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Metallopolymers

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The formation of highly disperse metal particles in a polymer medium is accompanied by the chemisorption interaction of their freshly formed surfaces with the polymer macromolecules. Such systems have several advantages over ordinary filled polymers, and have been termed "metallopolymers". Several methods of obtaining such systems—electrolytic, electroflotation, thermal, and mechanochemical—are surveyed. The nature and the mechanism of interaction between the surfaces of various metals and organic (also organosilicon) polymers are described in detail. The physicochemical properties of metallopolymers and possible fields of their application are discussed. A list of 175 references is included.

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I. INTRODUCTION

The development of new technology presents the chemistry of macromolecular compounds with the task of producing polymeric materials possessing several specific new properties. It has become necessary to combine the advantages inherent in polymers (low specific gravity, high elasticity and durability) with the electrical conductivity and magnetic, antifriction, catalytic, and other properties typical of metals and inorganic compounds.

Such polymeric materials can in principle be obtained in two ways: new polymers can be synthesised with several of the specified properties; and filled polymers, combining the valuable properties of their components, can be produced. Both lines of scientific research are being vigorously pursued at the present time [1-4], but polymeric materials containing various kinds of filler have already found wide practical application. The filling of polymers not only enables materials to be obtained with novel properties but also permits their physical, mechanical, and physicochemical characteristics to be varied in a controlled manner, with enhancement of the appearance and reduction in the price of goods made of plastics.

Several reviews [5-7] and monographs [8-10] have been published on the production, structure, and properties of polymeric materials containing various mineral fillers. Considerably fewer publications have appeared on the preparation and properties of polymers filled with metals of different kinds and degrees of dispersion [11]. Polymers filled with metals possess several quite specific properties (electrical, magnetic, catalytic) in addition to the above advantages inherent in polymers containing mineral fillers [12-14]. Furthermore, these two groups of filled polymers differ in the nature and the mechanism of the interaction at the solid–polymer interface [15,16].

Coarse powders, mixed mechanically with the polymer, are generally used as fillers, the particles of which form aggregates distributed non-uniformly through the polymer. During recent years systematic investigations have been made on new methods for obtaining metal-filled polymers and on the properties of the systems [17-20]. These methods consist essentially in forming highly disperse metal particles within the polymer, instead of introducing them ready made. The metal particles, having active centres on their surfaces at the instant of formation, enter into chemisorption interaction with macromolecules of the polymer within which they are formed. This leads to the production of two-phase systems having the most uniform distribution of highly disperse metal particles in the bulk of the polymer and in a stable state of aggregation. Such systems have been termed "metallopolymers". [18] Investigation of the physicochemical and mechanical properties of these systems has revealed considerable differences between metallopolymers and ordinary polymers filled with metals [21], these differences being due to the methods of preparation. The experimental results which have accumulated enable certain generalisations to be made concerning the methods of preparation, the mechanism of formation, and the properties of metallopolymers.

II. METHODS FOR THE PREPARATION OF METALLOPOLYMERS

Metallopolymers can be obtained by various methods provided that a fundamental condition is observed: highly disperse metal particles should be formed in the presence of polymers, with the appearance of chemisorption bonding between the macromolecules and the surface of the metal particles. At the present time the following methods—electrolytic, electroflotation, thermal, and mechanochemical—have been developed for the production of metallopolymers.

1. Electrolytic Method

Cathodic deposits obtained in the presence of suitable surface-active agents can be dispersed in hydrocarbon media to form stable concentrated sols.

The stability of such metal organosols is governed mainly by the degree of solvation of the metal particles by the surface-active agents. The latter compounds usually interact with the surface of colloidal metal particles, with the formation of chemically bound adsorbed films which are strongly solvated by the dispersion medium. The interaction between surface-active agents and metal particles should be limited to the formation of surface compounds firmly bound with the main mass of the metal particles. If chemical compounds of exactly stoichiometric composition are formed on the surface, and are soluble in the organic medium, the adsorbed films are unstable.

The stabilising films must be formed on the surface of the colloidal metal particles at the instant at which the latter are produced. Otherwise, the particles have time to coagulate, with the formation of coarse aggregates, which are not peptised on the subsequent addition of surface-active agents.

The above mechanism of formation of metal organosols operates also when the surface-active agents used are compounds of high molecular weight, whose macromolecules contain polar functional groups.

Examination of the structural–mechanical properties of polymer solutions showed[24] that even small additions of an active filler constitute centres for the formation of a continuous three-dimensional network, which arises from the adsorption and orientation of polymer molecules under the influence of the force field due to the filler particles. The ability of macromolecular compounds to form structures in solution and the cross-linking of a polymer on the introduction of a metal sol, together with the stability of these structures and their tendency to re-form after destruction, are the deciding factors responsible for the stability of a metal organosol.

The nature of the interaction between metal particles and macromolecules is also of substantial importance in determining the stability of the structural network of polymers in solution. Structure formation is most effective in the case of the irreversible adsorption of a polymer due to chemical interaction between the surface of the metal particle and the macromolecules.

An electrolytic method for obtaining metallopolymers in a double-layer bath with a rotating cathode[17] developed from the above investigations of the stability of concentrated metal organosols and ideas on the structural–mechanical properties of polymer solutions in the presence of fillers.

The essence of the electrolytic method is that, when aqueous solutions of appropriate salts (the lower layer of the bath) are electrolysed, metal particles deposited on a disc cathode rotating horizontally are transported to the upper, organic layer of the bath containing the polymer solution. This involves interaction between the metal particles and the polymer macromolecules. Polymer adsorbed on the cathode surface partly shields the latter, and electrolysis occurs only at active centres free from adsorbed molecules. Two processes—passivation and metal electrodeposition—take place. Passivation of the cathode increases its polarisation, which is a measure of the energy requirement for growth of the metal crystals and the formation of new centres of crystallisation[25,26]. Low cathodic polarisations correspond mainly to the activation energy for the transfer of metal ions from solution into the crystal lattice of the metal, i.e. crystal growth of the metal. Very often this energy is insufficient for the formation of new crystal nuclei, so that at low cathodic polarisations metals separate predominantly as coarsely crystalline deposits.

Adsorption of a polymer on the original cathode surface and also on the small metal crystals that are formed, together with the associated increase in cathodic polarisation, favours the formation of highly disperse metal particles, which become lyophilic with respect to the organic dispersion medium.

Rapid transfer of the metal particles creates favourable conditions for interaction between the polymer and the active centres arising on the freshly formed metal surfaces. The nature of the macromolecules has a substantial effect on the transfer of highly disperse metal particles to the upper layer of the bath. Thus with natural rubber of polyisobutylene highly disperse metal particles do not pass into the organic layer, but are concentrated at the interface between upper and lower layers; transfer to the organic layer becomes possible only as a result of inversion of the selective wetting by the addition of small amounts of simple surface-active agents, e.g. oleic acid[19].

If polymers having polar functional groups are present in the organic layer during electrolysis, the metal particles formed pass into the organic layer even in the absence of simple surface-active agents. The polar macromolecules are adsorbed irreversibly on the surface of the metal particles with formation of the corresponding surface chemical compounds[17]. Stable concentrated sols of metallopolymers can be obtained in this way. With a small content of highly disperse metal particles in the organosol, removal of the solvent yields solid or rubber-like products; with high (above 50%†) metal concentrations powders are obtained which can easily be processed.

A series of investigations[27–30] has been made on the effect of various factors—cathodic current density, temperature, electrolyte and polymer concentrations, nature of electrolyte and of polymer, pH of medium—on the current efficiency and the degree of dispersion of the metal particles formed at the cathode. All these relations are extremal in character. Optimum conditions for obtaining metallopolymers by the electrolytic method can be found experimentally for each metal–polymer system. The nature of the polymer has a decisive effect not only on the dispersion and yield of metal but also on its particle shape. Particles formed at the cathode usually have a strongly developed surface owing to their production as dendrites and other complicated forms with strong dimensional anisotropy[29–32].

2. Electroflotation Method

During electrolysis a solution of a surface-active agent of low or high molecular weight in an organic solvent is fed continuously through the pores of a stationary cylindrical cathode in a vertical position, and is sorbed at the electrolyte surface. The metal particles deposited on the strongly passivated cathode surface adsorb the surface-active substances from the organic medium, so that their surface becomes hydrophobic. The sorption of polymer molecules on the fresh particle surfaces favours their detachment from the cathode surface and flotation into the upper layer of the bath[33,34]. Flotation is promoted by a stream of nitrogen along the walls of the cathode during electrolysis. At the same time the nitrogen protects the highly disperse metal particles from oxidation.

The electroflotation method is more suitable than the electrolytic method for industrial use. On an industrial scale the latter method of obtaining metallopolymers in a two-layer bath with a rotating cathode encounters certain difficulties, caused by the need to design electrolytic cells with a rotating shaft and cathode, as well as current leads with a special device to prevent sparking. Moreover, the continuous production of metallopolymers is impossible in this case. The electroflotation method is free from these defects, and permits easy control of the degree of dispersion and the morphology of the metal particles formed at the cathode.

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†Percentages by weight are indicated here and subsequently.

3. Thermal Method

Several organic and inorganic compounds of metals, when heated in a reducing atmosphere or in a vacuum to a certain temperature, decompose with the separation of finely divided metal particles [35,36]. Decomposition of such compounds in an organic medium (oils, high-boiling solvents) may yield concentrated, highly disperse metal organosols [17,37].

Among compounds which decompose readily at comparatively low temperatures are certain salts of formic acid: when heated, they break down with the formation of disperse particles of the corresponding metal and volatile products (carbon dioxide, carbon monoxide, hydrogen) [36]. Silver, copper, nickel, cobalt, iron, and lead formates decompose in this way at temperatures not exceeding 250°C. [38,39] Differential thermal analysis has shown [40] that iron, nickel, and cobalt formates lose uncombined water at 102–103° and water of crystallisation at 115–137°C. The intense endothermic processes at 216°, 192°, and 203°C on the thermograms of these salts have been related to the corresponding decomposition points and the formation of finely divided particles of the metals. Chemical analysis of the metal powders showed them to contain on the average ~96.3% of the pure metal. Silver formate decomposes vigorously even at 64–67°C, [41] whereas copper formate begins to break down at 186°C. [42]

Freidlina and Bulanova established [36] that lead formate decomposes above 200°C with the separation of gaseous products, volatile liquids, metallic lead, and lead oxide. The thermograms show an intense double endothermic process at 240–260°C, ascribed to decomposition of the salt to metallic lead [43,44].

The conditions and the kinetics of the decomposition of metal oxalates, which also break down to yield the pure metals [45,46], have been considerably less investigated.

Among inorganic metal salts which decompose at relatively low temperatures with formation of a metal phase we mention the iron hexacyanoferrates. Mittasch [47,48] and Eisenhut [49], while examining the possibility of using decomposition products from iron ferrocyanides as catalysts for the synthesis of ammonia, showed that particles of α-iron are formed in a mixture of nitrogen and hydrogen above 300°C. Differential thermal analysis has established that all the following iron hexacyanoferrates—$Fe_2[Fe(CN)_6]$, $Fe_4[Fe(CN)_6]_3$, $Fe_3^{II}Fe_2^{III}[Fe(CN)_6]_3$, $Fe_3[Fe(CN)_6]_2$, $Fe[Fe(CN)_6]$, and $Fe_3^{II}Fe_4^{III}[Fe(CN)_6]_6$—decompose between 180° and 240°C. [50] Chemical analysis showed that the solid decomposition products of these salts contained 30–80% of highly disperse metallic iron with some iron carbide, the bulk of the metal being deposited during the first hour of reaction.

Thermoplastic polymers have been successfully used as the organic medium in the decomposition of such salts. The presence of the highly developed free surface of the metal particles at the instant of their formation in a polymer medium favours interaction of the surface metal atoms with functional groups and multiple bonds of the polymer, as well as with radicals formed by the partial thermal degradation of the macromolecules.

On this basis a thermal method was developed for obtaining metallopolymers [51,52], which consisted essentially in introducing easily decomposable metal salts into concentrated solutions of the polymers in a highly disperse state and precipitating the polymers with vigorous stirring. The washed and dried polymer containing particles of the salt was placed in a special apparatus [52], where it was kept in a vacuum at the optimum temperature for decomposition of the salt and formation of the metallopolymer. The time required for complete decomposition of metal salts in polymeric media is considerably longer than for the pure salts, owing to the poor thermal conductivity of polymers.

In contrast to ordinary mechanical mixtures of finely divided metals with polymers, metallopolymers obtained by the thermal method have a high degree of dispersion (1–5 μm) and a uniform distribution of metal particles in the bulk of the polymer, together with considerable irreversible adsorption of macromolecules on the surface of the metal particles at the instant of their formation. The quantity of irreversibly bound polymer is proportional to the metal content of the polymer and the duration of heating, and depends on the nature both of the polymer and of the metal [53]. The above differences between metallopolymers and ordinary mixtures have a favourable effect on the physicochemical, mechanical, and other properties characteristic of metal-filled polymeric systems [21,44,54–59].

The thermal method of obtaining metallopolymers is of especial interest in cases in which electrolytic methods are unsuitable owing to the sparing solubility of the polymer or the difficulty of depositing a highly disperse metal on the cathode. Another advantage of the thermal method is that solvent does not have to be removed before the metallopolymer is processed into articles.

4. Mechanochemical Method

The properties of polymers filled with coarsely divided metals are largely determined by the nature of the metal surface and the adhesive forces between the polymers and various metals [60]. The affinity of metal particles for a polymer can be increased by preliminary modification of their surface with substances of low molecular weight having a similar nature to the polymer [17,61,62], monomers capable of polymerisation on the solid surface [63–65], or directly by molecules of the polymer itself by means of mechanical, radiation, or other treatment of the coarse metal–polymer system [66]. Such treatment—in particular mechanical ones—produce cleavage of the polymer molecules with the appearance of free macroradicals, which may interact with the metal surface to form stable metal–polymer chemisorption bonds.

A mechanochemical method for obtaining metallopolymers has been based on these concepts. There are several varieties of this method—(*a*) the polymerisation of monomers on the freshly formed surface of the metal particles, initiated by active centres in this surface produced by the dispersion of metals in the monomers [65]; (*b*) the polymerisation of monomers on the surface of metal particles previously dispersed in a high vacuum (in an inert atmosphere or in the presence of substances which protect the metal surface from intense oxidation) [63,67]; (*c*) preliminary dispersion of metals in surface-active agents of low molecular weight, followed by the introduction of polymers containing active functional groups or multiple bonds, which promote chemisorption of the polymer on the surface of the metal particles [62,68]; (*d*) mechanical dispersion of metals in polymers [69,70]; and (*e*) simultaneous vaporisation of metal and monomer (polymer) in a vacuum, leading to the formation of highly disperse metal particles with macromolecules of the polymer chemisorbed on their surface [71,72].

Kargin, Plate, and their coworkers [73,74] investigated the processes of polymerisation occurring when metals, salts,

and oxides were subjected to vibrational milling in vinyl monomers. As a consequence of the exposure of energetically active faces the surface formed by grinding possesses considerable reactivity, which is apparent in a sharp increase in the adsorptive and chemisorption power. If monomers are present at the instant of formation of such a surface, the active centres in it of ionic or radical type interact with the monomer molecules to form a growing macroradical.

These workers investigated the polymerisation of styrene, methyl methacrylate, α-methylstyrene, acrylonitrile, and vinyl acetate on the surfaces of iron, nickel, chromium, and titanium during grinding, and proved by direct methods the formation of polymers grafted chemically to dispersed substances. The degree of conversion of the monomers increased with the duration of milling, the yield of polymer being small initially, after which it increased sharply. The degree of conversion at a constant time of dispersion depended on the proportions of the components: the highest yield of polymer was reached with small quantities of the monomer, this being associated with the better conditions for grinding.

The relatively coarse grinding of small quantities of iron with a phenol–formaldehyde resin [13,66,75] gave materials in which hardening of the resin was accelerated and its thermomechanical characteristics were improved. This can be explained by chemisorption interaction between active groups of the polymer [76] (phenolic hydroxyls, oxydimethylene groups) and the disperse metal particles.

With polyethylene and polystyrene [66] no appreciable change in properties was observed even on the introduction of considerable quantities of disperse iron. Only when concentrated solutions of these polymers were ground mechanically with the metal powder did interaction occur between the resulting macroradicals and active centres in the metal, as a consequence of mechanical degradation of the polymer macromolecules and "renewal" of the surfaces of the metal particles. The thermomechanical and mechanical characteristics of these systems varied not only with the conditions of mechanochemical treatment but also with the particulate form of the iron [77]: powders containing dendritic particles were more effective as fillers for polymers.

An optimum time of grinding was established [66] for the metal–polymer composition, since prolonged mechanical action on the system produces considerable degradation of the polymer.

Although the above papers give no direct proof of the occurrence of chemisorption interaction between polymers and metal particles when ground together, the effective improvement in several physicomechanical characteristics of these systems can be explained by the formation of surface compounds between polymers and metal, i.e. by the formation of metallopolymers.

Processes occurring at an interface between a metal and a polymer in dynamic contact have been surveyed [78]. The presence of the polymer was shown to promote finer subdivision of the metal (e.g. iron) in a ball mill. The explanation is that the polymeric molecules are activated chemically during loading, and interact with the exposed crystalline surfaces of the metal particles, diminishing their free energy, which leads to intense dispersion of the metal. Surface-active substances of high molecular weight, e.g. poly(methyl methacrylate), were considerably more effective than simple compounds, e.g. oleic acid.

The dispersion of metal powders in the presence of surface-active agents of amine type creates favourable conditions for the formation of chemically fixed adsorbed layers, consisting mainly of compounds of the type M–NH_2 or M–NH–M. [68] This makes interaction between metal particles and polymer macromolecules substantially easier, and promotes a uniform distribution of the particles in the polymer.

The introduction of highly disperse metal powders into polar rubbers (SKN-26, Nairit chloroprene rubber) improves their stability and also accelerates vulcanisation, as a consequence of interaction between the surface of the metal particles [79–81] and the polymer molecules at the instant of opening of the double bonds.

The above applications of the mechanochemical method of obtaining metallopolymers require only simple equipment, and will undoubtedly find wide use in industry in the very near future.

III. MECHANISM OF INTERACTION BETWEEN POLYMERS AND COLLOIDAL METAL PARTICLES DURING FORMATION

Several factors—nature of polymer and metal, chemical state of metal surface, conditions of contact between polymer and metal—govern the character of the interaction between polymer macromolecules and the surface of the metal particles. The present Section discusses various mechanisms of interaction at the interface between metal particles obtained by the above methods and the macromolecules of various polymers, leading to the formation of metallopolymers. In this connection it is necessary to consider also the changes occurring in the mechanism and the kinetics of polymerisation and polycondensation in the presence of highly disperse metals.

1. Metallopolymers based on Macromolecular Organic Compounds

Investigations of chemisorption interaction in the formation of metallopolymers have been made mainly on systems containing polymers having functional groups which are reactive towards metals and their oxides.

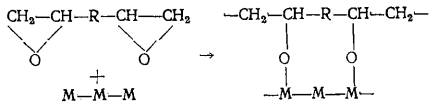
Epoxide–dian resins‡

During investigation of electrolysis in the presence of various polymers it was noted that the epoxide resin ED-5, in contrast to polymers not containing functional groups (polyisoprene, natural rubber), promotes migration of metal particles from the cathode into the organic layer with formation of a stable concentrated metal organosol [18,29,82]. In this case the metal particles are easily made lyophilic with respect to the organic dispersion medium.

Infrared-spectroscopic examination of the products of interaction of ED-5 resin with the metal (iron, lead, etc.) particles at the instant of their formation at the cathode showed a considerable diminution in intensity of the 915 cm^{-1} absorption band corresponding to bending vibrations of epoxy-groups [18], with an inverse relation between the concentration of metal in the polymer and the intensity of this band [18,27,83]. This undoubtedly proves that, at the instant of formation, the highly disperse metal particles

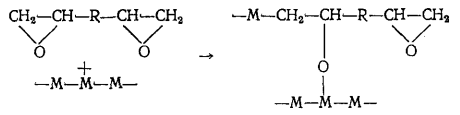
‡Dian = 1,3-diphenylpropane-*pp'*-diol (Ed. of Translation).

react chemically with macromolecules of the epoxide–dian resins. This evidently involves opening of the epoxy-rings:



Such a mechanism should yield three-dimensional structures, in which the highly disperse metal particles act as junction points. In fact ED-5 resin containing 12% of electrolytic lead but without the introduction of any hardening agent was completely hardened at 210°C in 90 min [83]; the pure resin had not hardened at this temperature after 10 h had elapsed.

Investigation of the mechanism of formation of metallopolymers from an epoxide resin and highly disperse palladium obtained by the electrolytic method yielded similar results [84,85]. Palladium metallopolymers exhibited new infrared absorption bands in the region of 440 and 420 cm^{-1}, whose intensity increased with the metal content of the polymer [86]. The appearance of these bands is obviously due to the formation of chemisorption bonds, not only of the C–O–M but also of the C–M type, during hardening [87]:



Differential thermal analysis shows that considerable thermal effects accompany the interaction of epoxide resins with highly disperse metals: they occur in the region of 190°C in the case of copper [42,88], 280–300°C with lead [89], at 293°, 322°, and 380°C with palladium [86], at 196–223°C with iron and cobalt [53], and at 186–198°C with nickel [53]. The intensity of these effects generally increases with increased metal content of the metallopolymer, while they move to lower temperatures on the differential thermal analysis curve.

The appearance of free radicals has been recorded [42,86,88] even at 200–210°C in the metallopolymers on the introduction of highly disperse copper, palladium, or lead into ED-5 epoxide resin, the majority of them being formed during the first 30–60 min of heating. The intensity of the electron spin resonance signal increased with rise in temperature, while the band width remained constant at 10.6–10.9 G. The appearance of this band can be attributed to the generation of macroradicals of the epoxide–dian resin accompanying formation of the metallopolymers. It is noteworthy that heating the pure resin to 260°C does not result in the appearance of radicals.

The radicals produced in metallopolymers based on an epoxide resin are extremely stable (their lifetime at room temperature is of the order of several months), which is obviously due to the formation of a rigid three-dimensional polymer structure. The lower temperature at which macroradicals appear in metallopolymers, in comparison with the pure resin, indicates not only polymerlike transitions in the polymer chains but also acceleration by the highly disperse metals of the thermal degradation of the polymers.

Kinetic investigation of the hardening of an epoxide resin by various highly disperse metals leads to the conclusion that the quantity of bound resin depends not only on the concentration of the metal and the time of heating at a given temperature but also on the nature of the metal (Table 1). Such substantial differences in the quantity of resin bound by different metals at a given hardening temperature and metal concentration in the resin are obviously associated with the electronic structure of the metal atoms. According to Trapnell [90] chemisorption on metals involves the formation of surface compounds with *d*-electrons of the metal atoms. Table 1 [27,29,42,82–89] shows that, during the chemisorption of the epoxide resin, the activity of the metals diminishes as the *d*-shells of the metal atoms become filled.

Table 1.

Metal	Metal in metallopolymer, wt.%	Hardening temp., °C	Bound resin, wt.%, after 2 h	6 h	12 h
Iron[a]	10	230	98.27	98.84	99.40
	20		98.32	93.03	99.48
	30		98.30	99.08	99.49
Nickel	10	230	75.80	96.39	98.30
	20		94.00	97.40	98.60
	30		94.40	97.88	98.88
Palladium	11	225	8.8[b]	74[e]	
	21.9		27.5[c]	92.7[b]	
	26		79.3	94.0	
Lead	12	240	92.0[d]		
Cadmium	10	220	21.0		
Copper	10	240	57.0		
	10	210	30.5		
	20				
	30		60.12		

[a]Identical results obtained for cobalt.
[b–e]Heated for 1, $1\frac{1}{2}$, $2\frac{1}{2}$, and 4 h respectively.

Cadmium and palladium possess comparatively low chemisorption activity, although the latter is a metal of variable valency. The high activity of lead in comparison with the other metals cited here is obviously due to its tendency to form covalent compounds, for the surface compounds formed by an epoxide resin with metals are of this type [16].

The suggested mechanism of the formation of metallopolymers is supported by a comparative study of the conditions under which the pure epoxide–dian resin and metallopolymers formed from it are hardened when exposed to γ-rays [91,92]. Whereas in the radiation hardening of the pure resin a decrease in the concentration of epoxy-rings is accompanied by an increase in the concentration of carboxyl and hydroxyl groups, the carboxyl content remains constant during irradiation of the lead metallopolymers, while the concentration of hydroxyl and epoxide groups decreases sharply. This is obviously due to the accelerating action of γ-rays on the chemisorption of the resin on the surface of the highly disperse metal particles.

X-Ray examination of the γ-irradiated pure resin and metallopolymers based on it indicates that increase in the duration of exposure produces increased ordering of the epoxide–dian resin molecules with the appearance of a quasi-crystalline structure [93]. The introduction of highly disperse copper into the resin promotes a considerable increase in the ordering of the macromolecules after irradiation, but this is not observed in the presence of lead.

Poly(vinyl acetate)

Several studies have been made [31,94–97] of the formation of metallopolymers of poly(vinyl acetate) $[CH_2.CH(OCOCH_3)]_n$ with highly disperse lead and palladium.

Investigation of the effect of the molecular weight of this polymer in the range 117 000–4000 showed that a decrease to ~ 13 000 was accompanied by an increase in the activity of the polymer during electrolysis. A decrease in molecular weight favours a diminution in the blocks of the mosaic of metal particles and also a decrease in size of the particles themselves. These phenomena are probably associated with the adsorption activity of poly(vinyl acetate) [98].

Study of the nature of the bond formed when a polymer is adsorbed on the surface of disperse metal particles indicates ion–dipole interaction between carbonyl groups of the poly(vinyl acetate) and the metal surface. Further evidence of this is the shift in the 1734 cm^{-1} infrared band to 1711–1706 cm^{-1} in the spectrum of the metallopolymer (at a palladium content of 5–10%).

Heating poly(vinyl acetate) metallopolymers produces marked cross-linking of the system [99,100], as a consequence of the detachment of acetate groups from the polymer and interaction of the resulting radicals with the metal surface to form an M–C chemisorption bond [86].

Increase in the concentration of metal, in particular palladium, in the polymer is accompanied by a considerable increase in the concentration of free radicals and a lowering of the temperature at which they are detected. The appearance of free radicals at extremely low temperatures (Table 2) [86] is evidence of chemisorption interaction of the highly disperse palladium particles with macromolecules of poly(vinyl acetate) in the formation of metallopolymers.

Table 2.

Pd in metallopolymer, %	Free radicals in metallopolymer, spins g^{-1}	Radicals detected at, °C
22.45	$4.75 \cdot 10^{17}$	180
47.25	$2.19 \cdot 10^{18}$	100
80.0	$3.40 \cdot 10^{18}$	30

Rubbers

The early publications showed [18–20,101,102] that polyisobutylene and natural rubber, possessing neither functional nor other active groups, do not interact directly with the surface of metal particles at the instant of their deposition on the cathode. A metal organosol is formed only in an oleic-acid solution of the polymer. In neither case did infrared spectroscopy detect a metal–rubber macromolecule chemisorption bond. However, investigation of the swelling and desorption of metallopolymers obtained in this way has established that irreversible adsorption of the polymer on the metal surface nevertheless takes place. In this case interaction between rubber macromolecules and the surface of the metal particles is evidently accomplished through an adsorbed layer of oleic-acid molecules [20].

Electrolysis in the presence of a carboxylate or other polar rubber produces direct chemisorption interaction between rubber macromolecules and particles of various metals [18,28,69]. The swelling and the desorption of such rubbers show this process to be irreversible, and infrared spectroscopy has established ion–dipole interaction between the metal and functional groups of the polymer. The band at 1720 cm^{-1} in the infrared spectra of the metallopolymer, corresponding to vibrations of the C=O group, shifts and diminishes in integral intensity with increase in the concentration of metal in the rubber and rise in temperature, which confirms a chemisorption mechanism of interaction between polar rubbers and metal particles. In this case the latter act as hardener, and promote the formation of a three-dimensional structure in the metallopolymer.

The hypothesis was put forward [74,103] that, when iron is ground in the presence of polyisoprene, the rubber macromolecules initially undergo rupture at the tertiary carbon atom as the weakest point in the chain, and the resulting macroradicals then interact with the metal surface. Investigation of the semiconductor properties of mechanical mixtures of polyisoprene with iron and of compositions where chemisorption interaction between polymer and metal takes place as a consequence of mechanochemical processes, and of the polymerisation of isoprene on freshly formed faces of particles of the metal, shows that chemisorption interaction between the components determines the type of conduction of the resulting systems.

Polystyrene

Metallopolymers have been prepared from polystyrene and highly disperse lead, copper [58], and silver [41] by the thermal method; bismuth and manganese [104] have been introduced by a mechanochemical method. The accompanying chemisorption interaction at the metal–polymer interface results in the formation of a stable three-dimensional structure in the polymer. Furthermore, heat-treatment of the polystyrene–metal system produces significant rises in the glass and flow points of the polymer even in the presence of small amounts of the metal. As in the case of an epoxide resin, the nature of the metal influences the bonding of the polymer and the change in its thermomechanical properties. Metallopolymers based on polystyrene and highly disperse metals are not formed by the electrolytic method, as in the case of non-polar rubbers.

The cathodic deposition of lead [43] and cadmium [104] in the presence of polystyrene and oleic acid in the upper layer of the bath is accompanied by interaction between polymer and metal particles only at the level of van der Waals forces, as was to be expected. The equilibrium swelling for such systems is independent of the content of highly disperse metal in the polymer, but the rate of swelling of filled specimens is even higher than that of pure polystyrene. The introduction of a highly disperse metal into polystyrene, in the absence of chemisorption interaction between them, obviously causes the formation of loose layers of polymer at its interface with the metal, which facilitates penetration of the solvent into the polymer and swelling of the latter [8].

Study of the polymerisation of styrene in the presence of highly disperse metals obtained by various methods is of interest in connection both with the mechanism of the formation of metallopolymers and with the polymerisation of monomers on a solid surface. The rate of polymerisation of styrene in the presence of highly disperse iron, chromium, bismuth, and manganese [106,107] increased, especially during the early stages, if the concentration of these metals did not exceed 1.5%. The yield of polymer also increased, but the variation in the molecular weight was extremal. The increases in the rate of polymerisation and in the yield of polymer are obviously explained by the catalytic action of highly disperse metals on the decomposition of a peroxide initiator of polymerisation. At the

same time, the high rate of formation of growing macroradicals leads to a decrease in the mean molecular weight of the polymer. This process was so intense that the softening point of the metallopolymer fell with increase in the concentration of metal in it [67].

The polymerisation of styrene in the presence of chloride salts is accelerated [108] by additions of colloidal palladium and gold. It is suggested [108] that the polymerisation of styrene, on the freshly generated surface of the colloidal metal particles, is initiated by the formation of π-complexes involving *d*-orbitals of metals with variable valency and vinyl groups of the monomer. It is supposed that the metal particles are not regenerated, but are bound similarly to fragments of an ordinary initiator: i.e. chemical grafting of the polymer on to the surface of the metal particles is assumed.

A Japanese study [109] of the polymerisation of styrene on combined catalysts of the activated metal–organic halide type confirms that polymerisation is most active with metals having a freshly formed surface.

Thus the introduction of highly disperse metals having an active surface into styrene undergoing polymerisation creates favourable conditions for chemisorption interaction between metal and polymer, which should have a significant effect on the physicochemical properties of the resulting polymers, despite the small amounts of metal introduced. The addition of 1.5% of manganese or bismuth to styrene undergoing polymerisation [55] raises the temperature at the start of thermo-oxidative degradation of the polymer from 280° to 337°C.

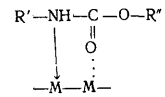
Nitrogen-containing Polymers (polyurethanes, polyamides)

The presence of tervalent nitrogen atoms of well defined π-donating character in a polymer chain should have a significant influence on the adsorption of these polymers on metal particles. In any case, hydrogen bonding may be expected between a hydrated or oxidised metal surface and amide groups in the polymer. However, Bills [110], in an investigation of the swelling of polyurethane–polyisobutylene filled with glass, salts, and also disperse aluminium and tin, did not observe any significant interaction between the polymer and the fillers. This was obviously due to the conditions of filling, which did not guarantee adequate and reliable contact between polymer macromolecules and the filler surface.

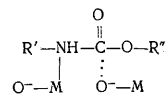
Examination of metallopolymers obtained from polyurethane rubbers and highly disperse cathodically deposited iron particles [111] support Trapnell's view [90] that coordinate interaction occurs at the interface between nitrogen-containing polymer and metal. The infrared spectra of these metallopolymers exhibit a shift to lower frequencies of the 1727 cm^{-1} band representing stretching vibrations of the C=O groups of polyurethane, the displacement being larger the higher the concentration of metal in the metallopolymer. Furthermore, the band in the region of 700 cm^{-1}, due to deformation vibrations of NH groups in the pure polymer, disappears, which may indicate that this bond is partly ionic in the metallopolymer.

Especially large differences in the spectra are observed in the range 600–400 cm^{-1}. Polyurethane exhibits several absorption bands, with maxima at 560, 518, and 495 cm^{-1}, these being due to deformation and out-of-plane vibrations of C–N bonds. The 560 cm^{-1} band is much weaker in the spectrum of the metallopolymer, and has shifted to the range 630–620 cm^{-1}. A new band appears in the region of 507 cm^{-1}, whose intensity increases with the metal content of the polymer; this band is due to stretching vibrations of the M–N bond.

Similar results have been obtained for metallopolymers based on capron [Soviet polyamide-6] and copper [112], iron, nickel, and cobalt [113,114]. These experimental results are consistent with the views of Rutzler [16] and Trapnell [90] on the nature of the adhesive bond between a nitrogen-containing polymer (nylon) and steel, according to which the interaction between metal and polymer involves the formation of surface coordination compounds—(1) with an unoxidised metal surface



or (2) with an oxidised metal surface



Chelate polymers

Chelate (coordination) polymers are similar to nitrogen-containing metallopolymers in the character of their interaction with metals.

Many chelate polymers containing conjugated bonds in their chain possess semiconductor properties [115]. The introduction of highly disperse metals, forming coordinate bonds with the polymer macromolecules, has a substantial effect on the type of conduction and the conductance parameters of these materials. Berlin et al. [115,116] worked out methods for obtaining, and investigated the electrophysical properties of, compositions consisting of disperse metals and chelate polymers. They used tetracyanoethylene as monomer [117], capable on polymerisation of interacting with metal surfaces to form polymeric chelate compounds.

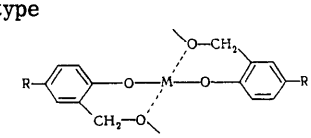
Information has been published also on the polymerisation of phthalocyanines [118], and the synthesis of polymeric Schiff bases and polyazaporphyrins [119] in the presence of powdered metals, accompanied by the formation of coordinate bonds between the surface of the metals and the polymeric molecules.

Since these polymers themselves possess several interesting semiconducting, electrical, and catalytic properties, the further addition of highly disperse metals should obviously intensify these properties in several cases or change their character.

Other organic polymers

The nature of the interaction between polyethylene glycol maleate phthalate, a polyester containing polar ester groups and unsaturated bonds, and the surface of cathodically deposited highly disperse iron has been investigated by infrared spectroscopy, which has established that double bonds are opened with the formation of a chemisorption C–Fe bond [120].

Interesting investigations have been made [121] on the mechanism of the interaction of metals with phenol–formaldehyde resins, which are able to form chelate bonds [76] of the type



with an oxide film on a metal.

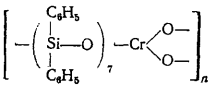
The possibility of forming chemisorption bonds with metals is not confined to polymers containing functional groups or unsaturated bonds. The thermo-oxidative degradation of polyethylene containing disperse iron is sharply accelerated at 240°C, with the formation of chemisorption compounds between macroradicals of the degraded polyethylene and iron.

2. Metallopolymers based on Organometallic Siloxane Polymers and Polyorganosiloxanes

Metallopolymers based on organoelementary siloxane polymers and polysiloxanes are of considerable interest because of the great thermal stability of the initial polymers, which can be still further improved by the introduction of highly disperse metals. Investigation of the mechanism of the formation of these metallopolymers is thus closely connected with problems of the thermal stability, thermal degradation, and stabilisation of the above polymers filled with highly disperse metals [124].

Polydiphenylsiloxanoxychromium

Polydiphenylsiloxanoxychromium has the cyclolinear structure



and possesses excellent thermal stability [125,126]. Metallopolymers have been obtained from it by a thermal method. The decomposition of lead formate in the polymer [127] at 240°C for 6 h yields a metallopolymer, whose structural forms differ considerably, according to differential thermal analysis data, from those described for the pure polymer [126].

Atkins et al. [128], who studied the thermal stabilisation of polydimethylsiloxane rubbers by metals, including lead, suggested that at high temperatures lead oxides rupture the chain of the siloxane polymer, and then react with the macroradicals thus produced, forming a new polymer containing lead in the main chain. Andrianov [129], in work on the stabilisation of cyclolinear polymethylphenylsiloxanes by metal oxides, showed that chrome yellow may cause rupture of silicon–carbon bonds and also the cleavage of rings in the polymer. Analogous changes obviously occur in the structure of polydiphenylsiloxanoxychromium on the formation of metallopolymers containing lead.

The infrared spectra of these metallopolymers reveal a direct dependence, on the concentration of lead in the polymer, of the decrease in integral intensity of absorption bands at 1050 and 1010 cm^{-1}, due to silicon–oxygen stretching vibrations in small rings, and a considerable strengthening of bands at 1090–1080 cm^{-1}, due to silicon–oxygen stretching vibrations in linear polymer chains [130]. Thus the spectroscopic results provide experimental evidence of ring-opening in polydiphenylsiloxanoxychromium under the influence of highly disperse lead. Furthermore, the infrared spectra of the metallopolymers contain a new band at 620 cm^{-1}, whose intensity increases with increased concentration of lead in the polymer. This band is obviously due to vibrations of the chemisorption SiO–Pb bond, formed by interaction between polymer radicals and the surface of the lead particles.

Both infrared spectroscopy and differential thermal analysis suggest that, when a mixture of polydiphenylsiloxanoxychromium and lead formate is heated at 240°C, polymer molecules are adsorbed on the freshly formed surface of the deposited lead particles, which catalyse ring-opening and obviously the detachment of phenyl radicals. The resulting macroradicals undergo chemisorption interaction with the surface of the lead particles, to form linear, branched, and perhaps cross-linked polymer macromolecules containing lead atoms as well as chromium.

Similar results have been obtained for metallopolymers based on polydiphenylsiloxanoxychromium and highly disperse iron formed by the thermal decomposition of iron ferrocyanide in the polymer [131].

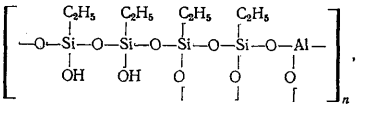
Investigations of the thermomechanical properties of these metallopolymers [132] have revealed no simple relation between softening temperature and concentration of metal in the polymer, such as occurs with linear organic polymers. At low metal concentrations (up to 4%) the softening point of the metallopolymers rises, as a consequence of the increased number of sorbed macromolecules on the solid surface. However, further increase in concentration (5–10%) is accompanied in all cases by a fall in the softening point. At higher metal concentrations the softening temperature either rises slightly or else remains unchanged.

The lowering of the softening point at metal concentrations of 4–10% is obviously due to intense decyclisation of the polymer under the catalytic influence of the highly disperse metals, with the formation of linear polymer molecules, which are more mobile than cyclolinear molecules. This process probably occurs to a considerable extent only when the metal concentration reaches 4%. It continues at concentrations above 10%, but is accompanied by intensified cross-linking of the polymer, so that only a slight rise in softening temperature of the metallopolymers is observed. This type of dependence of the softening temperature on the metal content in the polymer has been found with all metallopolymer systems based on cyclic and cyclolinear organometallic siloxane polymers [133].

Highly disperse metals are efficient catalysts of ring-opening in organometallic siloxane polymers. This is evident with polydiphenylsiloxanoxychromium in particular in the fact that the introduction of a small quantity of highly disperse metal (by the thermal decomposition of suitable salts in the polymer) makes the polymer capable of softening.

Polyethylsiloxanoxyaluminium and oligomeric αω-dihydroxypolydimethylsiloxane

Polymethylphenylsiloxane contains no active functional groups, and is therefore neutral in the electrochemical crystallisation of highly disperse iron [134]. Polyethylsiloxanoxyaluminium



which is a cyclolinear polymer, contains a sufficient number of hydroxy-groups [135] for metallopolymers to be obtained [30] by the electrolytic method. The electrochemical crystallisation of highly disperse cadmium in the presence of this polymer and the transport of metal to the

upper, organic layer of the bath are ensured by interaction between polymer hydroxyls and the surface of the cadmium particles deposited on the cathode.

Differential thermal analysis and infrared spectroscopy show that, when metallopolymers based on polyethylsiloxanoxyaluminium and cadmium are heated at 200°C, the radicals formed by the detachment of hydroxyls interact with highly disperse cadmium particles [30].

Investigation of the electrochemical crystallisation of highly disperse cadmium in the presence of $\alpha\omega$-dihydroxypolydimethylsiloxane—a reactive organosilicon oligomer—in the upper, organic layer of the bath [32] has shown that here also the metal particles interact with hydroxyls of the oligomer to form a chemisorption bond. This is accompanied by polycondensation of the oligomer under the catalytic influence of the metal particles formed at the cathode.

Polydiphenylsiloxane

Metallopolymers of the type described above have been obtained both from the ready made organometallic polymers and oligomers containing hydroxy-groups and by the polycondensation of hydroxylated organosilicon monomers (e.g. diphenylsilanediol) in the presence of highly disperse metals.

At temperatures above 200°C diphenylsilanediol undergoes condensation [136] with the liberation of water and benzene, owing to the occurrence of two reactions—(1) interaction of the monomer hydroxyls with elimination of water and formation of a siloxane bond, and (2) interaction between hydroxyls and phenyl radicals with elimination of benzene and formation of a siloxane bond.

In the polycondensation of diphenylsilanediol in the presence of highly disperse lead [137] and iron [50] obtained by thermal decomposition of lead formate and iron ferrocyanide in the monomer, reaction (1) predominates with increase in the content of these salts. This may be due to the action either of the liberated metals or of the salts themselves and their volatile decomposition products (formic acid, cyanogen), which are acidic in character.

Acids catalyse the condensation of this monomer with the formation of a cyclic trimer—hexaphenylcyclotrisiloxane—and the elimination of water.

The polycondensation of pure diphenylsilanediol at 240°C is a rapid process, complete within 15–20 min. This excludes any effect of the highly disperse metal on the process, since appreciable quantities of the metal are formed only on more prolonged heating. The kinetics of the condensation of the monomer and of the decomposition of the metal salts indicate that the salts catalyse condensation of the monomer with elimination of water and formation of the cyclic trimer. However, the infrared spectra of the final condensation products containing highly disperse lead or iron indicate the formation of linear products, the quantity of which increases with the concentration of metal in the polymer. This apparent contradiction between kinetic and spectroscopic results disappears if the cyclic trimers formed in the initial period of condensation open up under the influence of highly disperse metals in the second stage with the formation of linear macromolecules. The occurrence of two stages in the formation of metallopolymers from diphenylsilanediol is also confirmed indirectly by the dependence of the softening point of the metallopolymers on the concentration of metal, which is similar in character to that found with polydiphenylsiloxanoxychromium.

Since the salts and their volatile decomposition products affect the mechanism of the polycondensation of diphenylsilanediol, it was desirable to investigate its polycondensation in the presence of a highly disperse metal already introduced into it by the electrolytic method. The infrared spectra of diphenylsilanediol containing electrodeposited lead [139], in comparison with the spectrum of the pure monomer, show a considerable shift to higher frequencies (940–920 cm^{-1}) of the 890–845 cm^{-1} doublet, corresponding to deformation vibrations of the hydroxyl in the Si–OH bond [130]. The broad absorption band at 3200 cm^{-1}, due to hydroxy-stretching vibrations in the solid monomer [130], is also displaced to shorter wavelengths (3400 cm^{-1}). Such a considerable shift in these bands is obviously due to chemisorption of the monomer on the surface of the lead particles at the instant of their deposition on the cathode.

The energy of interaction of hydroxyls with the metal surface calculated from the shift [140] is ~7 kcal $mole^{-1}$, which corresponds in magnitude with the energy of a hydrogen bond. Chemisorption on a freshly formed lead surface diminishes the mobility of the monomer molecules and causes a redistribution of the electron density of all the bonds, which should affect the reactivity of individual groups in the molecules and the mechanism of condensation of diphenylsilanediol as a whole. The thermal condensation of diphenylsilanediol containing electrolytic lead, unlike its condensation in the presence of lead formate decomposing to the metal, takes place only by reaction (2)—with the elimination of benzene.

The above results suggest a mechanism for the polycondensation of diphenylsilanediol in the presence of highly disperse electrodeposited lead in which, at the instant of deposition of the lead particles, monomer molecules are adsorbed by one hydroxyl on the freshly formed metal surface. When the monomer is heated phenyl radicals, unhindered by adsorption, interact readily with the hydrogen atom of a hydroxy-group in an adjacent molecule, benzene being eliminated. This should yield mainly a linear polymer adsorbed by hydroxyls on to the metal. Under these conditions there is little likelihood of the formation of cyclic trimers, owing to the rigidity of the growing macromolecule adsorbed at one end. These conclusions are supported by infrared-spectroscopic examination of the metallopolymers.

Although the dependence of the softening point of the metallopolymers on the metal concentration is the same in character as that for cyclolinear and cyclic polymers, the fall in softening temperature in the concentration range 4–10% is considerably less pronounced, obviously owing to the formation of small amounts of cyclic molecules. It should also be noted that, for the same lead content, the absolute softening points of metallopolymers obtained by the electrolytic method are higher than those of specimens obtained by a thermal method. The probable reason is more effective interaction in the former case between the monomer—later also the polymer—and the highly disperse metal.

Briefly summarising the investigations on the mechanism of the formation of metallopolymers based on organoelementary polysiloxanes and polyorganosiloxanes, we note that all cyclic and cyclolinear polymers undergo ring-opening under the influence of highly disperse metals [133]. This may be accompanied by the formation of chemisorption bonds of the type Si–O–M between the macroradicals and the metal surface. Among the metals examined, highly disperse lead was the most active [50]. Linear polyorganosiloxanes containing functional groups react with highly disperse metals under ordinary conditions;

on heating such interaction involves chain breakage and incorporation of the heteroatom into the polymer chain [128].

IV. PHYSICOCHEMICAL PROPERTIES AND APPLICATIONS OF METALLOPOLYMERS

Chemisorption interaction with a highly disperse metal affects also the boundary layers of a polymer to a certain depth, appreciably changing its properties in compositions. The physicochemical properties and the applications of metallopolymers pose vast and many-sided problems, a full consideration of which could form the subject of a separate review.

Electrical Properties

The electrical properties of metallopolymers are determined by the nature and the concentration of the metal, the method of its introduction, and also the character of the interaction [150] between metal and polymer.

With metallopolymers based on rubbers (natural rubber and polyisobutylene) and highly disperse iron [19] cobalt, and nickel [20] obtained electrolytically, the conductivity increases only slightly as long as the metal concentration does not exceed 20–40%. The explanation is that, under the influence of the metal particles, the rubbers acquire an ordered network structure.

At higher metal concentrations the particles form chain structures and are in contact with one another; the conductance shows an avalanche-like increase. As the metal concentration increases to 80%, the systems become almost as highly conducting as metals, their conductance falling with rise in temperature. A similar type of conductivity has been found for the polystyrene–silver system [41] and for those formed by an epoxide resin with copper [57] and with iron [141].

The explanation of the sudden increase in conductance at metal concentrations exceeding 40% is that, in metallopolymers having low metal contents, the metal particles are mostly separated by distances exceeding their mean diameter, and the probability that particles will be incorporated into a chain of a certain length is small. At metal concentrations above 40% the distances between the particles become comparable with their diameter, so that the further addition even of small quantities of metal will lock a series of adjacent particles, and this is responsible for the sharp increase in conductance at these concentrations.

The conductance of metallopolymers is due not only to metal chain structures but also to the tunnel effect [57]. At energies corresponding to a particular voltage the current carriers are able to overcome the potential barrier of the polymer shell, when the number of carriers in the system will increase exponentially.

Several researches have shown that the mode of preparation of the specimens has a great effect on the conductance of metal-containing polymer systems. Thus raising the temperature and the pressure at which the samples were prepared leads to a considerable increase in the conductivity [151]. This effect is especially strongly developed in the region of plastic deformations of the systems.

If a magnetic field is applied during the formation of metallopolymers, which gives a directed orientation of metal particles in the polymer, anisotropy of the conductance is observed [152].

Levina et al. discovered [74,103] that the vibrational milling of iron in isoprene, which polymerises on the fresh faces of the metal particles, yields a semiconductor material having electronic conduction; if the vibrational milling is conducted in ready made polyisoprene, material having positive-hole conduction is formed. The character of the interaction between polymer macromolecules and iron particles must obviously be taken as responsible for the type of conduction.

Dielectric Constant

Experimental values of the dielectric constant and the loss angle for the metallopolymers formed by an epoxide resin with copper [57] and with palladium [153] differ from the theoretical values, which is explained by the presence of radicals fixed on the surface of the metal particles. The dielectric constant of the metallopolymers is diminished by chemisorption interaction and cross-linking of the epoxide resin on the metal surface, which leads to bonding of the epoxy-groups.

Formation of radicals is intensified during hardening, and the dielectric constant of the system increases. When the system is completely hardened, with formation of a dense three-dimensional structure, the kinetic mobility of the remaining free radicals diminishes, as also the dielectric constant and the tangent of the loss angle.

Catalytic Properties

The use of polymers as stabilisers and carriers of the active phase in hydrogenation catalysts has for a long time attracted the attention of many investigators [154–158].

During recent years Sokol'skii and his coworkers have made extensive investigations [159–167] on the hydrogenation of organic compounds, containing double and triple bonds, over platinum-group catalysts deposited as finely divided reduced metal powders on a polymeric carrier—polyacrylonitrile, polyvinyl alcohol, anid, poly(ethylene terephthalate). The selectivity and the activity of these catalysts are determined in considerable measure by the nature of the polymer [168]. This is evidently related to the deformation of the electron shells of atoms of the disperse metal adsorbed on polar groups of the polymer, and to the orientation of molecules of the unsaturated compound as it approaches the catalyst surface along the polymer chain, with the unsaturated groups located on the active centres of the metal [168].

Metallopolymers based on polydimethylphenylsiloxane and highly disperse electrolytic iron have been studied [169–172] as catalysts for the synthesis of ammonia. Thermostable polysiloxanes proved to be resistant stabilisers of the surface of the active phase (100–120 $m^2 g^{-1}$), and provided reliable protection against sintering of the metal particles. The above metallopolymers were comparable in efficiency with an industrial iron catalyst.

The great catalytic activity of metallopolymers based on an epoxide resin, poly(vinyl acetate), and highly disperse electrolytic palladium for the hydrogenation of unsaturated organic compounds remains almost unchanged on prolonged storage of the catalyst under ordinary conditions [86].

Investigation of the catalytic properties of metallopolymers requires further development both in the search for new systems suitable for definite catalytic reactions

and in the establishment of the interrelation between the semiconductor and the catalytic properties of metallopolymers [173].

Metallopolymers are used also in the purification of petroleum products from organosulphur compounds at normal pressures and temperatures [174,175].

Antifriction Properties

Metallopolymers find application as antifriction materials [56]. The combination of polymers, which possess low coefficients of friction or abrasion, with the highly disperse metals traditionally employed in friction joints (copper, lead, etc.) yields antifriction materials having low coefficients of friction and, what is very important, high thermal conductivity and good mechanical properties [60].

Thermomechanical Properties

Chemisorption interaction between polymers and metals greatly restricts the mobility of individual macromolecules and supermolecular structures [8] in contact with the surface of the metal particles, so that the softening and glass points of metallopolymers are particularly high [21] compared with those of ordinary filled polymers. The thermomechanical properties of a polymer are affected significantly not only by the type of interaction between polymer and metal but also by the concentration, degree of dispersion [66], particle shape [77], and nature of the surface of the filler. The high degree of dispersion and uniformity of distribution of metal particles introduced into polymers by the methods described above are already sufficient to ensure considerable differences in thermomechanical properties between metallopolymers [41] and ordinary filled systems.

The effect of the character of interaction between polymer and metal on the thermomechanical properties of the compositions can be clearly traced from the variation in the softening points of metallopolymers based on polystyrene [41,58,67], where interaction between polymer and metal surface is weak, and in those based on an epoxide–dian resin [21,84,85,141], poly(vinyl acetate) [99], and capron [112–114], where chemisorption interaction between macromolecules and metal surface has been established. At the same concentrations of different metals the softening temperatures of the second group of metallopolymers are always far higher. Furthermore, whereas the first group of metallopolymers exhibit an almost linear dependence of softening point on metal concentration, metallopolymers based on the epoxide–dian resin with copper [21] and especially iron [141] already exhibit a sharp rise in softening temperature at comparatively low metal concentrations, and then loss of deformability, which is associated with complete hardening of the resin by the metal.

Raising the temperature [99] and increasing the duration [84,85] of preliminary heat-treatment with the second group of metallopolymers will raise the glass and softening points for a given concentration of metal in them.

Mechanical Properties

Study of the thermomechanical properties of filled polymers provides a clearer idea of the processes that occur when a polymer interacts with metal particles and of their effect on the mechanical properties of metallopolymers.

The introduction of lead by the thermal method into an epoxide–dian resin [89] increases the breaking strength and the elongation (up to a certain concentration of the metal), as well as the modulus of elasticity of the specimens, lead serving in this case as hardener. Raising the lead concentration above an optimum value leads to the formation of a more brittle and rigid system, which sharply lowers the strength characteristics of the metallopolymer.

The particle shape of the metal also affects the mechanical characteristics of the compositions. Powders comprising dendritic particles are most effective in improving the mechanical properties of filled polymers [77]. The introduction of highly disperse aluminium, manganese, iron, and silicon powders [67], made lyophilic towards rubber, has a vulcanising and reinforcing action on compositions of chloroprene and butadiene–nitrile rubbers. The improvement of the mechanical properties of rubber [68,90,81] in the presence of highly disperse metals is obviously due to the formation of stable rubber–metal bonds.

Swelling

The introduction of a filler into polymer systems may form additional cross-link in the three-dimensional network, but may also decrease its density. These additional cross-links are usually broken by swelling, with a considerable increase in the apparent degree of swelling of the polymer [142]. Swelling of this character is found with metallopolymers based on polystyrene and lead [43,104], where only weak van der Waals interactions link polystyrene macromolecules and metal particles.

However, in the thermal preparation of metallopolymers from polystyrene and a more active metal, silver [41], when a stable three-dimensional structure can be formed by thermal degradation of the polymer macromolecules followed by chemical interaction between the macroradicals and the surface of the silver particles, the ability of the metallopolymer to swell diminishes with increase in the metal content. Chemisorption interaction of polymers with the surface of metal particles leads to a sharp restriction of the mobility of the polymer chains, owing to the formation of additional chemical cross-links in the polymer network.

The introduction of highly disperse iron into non-polar rubbers (natural rubber, polyisobutylene) produces a considerable decrease in their swelling, and specimens containing 80% of the metal hardly swell at all [19]. A similar pattern is observed with these polymers on the electrolytic introduction of nickel and cobalt [20]. When the same quantities of these metals are added to a rubber, the decrease in the equilibrium degree of swelling depends on the nature of the metal. Furthermore, equilibrium swelling is reached more rapidly with metallopolymers than with the corresponding pure polymers, owing to the loose packing of surface layers of the polymer in the former case [8].

Metallopolymers based on an epoxide resin and copper, prepared by a thermal method, also show a decrease in swelling with increase in the copper content from 1% to 40%. [52] The character of the swelling changes sharply at copper concentrations above 40%. Samples containing 50–60% of copper hardly swell at all in 180 min. The swelling of specimens containing 60% of copper is one-tenth of that observed with 40% of copper.

Theoretical values of the degree of swelling of metallopolymers based on poly(vinyl acetate) and palladium [99], calculated by means of the Flory–Rehner equation [142], exceed the experimental values, the difference being larger the higher the palladium content.

All this indicates that bonds formed between metal surface and polymer in the preparation of metallopolymers are not broken during swelling.

Thermal and Thermo-oxidative Degradation

The influence of highly disperse metals on the thermal and thermo-oxidative degradation of metallopolymers has been by no means fully investigated, although it is of great interest. The introduction of up to 33% of highly disperse iron into an epoxide resin somewhat increases the rate of thermal degradation of the latter, but aluminium has no appreciable effect on this process [143,144]. Polyethylene also undergoes considerably more vigorous thermo-oxidative degradation when filled with disperse iron [122].

Differential thermal analysis has been used to examine the effect of the concentration of various metals on the thermo-oxidative degradation of metallopolymers, in particular those based on the epoxide–dian resin with copper [21] and on polystyrene with bismuth, manganese, and lead [54,55]. In all cases an appreciable rise in the temperature at which degradation began was observed only at low metal concentrations (up to 1.5%). The same method has shown that the optimum temperatures for the start of the thermo-oxidative degradation of metallopolymers based on an epoxide resin were reached at contents of 40–80% of copper [21] and of iron [141]. Similar results have been obtained for systems based on natural rubber and various metals [145].

However, the use of differential thermal analysis will not give a complete understanding of the role of metals in the degradation of metallopolymers. Quantitative investigations are necessary on the loss of weight of specimens and the evolution of volatile products, and their nature and the structural changes in the solid residue must be established; these may give more definite information on the mechanism of the degradation of metallopolymers. The investigation of purely thermal degradation is especially important, since the degradation of metallopolymers in air leads to oxidation of the highly disperse metals, so that degradation of the polymer is then affected actually by the metal oxide.

The introduction of certain disperse metals retards the oxidative degradation of organosilicon polymers [126,146,147]. This was explained by the orienting influence of the particles, which are able to become centres for the formation of secondary structures: i.e. physical factors are regarded as having the predominant effect on thermal degradation. Other authors [148,149] are inclined to attribute the enhanced stability of polysiloxanes when filled with metals to the formation during degradation of a new polymer with the metal heteroatom in the chain: i.e. they explain the stabilisation effect by the chemical action of the metal. The role of the physical or the chemical factor is obviously decisive in each specific case, but the influence of the other factor can be by no means excluded.

The above methods of preparation, mechanism of formation, and physicochemical properties of products obtained by the interaction of polymer macromolecules with the surface of colloidal metal particles at their instant of formation indicate that a chemisorption bond is established in these products between polymer and metal. This allows such two-phase systems of limiting homogeneity to be classed as a separate group under the name "metallopolymers". The chemisorption interaction of the macromolecules with the metal surface, the high degree of dispersion of the metal particles, and also the uniformity of their distribution in the bulk of the polymer guarantee a considerable improvement in the physicomechanical and physicochemical properties of metallopolymers in comparison with ordinary polymers filled with metals.

The simplicity of the methods of preparation combined with the series of valuable specific properties of metallopolymers opens up wide possibilities for their application in the national economy. Metallopolymers based on film-forming and lacquer-depositing polymers may find application as corrosion-resistant and other protective coatings. The exploitation of, for instant, the magnetic, semiconducting, ferromagnetic, catalytic, and antifriction properties of metallopolymers is most promising in practical terms.

Detailed investigations are required on the mechanism of the thermal and thermo-oxidative degradation of metallopolymers obtained from a variety of metals and macromolecular compounds. Such investigations would serve as a basis for producing metallopolymers possessing high thermal stability, which would considerably expand their field of application.

Further examination of the mechanism of the formation of metallopolymers based on the most diverse classes of macromolecular compounds and various metals would make possible a general theory of the formation of metallopolymers.

Researches on the formation of metallopolymers by the polymerisation or polycondensation of monomers and oligomers on the freshly formed surface of highly disperse metals would be especially interesting for both theory and practice, involving both problems of polymerisation and structure formation on solid surfaces and those of the strengthening of filled polymers.

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