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Metallic Clusters in Polymer Matrices

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The methods of synthesis, the properties, and the structure of new composite materials based on polymers and on clusters of the transition metals are discussed. The properties of metal-polymer systems of this type are shown to be very different from those of ordinary metal-polymer systems, in which the metal particle size is greater than 100 μm. The effect of the clusters on the structure of the polymers is examined, and examples of the dependence of the electrophysical and magnetic properties of metal-polymers on the concentration of metallic clusters are given. 62 references.

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I. INTRODUCTION

Exploratory research on new types of material based on polymers for use in electronics has been intensified in the last few years both within and outside the Soviet Union. The outcome of much of this work has been polyconjugated polymers, such as polyacetyl, polyphenylene, polydiactylene, polypyrrole, etc.[1-3] Being dielectrics with a wide forbidden gap in the energy spectrum of their charge carriers these materials can be doped with electron acceptors (such as halogens, or arsenic or antimony pentafluorides) to give organic semiconductors and organic metals whose electrophysical parameters can be controlled between wide limits.

However, these polymeric materials are still far from being generally available, for a number of reasons, including the lack of large-scale methods of preparation of the initial polyconjugated polymers. We have therefore turned our attention towards the familiar and readily available polymers polyethylene and Teflon. The controlled addition of dopants of different chemical nature (both donors and acceptors) to these materials had be developed. Since the introduction of metal particles of various sizes into this type of polymer matrix had already been demonstrated, we initialy used clusters of the transition metals as dopants.

The expectation that this modification of polyethylene and Teflon could lead to new materials with interesting electrophysical properties was stimulated by a series of papers by Enikolopyan and co-workers[4,5], who showed that the injection mechanism of electrical conduction (which they had observed at high pressures) can be realised at ordinary pressures if the integration of metal and the polymer can be carried out at the "molecular level".

In this review we shall examine the methods of preparing single-phase metal–polymer composites from the inert polymer matrices Teflon and polyethylene (not containing multiple bonds) doped with metal particles of size comparable to the thickness of a single polymer chain. By this approach we have produced a new type of material (which we have termed "cluspols") in which metal clusters are accommodated within the natural cavities of the polymer matrix[6].

II. METHOD OF PREPARING METAL–POLYMERS

Industrial methods of preparing metal–polymer composites usually rely on metal powders (of fairly large particle size), which are added to a melt of the polymer with stirring. However, this method cannot give a uniform distribution of particles in the polymer, and furthermore it tends to degrade the stability characteristics of the composite.

Several alternative methods of preparing metal–polymers have been described: we shall examine some of them in detail.

1) The electrochemical reduction of metals from solutions in the presence of surface-active substances (SAS).[7-11] Polymers containing functional groups can play the role of the SAS. It has been shown[12] that even when the amount of active filler is very small its particles act as centres for the formation of a continuous three-dimensional network through the adsorption and orientation of the polymer molecules under the influence of the field of force of the filler particles. The influence of various factors on the current yield and on the dispersion of the metallic filler has been studied in detail[13-15]. The electro-flotation[16] and the electro-acoustic method[17] are variants of the electrochemical method of synthesis of metal–polymers.

2) The mechanochemical method of synthesis of metal–polymers[18,19] relies on the high adsorption and chemisorption activity of the surface created during the dispersion of a metal. Polymerisation processes during the vibratory milling of salts, metals, and oxides in the presence of vinyl monomers have been studied, and chemical grafting of the metallic particles to the polymer surface was observed during the milling of iron, nickel, titanium, and chromium.

It was reported[20] that the absence of reactive functional groups in the polymer affects the physicochemical properties of the polymer: for example, grinding finely divided iron with polyethylene (even in large excess) does not form a metal–polymer. Furthermore, the main properties of the resulting composite are strongly dependent on the dispersion conditions, and on the shape of the metal particles. Optimising the dispersion time is equally important, since excessively long mechanical treatment of the polymer system may cause mechanical degradation[21]. Thus the mechanical method of synthesis of metal–polymers is applicable mainly to polymers which contain functional groups or multiple bonds, and which can therefore generate chemisorptive interactions between the polymer molecules and the surface of the metal particles[22,23].

3) The displacement method depends on the fact that in the presence of polymers metals can be displaced from salt solutions and form metal–polymers if the electronegativity of the matrix is high enough. This method does not appear to have been widely used: the few papers which refer to it are reviewed in Ref.24.

4) The thermal method of metal–polymer synthesis is the most widespread at the moment[25–28]. It relies on the tendency of the slats of organic acids (formates, oxalates, etc.) and of many metal–organic compounds (MOC) to dissociate into the metal (or metal oxide) and give a volatile compound when heated. Thermoplastic polymers can be used as the organic host material for the decomposition of MOC, giving metal-filled composites as the reaction product.

Unlike the usual mechanical mixtures of polymers and metals, in metal–polymers prepared by the thermal method, the metal particles have a fairly high dispersion, they are evenly distributed through the bulk of the polymer, and the sorption of the macromolecules on their surface is strong and irreversible[29–36].

5) The plasmochemical method. Metal-containing composite materials have been prepared[37] by a high-frequency plasma technique in which the polymerisation process was carried out within the plasma chamber. Two methods of transferring the metal to the gas phase before incorporating it in the growing polymer have been proposed: evaporation of the metal (tin) in an inert gas atmosphere and decomposition in the plasma of a volatile compound of the metal [for example, $Cr(CO)_6$]. The products were analysed by the ESCA method, and it was found that the technique can produce highly dispersed metallic particles in a polymer, covering a wide range of metal–polymer compositions. It was also found that the metal particle size depends on the properties of the polymer: for example, in C_2H_4 the size of Sn particles was 150 Å, in C_6H_4 the size of Cr particles was 500–700 Å, and in C_2F_4 the size of Cr particles was 3000 Å.

Though this method seems very promising for the preparation of metal-containing polymers it does not appear to have been used for this purpose.

6) Cryochemical methods of synthesis of metal-containing polymers[38] are potentially very useful. They rely on the fast diffusion of metal vapours towards a cooled surface covered with a thin layer of polymer. Alternatively, the reaction is carried out in a rotating reactor, and the metal–polymer composite is obtained in the bulb of the rotating apparatus. Francis and co-workers[39,40] prepared metal-containing polymers of the poly(methyl phenyl siloxane) type (DC-150) and studied their u.v. spectra. Various metals (titanium, chromium, molybdenum, vanadium, and tungsten) were used as fillers. It was shown that at low concentrations of the metal in the polymer the metallic clusters are coordinated to the phenyl groups of the polymer to give compounds of the *bis*-arene type. Monatomic, diatomic, and triatomic metal clusters, both single and bimetallic (Cr_xTi_y, etc.) were obtained[40] in a matrix of poly(methyl phenyl siloxane). However, the metal–polymer composites thus obtained were found to be unstable if the temperature was allowed to rise to 25 °C or if the concentration of metal was increased.

Thus, in spite of the many methods of synthesis of metal–polymers already disclosed, new methods are needed for the preparation of materials stable under normal conditions and containing a narrow distribution of particle sizes in the range of 15–50 Å.

1. Effect of Dispersed Fillers on the Properties and Structure of Polymers

Let us examine more closely the structure of the polymer molecules, and calculate the effect of the introduction of relatively coarse metallic filler particles on some of the properties of the polymers.

The structure of polymers is characterised by crystalline regions (blocks, or stacks) randomly distributed within the amorphous mass. Orientational ordering of the crystalline fragments can be obtained by stretching or rolling the polymer[41].

The insertion of even relatively small metal particles (~250 Å) should cause substantial disruption of the polymer structure: in practice, the metal particles in metal–polymers are several orders of magnitude larger, and their influence on the polymer structure is correspondingly more marked.

The presence of metallic fillers of ordinary particle size (1–5 μm) can produce some specific properties in polymer materials (for example, enhanced thermal and electrical conductivity, higher magnetic susceptibility and specific heat, and resistance to ionising radiation). However, usefully large changes in properties are achieved only at high concentrations of the metallic filler[42]. Thus, in nickel–polyethylene composites the required electrical conductivity (5.8×10^3 Ohm^{-1} m^{-1}) could be achieved only at a concentration of metallic particles greater than 50 vol.% (90 wt.%). According to current views, the highest conductivity is observed when a substantial fraction of the sample volume is occupied by connected chains of electrically conducting particles with a cross-section equal to the area of contact of the particles. This type of material has only limited applications in technology because its properties cannot be optimised.

In the electrical conductivity scale of materials the extreme positions are occupied on the one hand by typical insulators such as Teflon and polyethylene, and on the other hand by typical metals such as copper and silver. The conductivity can be increased by 5–14 orders of magnitude in some materials by doping[1]. The doping (a special type of alloying) usually involves placing particles of the doping element in vacancies of the crystal lattice of the host material. The two types of particle should be comparable in size. From this formal analogy we can expect the doping of polyethylene or Teflon with metals to bring their conductivity into the typical semiconductor range.

Thus the problem of controlling the electrophysical properties of Teflon or polyethylene reduces to introducing into these polymer matrices dopants comparable in size to the vacancies (or holes) in the initial polymer.

Let us consider once again the structure of the polymer matrices. Polyethylene and Teflon are typical semi-crystalline polymers, with a crystallinity of 60–85% and 75–80% respectively. The molecules in the polymer chain form a planar zig-zag structure with an angle of 112° between the units. In the case of polyethylene the self-repeating unit consists of two CH_2 groups. The polytetrafluoro-ethylene molecule has a more complex zig-zag structure because of the fairly large size of the fluorine atoms[43].

The crystalline part of the polymer structure usually consists of platelets 10–20 μm wide and ~100 Å thick. The main axes of the chains are found to lie at right angles to the plane of the platelets. The thickness of the platelets is much smaller than the chain length. Thus one molecule of polyethylene (with a mass of 50000 and a length of 4500 Å, say) repeatedly crosses the boundaries between crystalline and amorphous regions. Even the crystalline parts of the polymer contain a large number of holes (or defects): these include stacking faults, irregular arrangement of tapes, plates, etc., and therefore the microcrystallites in polymers are usually treated as formations with a high concentration of defects[44].

The amorphous regions in the polymer structure are even "looser", and contain a larger number of natural "holes": the bond between the chains is weaker than in the crystalline blocks, giving greater mobility to the amorphous segments of the molecules.

2. Method of Synthesis of Composite Materials of the "Cluspol" Type

We shall now consider the methods of forming metallic clusters in the natural holes of polymeric matrices by the fast monomolecular thermal decomposition of solutions of metal compounds in a melt of the polymer.

According to modern views, melts of polymers consist of distinct spherulites which retain (in a slightly distorted form) the original platelets or lamellae as unchanged constituents. In other words, the melt retains the short-range order of the initial polymer structure, but the pre-existing holes become accessible for the insertion of metallic particles[45].

The thermal decomposition of metal compounds has been studied widely, under various conditions. In some cases it was shown to be a good method of preparing highly dispersed and very pure metal particles[46]. An overall scheme of thermal decomposition with formation of volatile ligands and a "hot" metal atom M* is given below. The cluster of metal atoms M_n which begins to grow in the melt is stabilised in the polymer matrix. A specific example [the thermal decomposition of $Fe(CO)_5$] is also given.

$$ML_n \rightarrow M^* + nL$$
$$mM^* \rightarrow [M]_m \text{ (cluster)}$$
$$Fe(CO)_5 \rightarrow Fe + 5CO$$
$$\Delta G_{400K} = -8.98 \text{ kcal mole}^{-1}; \Delta G_{600K} = -36.82 \text{ kcal mole}^{-1};$$
$$\Delta G_{1000K} = -92.50 \text{ kcal mole}^{-1}$$
$$15Fe + 4CO \rightarrow Fe_3O_4 + 4Fe_3C$$
$$Fe_3O_4 + 6CO \rightarrow Fe_3C + 5CO_2$$
$$CO \rightleftarrows 0.5CO_2 + 0.5C$$

It is found that an increase in temperature causes an increase in the extent of decomposition of the carbonyl by the main reaction, and correspondingly lowers the yield of side-products[47].

In some recent work the thermal decomposition of metal carbonyls has been used as a source of pure metals (polymer fillers). Thus the preparation of zero-valent iron by the thermal decomposition of $Fe(CO)_5$ in a solution of "functional" polymers has been described[27,48]. It was shown that polymers containing functional groups act as catalysts for the thermal decomposition of $Fe(CO)_5$ to iron(0) through an intermediate of the butadienyl–$Fe(CO)_3$ type, whereas in polymers without functional groups the thermal decomposition goes through the disproportionation of $Fe(CO)_5$. The average size of the iron particles in the composites was ~70–80 Å.

Ultra-dispersed particles of Fe_2O_3 were obtained[49–51] by thermal decomposition of $Fe(CO)_5$ under oxidising conditions in polymers not containing functional groups (polyethylene, polytetrafluoro-ethylene, polypropylene). The preparative method consists in the adsorption of $Fe(CO)_5$ on the surface and in the bulk of the polymers, followed by thermal oxidation at 105 °C in air. The value of this method in the preparation of stable composites of iron(III) oxide and polymers was convincingly demonstrated. The average size of the Fe_2O_3 particles was 30–80 Å.

For the reasons mentioned above the formation of metallic clusters in a polymer melt was carried out at the highest permissible melt temperature, well in excess of the incipient thermal decomposition temperature of the compound. Additional requirements included the highest possible dilution of the solution of metal-containing compound in the thermal decomposition step and the fastest and fullest possible removal of the volatile ligands from the reaction mixture. The proposed method was tested with several types of polymer and different metal compounds (iron, cobalt, molybdenum, and chromium carbonyls, π-allyl compounds of the platinum metals, and acetates, formates, and other metal compounds)[6]. The metal–polymer materials prepared in this way can easily be shaped by moulding. The products included films of high-pressure polyethylene HPPE + M (where M = Fe, Cr, Ni, Cu) prepared at 125 °C and 150 atm, and sheets and rods of polytetrafluoro-ethylene PTFE-40 + Fe prepared at ~280 °C and 150 atm.

The method has been repeatedly shown to be applicable to a wide range of polymer matrices with different types of compounds and different metals, as well as metallic mixtures, alloys, oxides, sulphides, etc. The resulting powders can be formed into articles of any shape by standard methods. Thus we have developed a method of producing a new type of material for which the technical term "cluspol" has been proposed.

The detailed structural features of these materials, including the distribution of the metal particles, their state of oxidation, interactions with the polymer matrix, etc. were studied by a wide range of physicochemical and analytical methods (DTA, X-ray phase analysis, low-angle X-ray diffraction, i.r. spectroscopy, NMR spectroscopy, and Mössbauer spectroscopy).

On the whole, the most sustained and detailed studies were made on high-pressure polyethylene and Teflon-40 containing iron clusters. Samples containing other metals or other matrices received only occasional study.

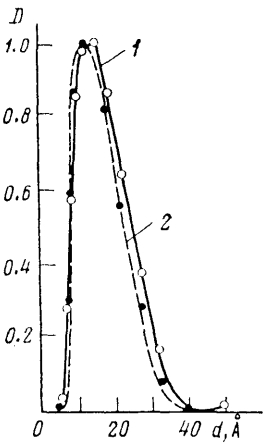


Figure 1. Size distribution of chromium clusters in a Teflon-40 matrix containing 1.0 (*1*) and 5.0 wt.% of Cr (*2*).

III. STRUCTURE AND PHYSICOCHEMICAL PROPERTIES

1. X-Ray and Mössbauer Studies of Metallic Clusters in Polymer Matrices

Metal lines cannot be detected by X-ray phase analysis in "cluspol" materials until the concentration of metal exceeds 10%. Samples containing less than 10% of metal were studied by the low-angle X-ray diffraction method[6]. A typical distribution is shown in Fig.1. Chromium in Teflon-40 gave a particle size distribution curve with a single narrow maximum at $d \cong 12.1$ Å. In the case of iron clusters in a polyethylene matrix the picture is more complex: at low concentrations we again find a narrow distribution with a maximum at 14.8 Å,

but at higher iron concentrations a second, flat maximum appears in the curve at $d \cong 70$ Å (Fig.2). A further increase in the concentration of metal in the material shifts the peak towards larger cluster sizes, but even in this case more than 80% of the clusters have a diameter smaller than 40 Å.[6]

The low-angle X-ray diffraction method can be used to determine the periodicity of the distribution of clusters in the matrix: typical results[6] for iron clusters in polyethylene are shown in Table 1. We note that at high concentrations the average distance between clusters is not more than two or three cluster diameters. The size of the iron clusters was determined by the static magnetic susceptibility method. From the plots (Fig.3*b*) of the specific magnetisation against temeprature for different iron concentrations we note that the downward slope is steeper than for massive iron (which has a Curie temperature of ~1000 K). A size dependence of the Curie temeprature cannot be excluded for very small particles.

Table 1. Periodicity (l) of the distribution of iron clusters in high-pressure polyethylene[6].

[Fe], wt.%	l, Å	[Fe], wt.%	l, Å
1.10	315±30	8.08	110±5
2.64	220±12	29.6	90±5

By measuring magnetisation in small fields the size of the iron clusters in the polymer matrix was determined on the assumption that the separate clusters display supermagnetism[52]. We know that the number of iron atoms (n) in a superparamagnetic particle, its volume (V), and its size (r) can all be determined from the initial slope of the experimental magnetisation curve:

$$n=\mu/2.2\ \mu_B;\ V=nM_B(\mathrm{Fe})/N_A\rho$$

where μ is the magnetic moment of the superparamagnetic particles, $2.2\mu_B$ is the magnetic moment of the Fe atom, and ρ is the density. We note from Fig.3*a* that the initial linear portion is most developed in the sample with an iron concentration of 3 wt.%. For this composition the following results were obtained: $n = 286$, $V = 3401$ Å^3, and $r = 15.1$ Å. The deviation from linearity arises because of the presence (in addition to the main group of supermagnetic particles ~15 Å in size) of a smaller number of larger particles which contribute ~5% to the toal magnetisation. These results are fully consistent with those obtained by low-angle diffraction on the same samples.

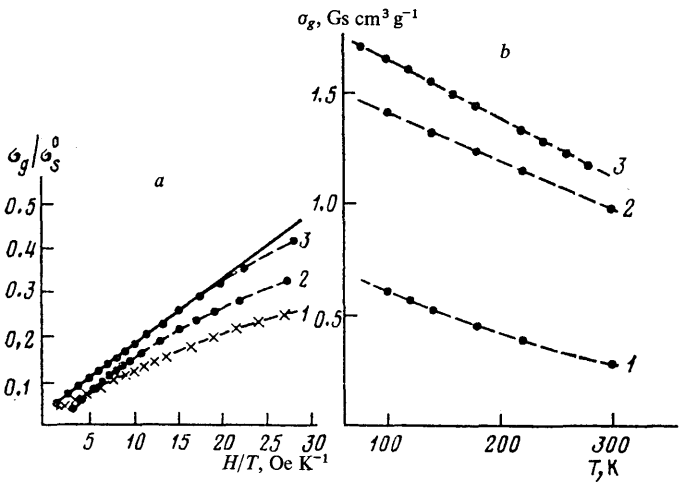


Figure 3. (*a*) Plot of the ratio σ_g/σ_s^0 (where σ_s^0 is the saturation magnetisation at 0 K) against H/T, and (*b*) temperature dependence of the specific magnetisation σ_g, for samples of polyethylene with different iron content: *1*) 1.0, *2*) 2.0, *3*) 3.0 wt.%.

The presence of iron clusters in these materials is confirmed by the Mössbauer spectra of "cluspol" samples. In the typical spectra shown in Fig.4 the main component at 300 K is a doublet with a quadrupole splitting of 0.6–0.9 mm s^{-1} and an isomeric shift of 0.6–0.7 mm s^{-1}. The parameters of the spectrum differ from the values for both α and γ

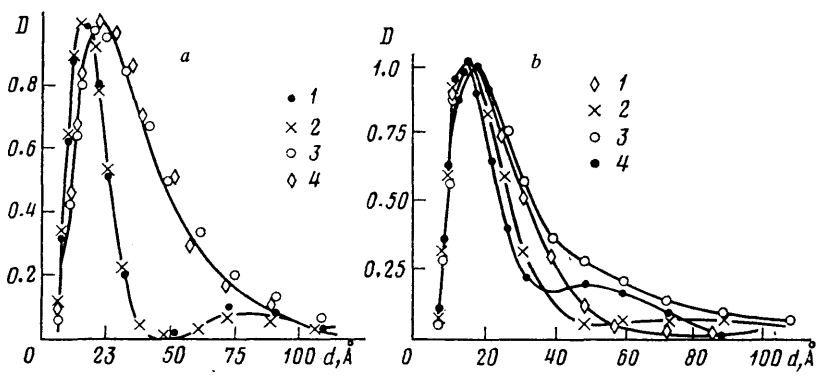


Figure 2. Size distribution of iron clusters in a high-pressure polyethylene matrix (*a*) and in Teflon (*b*); Fe content of the HPPE matrix: *1*) 0.7, *2*) 1.0, *3*) 5.0, *4*) 7.0 wt.%; Fe content of Teflon; *1*) 1.0, *2*) 5.0, *3*) 25.6, *4*) 10.0 wt.%.

iron (whether massive or in thin-film form)[55,54], and they agree with the parameters of the Mössbauer spectra of iron clusters in an argon matrix[55].

Thus the available data convincingly show that the proposed method gives metallic clusters with a narrow size distribution, and that these clusters are stabilised in the polymer matrix.

2. Effect of Metallic Clusters on Polymer Structure: NMR Studies

The nature of the interaction between metallic clusters and the polymer matrix, and the resulting changes in the matrix, were studied by NMR. The NMR spectra of the initial polyethylene samples are symmetrical, and consist of a broad and a narrow component (Fig.5). The narrow component is associated with the amorphous part of the polymer, the broad component with the crystalline part. An increase in the concentration of metallic clusters produces marked changes in the NMR spectra. Initially the intensity and the width of the narrow component are affected, but at higher concentrations the broad component begins to expand rapidly and beyond a certain metal concentration the NMR spectrum can no longer be measured[56].

Both the crystalline and the amorphous regions of the polymer can act as localisation sites for the clusters. The processes by which the metal particles are incorporated into the polymer can be monitored by analysing the NMR spectra.

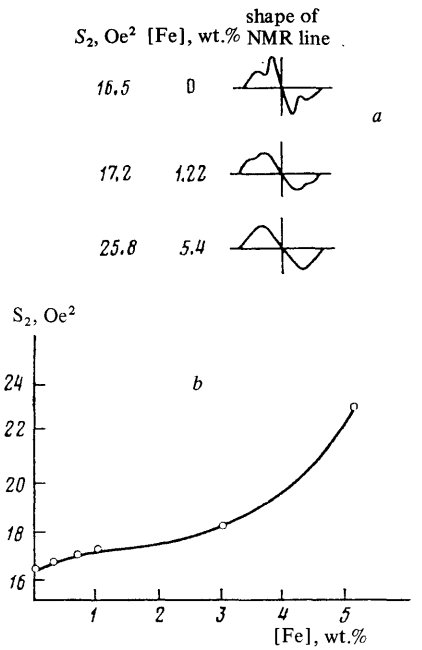


Figure 5. Effect of increasing the iron content on the shape of the NMR line (*a*) and on the value of the second moment S_2 (*b*) for composite polymers based on polyethylene.

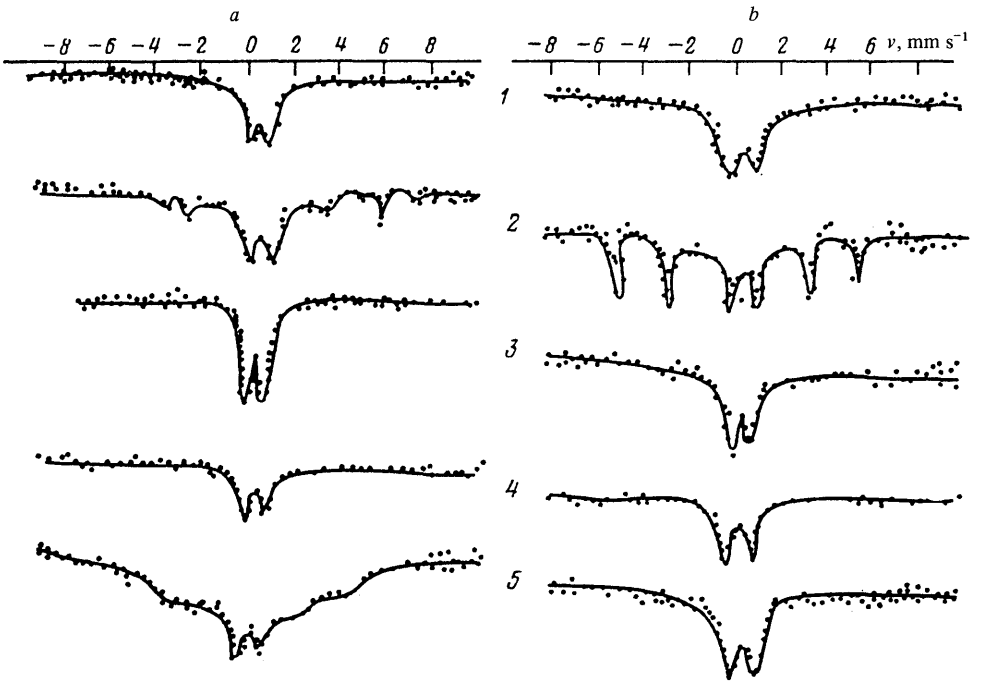


Figure 4. Mössbauer spectra of "cluspol" materials: (*a*) PE + Fe, (*b*) PTFE + Fe. Metal concentration: *1*) 3.0, *2*) 5.0, *3*) 7.0, *4*) 10.0, *5*) 30.0 wt.%.

Thus, as we have already pointed out, the narrow component is the first to be affected in the PE spectrum. Since the NMR spectra give information on the mobility of molecular chains, the decrease in intensity and increase in width of this component indicate changes in the segmental motion of the molecular chains in the amorphous phase, and also in the rotational and diffusive motions of the CH_2 groups about the fixed axes[57]. Thus the NMR results confirm that the formation of metallic particles begins in the amorphous regions, which are "looser" than the crystalline regions.

The introduction of metallic clusters makes the material more monolithic (more "pseudo-crystalline"), and also more thermally stable.

Table 2. Effect of the presence of iron clusters on the melting points of composites.

Sample	[Fe], wt.%	T_f, °C	Sample	[Fe], wt.%	T_f, °C
PP (atact.)*	0	89.0	PP (atact.)	30	155.0
PP (atact.)	3	123.0	PP* (isotact.)	0	158.0
PP (atact.)	5	145.0	PP (isotact.)	5	166.0

*Sample heated and treated in the same way as in the preparation of "cluspols" except for the addition of the MOC.

Direct experimental measurements of the thermal stability of the polymers (Fig.6) show that the addition of small amounts of metal raises T_{dec} by 50–80 K. More interesting results were obtained with atactic polypropylene (PP), which is a waxy substance with a softening temperature of ~90 °C. The addition of even very small amounts of iron to this material causes a sharp rise in the melting point, which can be made to approach the melting point of isotactic polypropylene (Table 2).

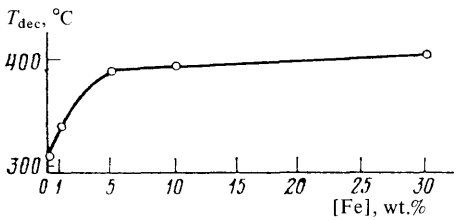


Figure 6. Effect of the addition of iron clusters on the thermal stability T_{dec} of polyethylene.

Since thermal stability is often related to molecular mobility, we should examine the dynamics of the polymer chains. The temperature dependence of the spin–lattice relaxation time (T_1) of the protons has been studied in a sample of LPPE (low-pressure polyethylene) containing ~30 wt.% of iron (particle size ~20 Å). Temperature plots of the spin–lattice relaxation times in the initial PE and in LPPE + 30% Fe are shown in Fig.7. This behaviour of T_1 reflects an average of the molecular mobility characteristics of the two phases (crystalline, and amorphous). The minima at 260 and 280 K for PE and PE + 30% Fe respectively can obviously be ascribed to the segmental motion of the polymer chains, whose thermodynamic characteristics tend to describe the thermal stability of the PE. In the temperature region of the minima in T_1 the correlation frequency (ν_c) of the molecular motion is equal to the spin precession frequency ν_0 (~40 MHz). The depth of the relaxation minimum in this case is a measure of the amplitude of the segmental motion of the polymer chain elements as well as of the change in the relative amount of the phases with different molecular mobility.

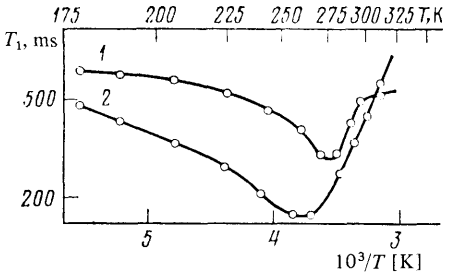


Figure 7. Temperature dependence of the spin–lattice relaxation time in the initial polyethylene and in polyethylene containing 30 wt.% of iron: *1*) initial LPPE, *2*) LPPE + 30%.

Thus the shift of the relaxation minimum in the high-temperature region of PE + 30% Fe, and the increase in T_1, denote the same effect: a strongly hindered segmental motion (as compared with the initial PE), and a correspondingly lower displacement amplitude. Since the amorphous phase has a higher molecular mobility, the motion of the polymer chains is suppressed in this phase at first, and the thermodynamic characteristics change towards those of the crystalline phase. However, conversion of the amorphous phase into a crystalline phase by the addition of finely divided iron seems unlikely. More probably, the very small iron particles are deposited initially in the amorphous, looser regions of the PE sample, where they suppress the molecular motions both by decreasing the free volume and (possibly) by forming chemical bonds with the matrix. This process, which increases the thermal stability, should be accompanied by changes in all the spectral characteristics, including the spin–lattice relaxation time, the specific heat, and the mechanical properties at ordinary temperatures.

Very surprising results were obtained by comparing the melt-flow indices of polyethylene and polyethylene with 20% of iron: the average flow decreased from 6.12 g to 0.049 g, i.e. more than 100-fold.

3. Some Physicochemical Properties of Materials of the "Cluspol" Type

The polymer matrices (polyethylene and Teflon) are relatively inert towards corrosive media. The interaction of powdered "cluspol" materials with hydrochloric and with hydrofluoric acid (diluted with water in a ratio of 1:1) and with bromine at 50 °C for 5 h has been studied[6]. No significant breakdown of the material was noted, but the colour of the powder changed from black to dark grey, and a small amount of metal was transferred to the solution. Thus, at

an iron concentration of 7.39 wt.%, 14% of the iron originally present was extracted into the solution.

The low-angle X-ray diffraction curves for these samples (Fig.8) show that acid treatment of the HPPE + Fe material tends to wash out the clusters with $d \geq 60$ Å. In the NMR spectra of the treated smaples a narrow component appeared with the broad component, though it had been previously established that this NMR component does not occur in polyethylene containing more than 3 wt.% of iron. These results suggest that the localisation sites of the larger ($d > 60$ Å) clusters are in the outer, mainly amorphous regions of the polymer particles. The remaining clusters (15–20 Å in diameter) are formed in the holes of the structure and are strongly held there. In polyethylene the localisation sites of the 15–20 Å clusters are probably crystal defects (in the crystalline regions) and holes (in the amorphous phase).

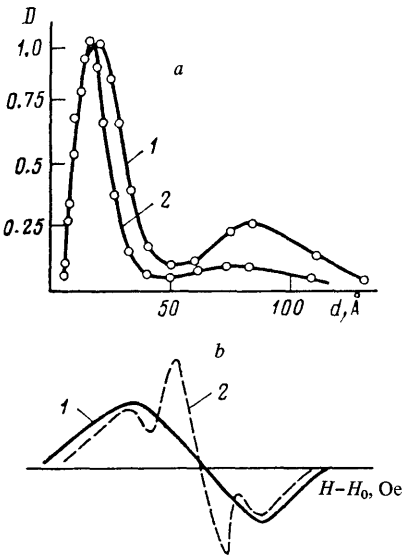


Figure 8. Changes in particle size distribution from low-angle X-ray diffraction results (*a*) and from the shift in the NMR spectra (*b*) produced by acid treatment of "cluspol" samples: *1*) initial sample, *2*) sample treated with HCl.

Thus we have developed a method of preparing "cluspol" materials containing metallic clusters with a narrow size distribution in polymeric matrices of the polyethylene and Teflon type. We have shown that the method is applicable to a wide range of metals and to different matrices. From a combination of physicochemical and structural studies we conclude that the metal clusters are located in natural holes of the polymer matrix, where they interact strongly with the matrix. The properties of the material and its physicochemical characteristics (magnetic, electrical, etc.) do not point to the presence of a metallic phase. The strong cluster–polymer interaction produces quasi-crystalline properties in the polymer matrix. Thus the materials of the "cluspol" type can be treated as single-phased metal–polymers in certain ranges of metal concentration.

Studies of the properties of these materials have only recently started: two types of characteristic (electrophysical, and magnetic properties) have been examined.

4. Electrophysical Properties of "Cluspol" Materials

The polymer matrices used for the preparation of "cluspol" materials are typical dielectrics. The addition of metallic particles to dielectrics in order to obtain electrically conducting polymer composites has long been a standard procedure in industry (in particular, electronics and radio), to give electrically conducting coatings, adhesives, etc.[58,59] The metal content of these composites is usually several tens of per cent by weight, and the particle size of the metal varies from a fraction of a micrometer to tens of micrometers.

Table 3. Electrical resistivity of "cluspol" composites.

No.	Sample	[Fe], wt.%	*R*, Ohm m
1	Teflon-40	20	10^{13}—10^{14}
2	Teflon-40	30	14
3	HPPE	20	$2.4 \cdot 10^2$

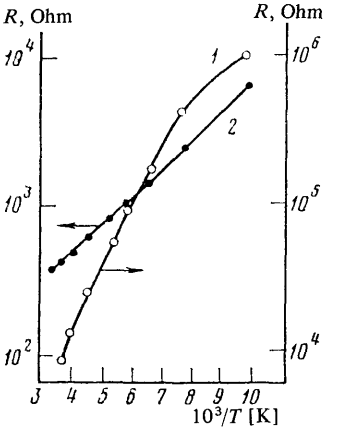


Figure 9. Resistance of "cluspol" samples against reciprocal temperature: *1*) PTFE + 30 Fe, *2*) HPPE + 20% Fe.

In "cluspol" materials the metallic clusters are accommodated in natural holes of the polymer matrix, at average distances from each other of 90–220 Å (depending on the metal concentration). This configuration of the clusters excludes the possibility of direct contact between metal particles and the formation of electrically conducting channels. Our electrophysical measurements on samples of "cluspol" materials (see Table 3) show that the addition of iron clusters to the polymer matrix can lower its electrical resistivity from 10^{15}–10^{16} Ohm m (a typical value for polymers such as HPPE and PTFE) to as little as 14 Ohm m (a typical semiconductor value).

These results also show that the resistance is very sensitive to the sample preparation conditions. For example, sample No.2 was prepared by pressing the powder into a cylinder at 120 atm and 280 °C, and used to study the variation of resistance with reciprocal temperature. We note from the results (Fig.9) that the electrical conductance increases with temperature in the experimental temperature range. The

plot is very similar to comparable plots for typical semiconductors.

Thus the electrophysical properties of polymers can be controlled between wide limits by introducing metallic clusters into natural holes of the polymer. However, more detailed and comprehensive studies of these effects are needed.

5. Magnetic Properties of "Cluspol" Materials

The static magnetic properties were measured for concentrations between 0.1 and 30 wt.% of iron at temperatures between 1.6 and 300 K with fields of up to 10 kOe (Fig.10). A characteristic temperature (T_m) corresponding to a maximum in the plot of magnetisation against temperature was observed in all samples cooled from 300 K to 4.2 K in the absence of a magnetic field. This maximum disappears if the sample is cooled in a field[60,61].

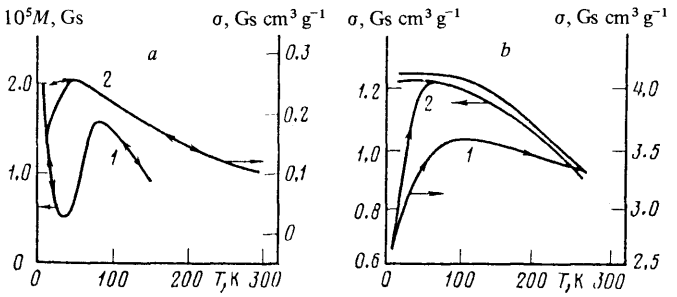


Figure 10. Temperature dependence of the magnetisation of samples containing different amounts of metal: (*a*) *1*) PTFE + 1% Fe, H = 10.2 kOe; *2*) PTFE + 5% Fe, H = 10.2 kOe; (*b*) *1*) PTFE + 30% Fe, H = 1.9 kOe, *2*) HPPE + 30% Fe, H = 1.3 kOe.

The magnetic properties are determined by the ensemble of superparamagnetic particles of the given metal, whose crystal structure differs from that of the massive metal. For the PE + Fe samples we have shown[56] that the change in structure is caused by the influence of the polymeric macromolecules; analogous effects are reported in Ref.62. The change in crystal structure of the particles produces sharp changes in magnetic properties. In iron and cobalt the effective anisotropy constant of the crystal field is increased[61]. Below the temperature T_m, determined by the locking temperature T_{lock}, the magnetic moments of the iron and cobalt particles are "frozen" in the anisotropic crystal field. The presence of T_{lock} makes the magnetic properties of the sample a function of the cooling conditions (as in the case of the spin glasses). In the PE + Cr samples the magnetic moments of the particles remain unfrozen down to 1.6 K (possibly because of their very small size). The iron metal–polymers contain, in addition to particles with $d \geqslant 100$ Å, much smaller particles which remain supermagnetic down to 1.6 K.

Thus our results show that the exchange and other collective interactions between particles of metallic clusters are retained in "cluspol" materials.

IV. POSSIBLE APPLICATIONS OF "CLUSPOL" MATERIALS

At the present stage of development insufficient data are available for the fields of application of the new material to be identified. It appears likely, however, that these materials will be exploited as thermally stable materials, as magnetic materials with properties similar to those of amorphous magnets and spin glasses, and as a new class of semiconducting polymers offering a wide range of parameters.

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