition layer not only when the original concentration of the soot in the mixture is varied, but also by changing the parameters of the electrostatic field. This must necessarily be taken into consideration in the production of electrically conducting coatings made out of dispersed polymer compositions by electrodeposition methods.

NOTATION

E, electrostatic field strength, MV/m; τ, deposition time, sec; M, specific mass of deposition layer, kg/m^2; q/m, integral charge of deposited layer, C/kg; I, current strength, A; S, area of measurement probe, mm^2; d, thickness of deposited coating, mm; U, voltage drop between probe and substrate, V; R_i, specific intermediate resistance, $\Omega\cdot$mm^2/mm; ρ_v, specific volume resistance, $\Omega\cdot$m; C, concentration of soot, mass %.

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