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Advances in the Production of Thermostable Antifrication Plastics

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Methods of producing self-lubricating antifriction plastics are examined. Filling with a solid lubricant a polymeric binder that does not possess a low coefficient of friction when unfilled is a promising development. The principal physicochemical requirements to be met by a polymer to be used as a binder are formulated. Possible chemical changes undergone by the polymeric binder and the filler during friction are discussed. Published information on the effect of the chemical nature of the polymeric binder on the properties of antifriction materials is summarised. The Review concludes with 211 references.

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I. INTRODUCTION

Many polymeric antifriction materials are known that can be used in friction units. Polymeric materials are far more effective in their antifriction properties than are antifriction alloys[1-6], graphitic and oil-filled bronzes[7]. Polymeric antifriction materials are distinguished by the ease of production of articles, low specific gravity, good antifriction properties, and the possibility of modifying the properties of the polymers by simple technical operations. They can be applied to friction units in various ways—by coating a metal surface with a thin layer of the polymer, making parts from blocks of the polymer with and without fillers, or impregnating a porous metal base with the polymer[8].

Materials possessing antifriction properties now face increasingly severe demands—high heat resistance and thermal stability, vibration strength, radiation resistance, good machinability. They should ensure the functioning of friction units under extreme conditions—high and low temperatures (from +500 to −200°C), corrosive media, high vacua, great speeds, and high unit loads. The use of liquid lubricants under these conditions is ineffective.

The attention of investigators has therefore been attracted to multicomponent materials, in which the functions of structural material and lubricant are combined. The production of such materials having specified properties is an extremely complicated task. Account must be taken of the nature of the polymeric binder, the properties, composition, and quantity of fillers added, and also the chemical and physicochemical processes involved in interaction between polymer and fillers[9-15].

Numerous investigations have been made on the friction of solids, including polymeric antifriction materials, which have been summarised in monographs[16-28], proceedings of conferences[29-31], reviews[32-36], and individual papers[37-42]. However, this research has been concerned with problems of the mechanics, technology, and physical chemistry of filled systems. Considerably less attention has been paid to chemical aspects of the production of antifriction plastics.

The present Review examines the influence of the chemical nature of the polymeric binder on the properties of antifriction materials, and also on the chemical and physicochemical changes undergone by the components during friction.

II. PRODUCTION OF THERMOSTABLE SELF-LUBRICATING ANTIFRICTION PLASTICS

Self-lubricating antifriction plastics can be obtained in two fundamentally different ways. A method widely discussed in the literature is to produce materials based on polytetrafluoroethylene[21,43-52], Thiokols[53,54], and other polymers possessing good lubricating properties and low coefficients of friction (~0.1). In this case the lubricating principle is the polymer itself, while the introduction of fillers merely improves its physicomechanical properties—by enhancing thermal conductivity, wear resistance, hardness, strength, and heat resistance, and by diminishing cold flow.

The second method is to obtain materials based on polymers having a comparatively high coefficient of friction (0.1–0.5). Such polymers include polyhydrocarbons, halogenated polyhydrocarbons, polyamides, polyesters, polyurethanes, phenolic resins, etc. Solid or liquid lubricants are generally included in the composition of such polymers for use in dry friction units. This process was made possible by research on highly filled polymers undertaken during 1949–1950 by Rebinder and his school[55,56]. This second method is most promising, since it opens up wide opportunities of purposeful searching for binders among a large number of known and new polymers.

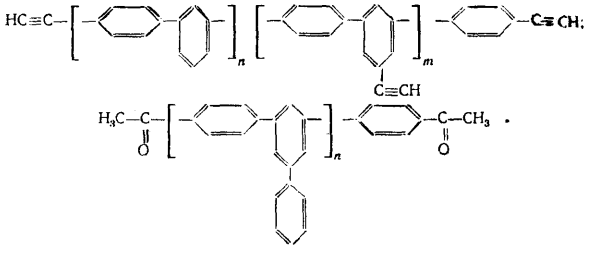
In order to solve the problem of producing the heat-resistant and thermostable self-lubricating antifriction plastics required by modern technology a broad research programme on filled antifriction polymer systems has been followed under the direction of V. V. Korshak in the Institute of Hetero-organic Compounds of the USSR Academy of Sciences. These investigations included study of the influence of the chemical structure of the polymers, their physical structure, and also the chemical nature of the filler and the strength of polymer–filler bonding on the properties of the antifriction plastics, study of the behaviour of filled systems during friction at high temperatures, as well as aspects of structure formation and the synthesis of network polymers in the presence of fillers under processing conditions, and study of the properties and the stabilisation of filled polymers.

Advances made in the synthesis of thermostable polymers, establishment of the relation between the chemical

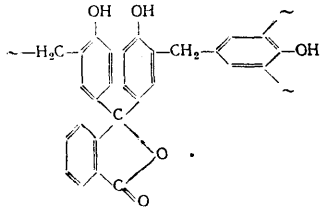
structure of polymers and their properties, and the hetero-unit character of polymers have offered wide opportunities for the production of antifriction plastics[57–59]. Both thermoplastic and thermosetting polymers of diverse chemical structure have been used as binders in the development of self-lubricating antifriction plastics. Choice has concentrated mainly on members (see List) of new classes of thermostable rigid-chain organic and hetero-organic polymers containing rings in the chain, bulky side-groups, hetero-groups, cross-links (such polymers include polyphenylenes, phenolphthalein–phenol–formaldehyde polymers, polyarylates, polyimides, polybenzimidazoles, polybenzoxazoles, polyphenylquinoxalines, polyoxadiazoles, polycyanates, etc., as well as polymers containing boron, silicon, phosphorus, or sulphur). Korshak and his coworkers[60–67] have used these polymers to develop new thermostable antifriction materials possessing several valuable properties.

A. Carbon-chain Polymers

1. Polyphenylenes[65,88,91]

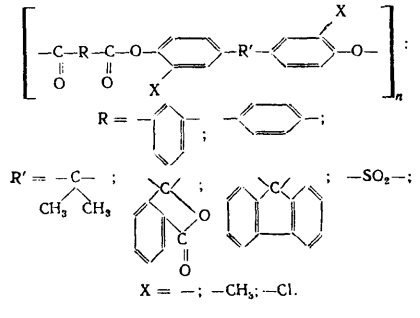


2. Phenolphthalein–phenol–formaldehyde polymers[66,70,82,91]



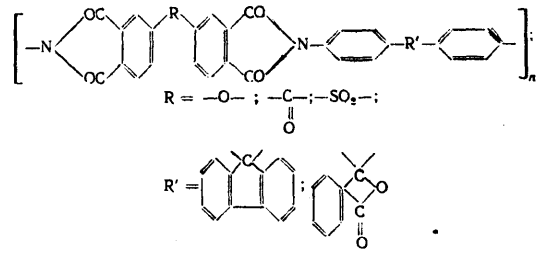
B. Heterochain Polymers

1. Polyarylates[71,72,81,82,91]

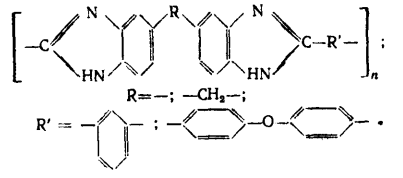


C. Heterocyclochain Polymers

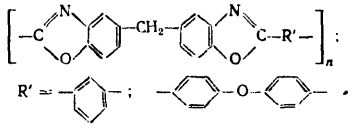
1. Polyimides[71,74,82]



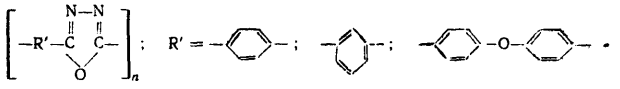
2. Polybenzimidazoles[73]



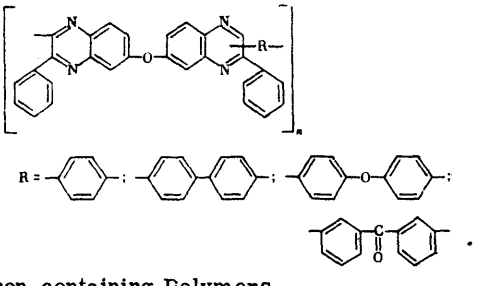
3. Polybenzoxazoles[91]



4. Polyoxadiazoles[60]

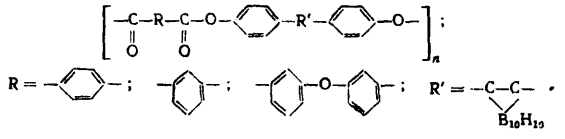


5. Polyphenylquinoxalines[74,79,87,90]

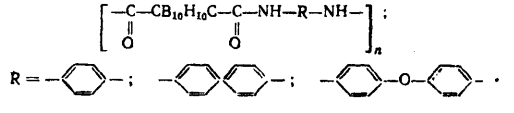


D. Boron-containing Polymers

1. Polyarylates[68,75,93–96]

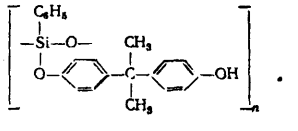


2. Polyamides[68,75,93–96]

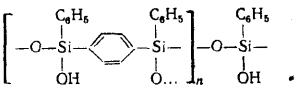


E. Silicon-containing Polymers

1. Polymer B-1[63]

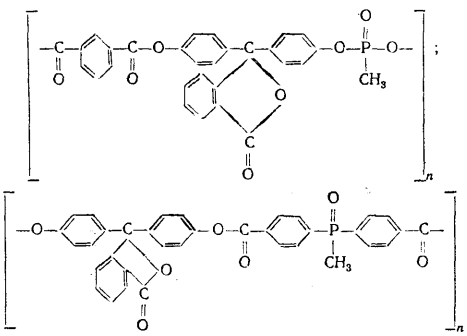


2. Polyphenylenephenylsiloxane[76,91]



F. Phosphorus-containing Polymers

1. Polyesters[78,81,91]



Substantial attention was paid to the behaviour of filled polymer systems during friction at high temperatures and to revealing the role of the polymeric binder, since under these conditions the system undergoes considerable changes in physicomechanical and antifriction properties[80–86]. Studying the thermal friction properties of several thermostable polymers—polyarylates, polyimides, a phenolphthalein-phenol–formaldehyde polymer—filled with molybdenum disulphide, Korshak et al. have shown[81,82,91] that all the filled polymers have a common type of temperature dependence of the coefficient of friction characterised by several friction zones— respectively of minimum coefficient, increasing coefficient, unstable friction, and decreasing coefficient[82] (Figs. 1 and 2)— rapid growth in the coefficient being observed considerably below the glass point of the polymers.

Investigation over a wide temperature range of the relaxation and thermal cohesive properties of self-lubricating antifriction plastics based on polyarylates and polyimides has shown[82] that the temperature limits of variation in these properties coincide with the temperature boundaries of the friction zones. Analysis of the behaviour in thermal friction tests of many filled systems based on polymers of diverse chemical structure, study over a wide temperature range of the relaxation and thermal cohesive properties of the polymers, and determinations of molecular mass and intrinsic viscosity before and after tests under various conditions suggested to Korshak et al.[82] that the temperature variation of the coefficient of friction is governed largely by the structure and properties of the polymeric binder. On the basis of their results they formulated the main physicochemical requirements to be met by polymers used as binders in the development of thermostable antifriction plastics—high heat resistance, thermal stability, and resistance to thermal oxidation, and absence from the chemical and physical structure of such polymers of mobile fragments capable of passing into a labile state at temperatures below the limit of their heat resistance— which are largely satisfied by polymers whose chains contain rings, bulky side-groups, hetero-groups, polar bonds.

In the development of thermostable self-lubricating materials based on thermoplastic polymers close attention has been paid to the influence of the chemical structure of

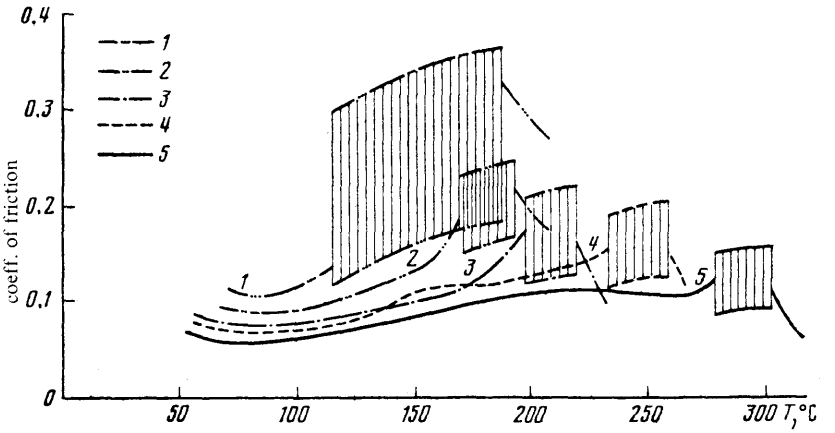
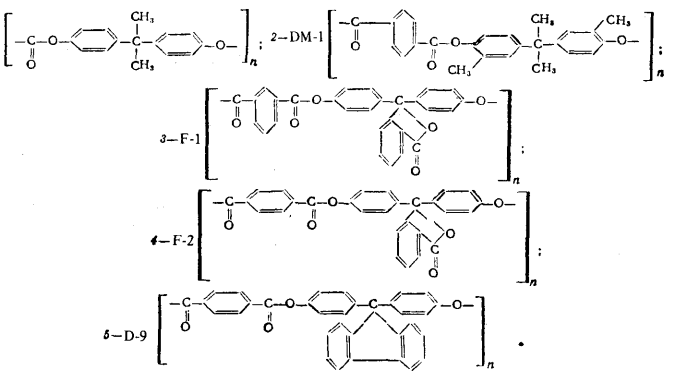


Figure 1. Thermal friction properties of self-lubricating antifriction plastics based on polyarylates of diverse chemical structure: *1*) Diflon.



the monomer unit on the thermal friction properties of the filled systems. With polyarylates of diverse chemical structure as example Korshak et al. [81] have shown that the presence of card [large, planar] groups such as phthalide and fluorene tends to extend the temperature limits of the zone of stable and low coefficient of friction (Fig. 1). Isomerism between dicarboxylic acids (isophthalic and terephthalic acids were used) displaces the "seizing" zone by 30–50 deg to higher temperatures on passing from the *meta*- to the *para*-isomer. Intensifying interchain interaction in the polyarylate macromolecule by introducing polar substituents (chloro) into the aromatic ring system of a diol increases the coefficient of friction of the materials throughout the temperature range. The results indicate that the temperature limits of effective application of self-lubricating antifriction plastics are extended withincrease in the rigidity of the polyarylate macromolecules due to increase in the number of aromatic rings, to the presence of card groups[81].

A factor tending to diminish the mobility of the polymer chains is the presence of fused ring systems (benzoxazole, benzimidazole, pyromellitimide) in the monomer unit, which leads to a considerable increase in the heat resistance of polymers. In such polymers the heat resistance usually surpasses the thermal stability, so that in most cases they do not melt, which hinders their processing[58]. In several cases introduction into the chain of mobile units — "hinge" heteroatoms (oxygen, sulphur) bulky substituents, or such hetero-groups as carbonyl and sulphonyl—yields polymers possessing quite high heat resistance while capable of softening below the decomposition point. Fig. 2 illustrates results of thermal friction tests on self-lubricating antifriction plastics based on polyimides containing such "hinge" hetero-groups and -atoms. Comparison of Fig. 1 and 2 shows that such plastics posses higher coefficients of friction than those based on polyarylates, owing to the strong intermolecular interaction of the polymer chains[81,82,91]. The chemical nature of the "hinge" hetero-atom or -group in the monomer unit in the polyimide has a significant influence on the thermal friction properties. Thus the introduction of oxygen atoms into diamine and dianhydride components, by conferring enhanced flexibility on the polymer chain, increases the coefficient of friction and narrows the temperature limits of the zone of minimum coefficient. Increasing the rigidity of the polyimide chain by introducing bridging hetero-groups (carbonyl and sulphonyl) into the dianhydride component or bulky substituents into the diamine component increases the hardness of the material, lowers the coefficient of friction, and extends the temperature limits of the friction zones.

The mobility of the chains can be diminished also by the formation of cross-linked structures. The possibility has been investigated of forming network polymer structures from oligomers (reactophenes, acephenes, phenol-formaldehyde oligomers)[65,66,70,88], from polymers (polyphenylquinoxalines, polyimides)[82,89–91] in the presence of fillers. Korshak et al.[66,82] have shown for a self-lubricating antifriction plastic based on a phenolphthalein–phenol–formaldehyde polymer (FF-40) that the coefficient of friction increases, while wear diminishes, with increase in the degree of hardening of the polymer. The start of the increase in the coefficient at moderate temperatures (~80°C) and within a narrow temperature range (80–90°C) was attributed[66] to the peculiar structure of phenol–formaldehyde polymers, to the presence in the three-dimensional network of two types of junctions—chemical (stable) and physical (labile), formed by hydrogen bonds.

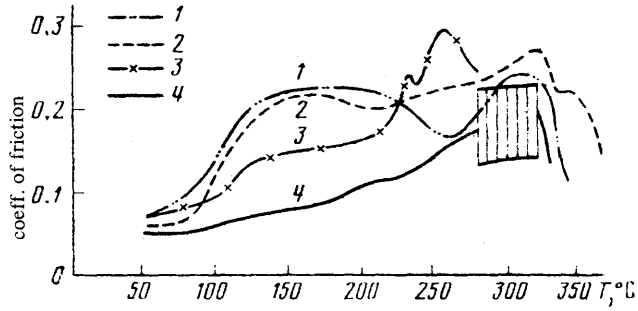
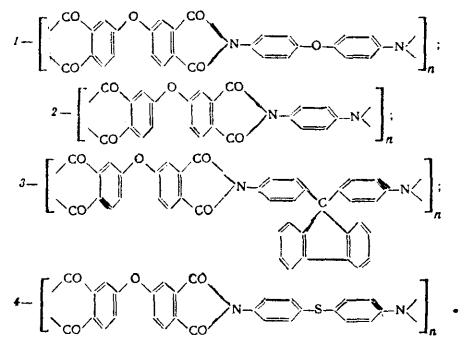


Figure 2. Thermal friction properties of self-lubricating antifriction plastics based on polyimides of diverse chemical structure:



Antifriction plastics based on a slightly hardened polymer exhibit unstable friction and an increase in the coefficient in the temperature range in which the material softens with increase in the thermal cohesive strength. Increase in the degree of hardening of a phenolphthalein–phenol–formaldehyde polymer is accompanied by increase in the viscosity of frictional contact in the zone of incipient softening. However, the cohesive bonding strength is still quite low, so that friction in this zone is stable in character[66].

The use of polymers capable of forming cross-lined structures during processing offers wide opportunities for obtaining new thermostable self-lubricating antifriction plastics with good physicomechanical properties. The possibility of forming a cross-linked structure by means of agents containing reactive groups (terephthalaldehyde, pyromellitonitrile, etc.) has been examined on polyphenylquinoxalines, which are cyclochain polymers; "self-cross-linking" polyphenylquinoxalines, which contain reactive carbonyl groups, have also been used for this purpose[89–91]. Materials based on cross-linked polymers possess a stable coefficient of friction and greater wear resistance at high temperatures.

Considerable attention has been paid to the effect of the chemical nature of the monomer unit in hetero-organic polymers on the antifriction properties[66]. Use of these polymers as binders is not only of theoretical but also of practical interest, since many of them possess high heat resistance and thermal stability, as well as several spe-

cific properties, i.e. incombustibility, radiation resistance, water repellency. The properties of the self-lubricating antifriction plastics are determined not only by the nature of the heteroatom but also by the conditions of formation of the filled system and the chemical structure of the monomer unit[81].

The use as binders of polymers containing carborane groups, which have a considerable effect on the behaviour of the polymers at high temperatures, is of great interest for the production of thermostable self-lubricating antifriction plastics[92–94]. Examination of polyamides and polyesters containing 1,2-, 1,7-, and 1,12-dicarbadodecaborane groups has shown[93–96] that at 400–500°C these polymers form "secondary" structures (pyropolycarboranes), which are thermostable, undeformable, cross-linked polymeric products. The structure and the properties of pyropolycarboranes depend on the method of synthesis, the isomerism of the carborane ring system, and its position in the monomer unit. The strongest tendency to form thermostable, undeformable pyropolycarboranes is exhibited by a polyamide containing 1,7-dicarborane and a polyester containing 1,2-dicarborane in the diol part of the macromolecule. Two types of filled antifriction materials—(*a*) thermoplastic, showing high wear resistance and thermal stability during friction (up to 350°C), and (*b*) cross-linked, undeformable and capable of operating under conditions of dry friction at 350–400°C— can be based on carborane-containing polymers. Korshak et al.[68,75] have used carborane-containing polyamides and polyesters with fillers to obtain new heat-resistant thermostable self-lubricating antifriction plastics that can be employed in dry friction units in the absence of a liquid lubricant up to 400°C. The decrease in the coefficient of friction at 300 to 400°C is largely due to the ability of carborane-containing polymers to evolve hydrogen at these temperatures[91].

Polymers containing silicon, phosphorus, or sulphur have been used to produce self-lubricating antifriction plastics[63,76,81]. Phosphorus-containing polymers and monomers possess the interesting property that filled systems can be stabilised and modified, which permits considerable extension of the temperature limits of application of the materials.

Great attention has been paid to establishing the relation between the chemical structure of a polymer and the wear resistance of filled systems based on it. Results obtained by Korshak et al.[91] show that the production of thermostable wear-resistant materials is a complicated problem, which cannot be solved merely by using more thermostable binders and fillers, since increasing the rigidity of the polymer chain leads to a considerable increase in the viscosity of the melt and raises the processing temperature right up to incipient thermal degradation of the polymer.

The physical structure of rigid-chain polymers, formed either during synthesis or on subsequent heat-treatment, has a significant influence on thermal friction properties. Korshak et al.[97] have examined polyarylates of different supermolecular structure filled with molybdenum disulphide, and have shown that, because of the greater elasticity and lower hardness of a polymer having a fibrillar structure, the coefficient of friction is higher for such specimens than in the case of a globular structure, throughout the temperature range. The depression of the operating temperature limits under friction conditions for a self-lubricating antifriction plastic based on a polyarylate having a fibrillar structure is due to the greater temperature sensitivity of the more complicated fibrillar supermolecular structures.

Investigation of the influence of supermolecular structure on thermal friction properties when poly-*m*-phenyleneisophthalamide (Phenylone) was used as binder[98] led to the development of novel antifriction plastics based on self-reinforcing polymers having the same chemical structure but differing in type of supermolecular structure, which resulted in an optimum combination of frictional and strength properties[72].

Belyi et al.[99–101] made widespread use of a tribometric method to study the influence of supermolecular structures on the friction of polymers and also to investigate self-lubricating compositions comprising polymers and dry lubricants. These studies make it possible to assess the mechanism of the friction of self-lubricating materials, and the influence of the components, their nature, dispersity, and physicomechanical properties on the frictional behaviour of a composition material.

Thus both the chemical structure of monomer unit and macromolecular chain and the physical structure of the polymers influence significantly the thermal friction properties of filled systems. At the same time the filler also has an important role in determining the structure and the properties of the systems: it should ensure not only good lubricating properties but also adequate strength of the materials[84,86,97,102,103]. The structure and the properties of a filled system depend on both the nature and the quantity of a filler. All materials of various degrees of filling can be divided into two groups with respect to their lubricating power[71,103]: the first comprises self-lubricating antifriction plastics containing at most 15–30% of polymer, which possess a low coefficient of friction (0.04–0.12) and high wear resistance; the second group of specimens, containing >15–30% of polymeric binder, is characterised by an unsteady régime in the case of dry friction and a high coefficient. The boundary of "self-lubricating power" depends on the chemical structure of the binder, and is displaced towards higher polymer contents with increase in the rigidity of the macromolecular chain. Within the limits of "self-lubricating power" all materials possess high wear resistance.

Table 1. Variation of molecular-mass characteristics of polyarylate F-1 during friction of self-lubricating antifriction plastics[138] (conditions of frictional contact: p = 2 kgf cm^{-2} and v = 2 m s^{-1}).

Medium	T, °C	F-1-MoS_2		F-1-MoS_2-Cu	
		M*	$[\eta]$ in C_2HCl_3	M	$[\eta]$ in C_2HCl_3
Argon	~50	14000 (44000)**	0.160 (0.284)**	34500 (27100)	0.356 (0.317)
Argon	120	17500	0.185	28500	0.295
Air	~50	23600 (44000)	0.165 (0.284)	29500 (24600)	0.300 (0.265)
Air	120	24000	0.40	66900	0.265

*Molecular masses M determined from the scattering of light.

**Initial values given in parentheses.

The fillers or solid lubricants[104] used have been molybdenum disulphide[105,106], graphite[107], tungsten disulphide[108], fluorinated graphite[109], metal sulphides[110], boron nitride[111], oxides of lead, molybdenum, cobalt, zinc, tin, copper, and

other metals, fluorides of metals, and other solid materials[112].

In the creation of multicomponent self-lubricating antifriction plastics account must be taken of the complicated chemical and physicochemical processes occurring in the polymeric binder, the fillers, and also the boundary layers in the contact zone between binder and fillers on formation of the filled system. The mechanical characteristics of filled polymers largely depend on the adhesion at the polymer–filler boundary[9,10,15,29,113,114]. The interfacial interaction has a special character[98], apparent in the orientation of thin polymer films along the faces of the filler crystals (molybdenum disulphide). These films are assumed to effect cohesion between the filler crystals. In some cases a film may be several micrometres thick even with a high filler content. The filler may have either a plasticising or a strengthening effect depending on its chemical nature and its content[83].

III. CHEMICAL REACTIONS OF POLYMERIC BINDER AND OF FILLER DURING FRICTION

Modern self-lubricating antifriction plastics are essentially filled multicomponent polymer systems in which solid lubricants are accompanied by various powdered fillers— metal powders, powdered coke, quartz, titanium dioxide, etc. — and also fibrous fillers (cellulosic, asbestos, etc.). During operation both individual components and the antifriction system as a whole undergo chemical and physicochemical changes. The operating temperature limits in friction units are determined both by the chemical structure of the polymeric binder, its heat-resistance and thermal stability, and by the nature of the filler, its dispersity, particle shape, activity towards the polymer, proportions of components, and several other factors[102].

The creation of new wear-resistant thermostable self-lubricating antifriction plastics is impossible without a detailed study of the behaviour of the initial components and the filled systems at high temperatures as well as during friction. Relatively little work has been done on the chemical and physicochemical changes occurring in filled polymer systems during friction at high temperatures: greater attention has been paid to the behaviour of pure polymers during friction.

Study of the mechanism of frictional transfer during contact between a polymer and another polymer, a metal, or another material is of both scientific and practical importance[19,33,34]. During friction between a metal and a polymer the latter is transferred to the metal surface, on which it forms a monolayer[115]. Under heavy-duty conditions metal is transferred to the polymer[116,117]. Sviridenok et al.[118] have used an adhesion–deformation mechanism of frictional interaction of solids[16,25] as a basis for the investigation of transfer between polymers differing in adhesive power and cohesive strength, such as polytetrafluoroethylene, polyethylene, poly(methyl methacrylate), polyhexanamide, and poly(ethylene terephthalate). Adhesive power was assessed from the critical surface tension, which established three characteristic types of contact—non-polar–non-polar (polytetrafluoroethylene–polyethylene), non-polar–polar (polytetrafluoroethylene–poly(ethylene terephthalate), polyhexanamide), and polar–polar (poly(methyl methacrylate)–polyhexanamide). Infrared spectroscopy shows[118] that transfer takes place from a less polar to a more polar polymer, and is accompanied by breakdown of the initial material. At the same time changes occur in the surface layer of the other material. The nature of the interacting materials also has a significant influence on transfer. Thus, when a highly polar polyhexanamide film is used together with polytetrafluoroethylene, a strong, continuous layer of the latter 1 μm thick is formed on the film surface. Increase in the duration of contact and in the loading result in amorphisation of the material owing to breakdown of macromolecules in the surface layer. It is assumed that highly reactive radicals of the type CH_2. .C'H.NH.CO are formed during friction. Other workers have also noted the possibility of the occurrence of free-radical reactions in the course of frictional interaction[116,117].

In the region of contact, processes affecting the properties of the surface layers of the rubbing bodies take place under the influence of friction. In the case of a metal–polymer pair this applies both to the polymer and to the metal. At the site of contact an extremely thin third body is formed, with properties determined by the frictional conditions[23]. Its formation is due to coating of the harder body with a thin layer of the softer material, adsorption of a polar lubricant on the surface, formation of stable chemical compounds, etc.

The deformation and thermal processes accompanying the friction of polymers tend to promote tribochemical phenomena[119,120], complicated multistage processes involving activation of the rubbing surfaces by mechanical deformation (i.e. actually the supply and absorption of mechanical energy) and various physicochemical processes occurring under the influence of mechanical activation, which favour the conversion of mechanical into chemical energy[121]. Mechanochemical reactions occur in stages[117,121–124], involving changes of a morphological, supermolecular character (mechanical disaggregation) followed by changes at a molecular level (mechanical degradation), and such degradation leads to chemical reactions[125–127] determined by the polymer structure. Processes occurring under the influence of mechanochemical factors have been studied in polyamides[128–130], phenol–formaldehyde polymers[129], polyethylene[131–136], poly(ethylene sulphide)[132,133], polyformaldehyde[134], poly(ethylene oxide)[133,137], polystyrene[134–136], and poly(methyl methacrylate)[134–136].

Study of the behaviour of filled polymer systems during friction, especially at high temperatures, has established an interconnection between thermochemical and tribochemical reactions in the polymeric binder and in the filler system[138–142]. The friction of filled self-lubricating antifriction plastics entails formation of surface films of the antifriction material both on the surface of the specimen and on the steel counterbody, between which rubbing then occurs[82,138,139]. The character of the films depends on the conditions of frictional contact. X-Ray diffraction and local X-ray spectroscopy have established[139] that the surface films on the counterbody correspond in chemical composition with the antifriction material. Korshak et al.[139] have examined the behaviour during friction of a self-lubricating antifriction plastic based on a polyarylate, and have shown that the polymeric binder undergoes considerable chemical changes depending both on the conditions of frictional contact (atmosphere, temperature) and on the nature of the fillers. Table 1 shows that the friction in argon of an antifriction plastic comprising F-1 polyarylate (based on isophthalic acid and phenolphthalein) and molybdenum disulphide as filler entails a decrease in the molecular mass of the polymer and a proportionate decrease in the intrinsic viscosity (in comparison with the initial values), which indicates the occurrence of degradative processes in the polymeric binder. In an oxidising environment (friction in air) cross-linking degradative pro-

cesses occur in the polymer, leading to some branching of the macromolecular chains.

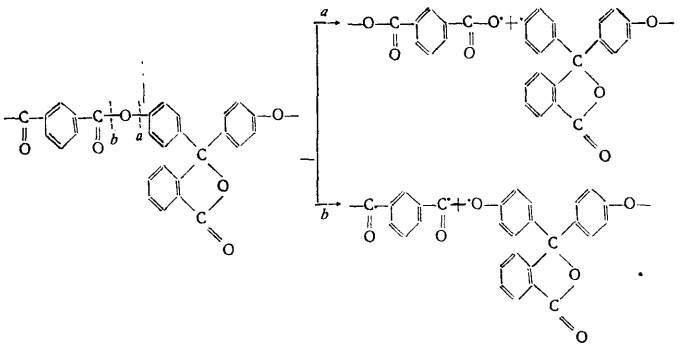
Linear wear on friction is less in argon than in air (Table 2), owing to oxidation of molybdenum disulphide in the latter with impairment of its lubricating properties, as well as mechanical degradation in the polymeric binder. Raising the temperature at the frictional contact intensifies mechanical degradation and diminishes wear resistance of a self-lubricating antifriction plastic comprising F-1 polyarylate and molybdenum disulphide. The presence of copper powder changes the character of the mechanical degradation processes on friction both in argon and in air. When the temperature at the frictional contact is 50° C, cross-linking degradative processes occur in the polyarylate leading to branching and some increase in length of the polymer chain. The wear resistance of the ternary system is greater in argon than in air. Raising the temperature to 120° C intensifies mechanical degradation on friction in air, owing to formation of a partly cross-linked structure. As a consequence the wear resistance of the antifriction material diminishes.

Table 2. Wear resistance of self-lubricating antifriction plastics based on polyarylate F-1 and various fillers[138].

Medium	T, °C	Linear wear, $10^9 I$*	
		F-1-MoS_2	F-1-MoS_2-Cu
Air	50	2.0	1.05
Air	120	3.8	2.2
Argon	50	1.5	0.5
Argon	120	2.7	1.2

*Ratio of height of layer worn away to friction path during surface friction.

Tribochemical reactions in a polyarylate filled with molybdenum disulphide are assumed to occur in argon according to the scheme[139–141]



Increase in the degree of branching of the polymer followed by cross-linking of the macromolecules may occur also as a consequence of cleavage of the lactone ring.

An antifriction filler undergoes considerable changes during the rubbing process, apparent in variation in particle size, some decrease in thermal stability, and chemical interaction with the contacting surfaces and accompanying fillers, which has a significant influence on the lubricating properties of the plastic systems[140]. Thus X-ray diffraction at room temperature has revealed the presence of ferrous sulphide in the surface film formed on the steel counterbody during friction of the F-1–MoS_2 system[139]. When copper is present, however, ferrous sulphide is not detected, owing to the greater strength in this case according to the physicochemical characteristics) of polymer–filler bonding. Infrared spectroscopy, X-ray diffraction, and dynamic thermogravimetric analysis have shown that compounds in which interstitial copper atoms are present in the molybdenum disulphide lattice are formed during friction in the range 110–180° C, with a consequent increase in the coefficient of friction[138,139].

Table 3. Composition of surface films formed on steel during friction of ASP self-lubricating antifriction plastic[138,139] (test conditions: p = 2 kgf cm^{-2} and v = 2 m s^{-1}).

ASP	T, °C	Time, h	Crystallite, Å	Product
F-1-MoS_2	50	2	335	FeS
	120	10	335	FeS
	200	10	430	MoO_2
F-1-MoS_2-Cu	50	2	103	—
	120	2	61	—
	200	10	47	MoO_2, CuS

Raising the temperature at the rubbing contact to 200° C produces a sharp change in the character of the thermal friction curves. Diffractograms of the surface film obtained during friction (Table 3) showed the formation of new tribochemical reaction products. The surface film formed from the F-1-MoS_2 antifriction plastic contained molybdenum dioxide, an oxidation product of the disulphide. Its formation was confirmed by electron diffraction of the film[139]. The presence of copper in the system has a more marked effect on the friction curves at temperatures above 200° C. Tribochemical processes occur more vigorously in the surface films, which contain not only molybdenum dioxide but also small quantities of copper(I) sulphide[138,139].

Thus the composition and the nature of the filler have a significant influence on the formation of surface films when antifriction plastics are subjected to rubbing, and also on the tribochemical reactions occurring both in the polymer binder and in the system of fillers.

IV. PROPERTIES OF THERMOSTABLE ANTIFRICTION PLASTICS

The present Section is a brief survey of the properties and fields of application of a few groups of antifriction materials based on thermostable polymers.

1. Self-lubricating Antifriction Plastics based on Phenol–Formaldehyde Resins

Pheno-formaldehyde resins are widely used as binders in the production of antifriction plastics[66,69,70,143–151]. These polymers find widespread application in industry by

virtue of a combination of valuable properties, primarily thermal stability, heat resistance, and wear resistance[152,153].

Phenoplasts—phenol–formaldehyde resins—are most commonly used with various fillers— such as glass fibre, cotton-wool[154], cotton waste[155], pressboard[156], asbestos fibres[157], etc.— in the manufacture of parts of friction units. Good lubricating properties are conferred on phenoplasts by introducing various solid lubricants, such as molybdenum disulphide, graphite, boron nitride, and polytetrafluoroethylene[158–161]. Another common material for friction units is textolite (resin-impregnated fabric laminate), of which ball-bearing cages and parts for electric motors, pumps, and motor vehicles are made. Textolite is used in friction units with a lubricant. Introduction into textolite of molybdenum disulphide, titanium dioxide, graphite, or selenides or tellurides or their mixtures enables the working capacity of a friction unit to be increased without application of an additional lubricant[162].

Among disadvantages of phenol–formaldehyde resins we must include brittleness and instability towards vibrational overloads; those of reinforced materials based on this thermosetting plastic are low heat conductivity, absorption of several liquids, and high coefficient of thermal expansion.

2. Self-lubricating Antifriction Plastics based on Polyamides

Among heterochain macromolecular compounds the best known as antifriction materials are polyamides[163–167]. These are widely used in mechanical engineering for the production of pinions, bearings[168–170], and cages, as well as various wear-resistant parts[171].

The coefficient of friction of polyamides and their wear resistance depend on the load and the sliding rate[172]. Study of the dry friction of polymers having various chemical structures showed[172] that the coefficient for low-pressure polyethylene increases with rise in temperature less sharply than for polyamides, but for polytetrafluoroethylene it decreases. The type of variation in the case of polyamides was attributed[172] to their structure: the presence of polar groups and hydrogen bonds produces a marked increase in energy of molecular cohesion, which intensifies intermolecular interaction and that between the surfaces during friction, the latter increasing with rise in temperature owing to rupture of the interchain hydrogen bonds of the polyamides. A considerable increase in the coefficient of friction is observed at some "critical" load characteristic of each polymer. With this change in the coefficient with load the polyamide sticks on the steel surface and the intensity of abrasion diminishes. Thus a sharp increase in the coefficient of friction of capron to ~0.9 at a sliding rate of ~1 m s^{-1} coincides with the appearance of adhesion of the polyamide on the steel.

The application of polyamides in pure form as structural materials in friction units is restricted by their strongly hygroscopic character, low heat conductivity (0.25–1.0% of those of metals), large coefficient of linear expansion (9.8×10^{-5}), low hardness, dimensional instability, and moderate load capacity at low temperatures[173,174]. Such defects of polyamides are eliminated by the introduction of various fillers, such as graphite[175,176], molybdenum disulphide[165,176,177], boron nitride, metal powders, fibrous fillers[178], and polytetrafluoroethylene[175,176]. Fillers enhance the rigidity and the compressive strength of polyamides, lower the water absorption and the coefficient of linear expansion, and improve considerably the frictional properties.

Thus the introduction of polyethylene into antifriction compositions based on polyhexanamide helps to separate steel and polyamide surfaces undergoing active molecular interaction and to create under heavy-duty régimes conditions for transition from external to internal friction, ensuring prolonged functioning of the dry friction unit with such operation[179].

An important defect of antifriction plastics based on polyamides is their relatively low heat resistance. The operating temperature range for polyamides is 80–140°C. With rise in temperature the antifriction properties deteriorate continuously. Capron and its compositions can be used[163] in friction units at surface temperatures not exceeding 100°C, P-68 polyamide up to 130°C, and AK-7 mixed polyamide up to 140°C.

3. Self-lubricating Antifriction Plastics based on Polyimides

Among cyclochain polymers polyimides are the most widely used as antifriction materials[71,72,74,180–193]. Aromatic polyimides have very high thermal and thermo-oxidative stability. They can be used at temperatures from −150 to +370°C. Polyimide materials surpass all known plastics in wear resistance, which permits their use in unlubricated bearings. Polyimides are highly resistant to radiation, sunlight, and solvents. Their low volatility in a vacuum makes them promising antifriction materials for use in friction units operating in space. Polyimides filled with graphite or molybdenum disulphide are used for the manufacture of ball-bearing cages[181,189,191,192,194].

Investigation of the influence of moisture on the antifriction properties of a polyimide–steel system shows[195] that entry even of a minute quantity of water is accompanied by a sharp increase in the coefficient of friction and in wear. The variation in the antifriction properties of polyimides and compositions based on them is due to the occurrence of mechanochemical processes at the rubbing surface under the influence of the medium.

4. Self-lubricating Antifriction Plastics based on Epoxy-polymers

Epoxy-polymers are finding increasing application as binders for antifriction materials[196–204]. Bearings based on epoxides are usually employed at temperatures from −50 to +230°C, but under large mechanical loads the upper limiting operating temperature is only 155°C.[153] The fillers generally used in epoxide antifriction materials are graphite, molybdenum disulphide, metal powders and oxides, quartz sand, and also fibrous fillers. An epoxy-plastic filled with graphite or molybdenum disulphide[204] possesses high compressive strength, a low coefficient of friction (0.08–0.09), and heat resistance up to 200°C.

To improve the physicomechanical properties, heat resistance, and lubricating properties epoxy-resins are used in compositions with polyarylates[205], phenol–formaldehyde[206,207] and silicone[200,208] resins, polysulphides[209], or rubbers[210]. A special advantage of materials prepared from epoxy-resins is their ability to harden at room temperature and serve as an antifriction liner.

5. "ASP Plastics"

The scientific principles of the production of thermostable antifriction materials developed by Korshak et al. have enabled several new antifriction plastics to be obtained, among which we must note the "ASP plastics"[211] of various brands (AMAN, TESAN, ESTERAN, VILAN, etc.). These are multicomponent filled systems, in which the binders are polymers possessing a combination of necessary properties— thermal stability, resistance to heat, radiation, and chemical attack, and technical suitability for processing. In their combination of properties the ASP plastics considerably excel known dry friction materials— plastics based on polytetrafluoroethylene and fillers (Table 4).[211]

Table 4. Temperature ranges of application of lubricating materials.

Lubricant	T, °C
Liquid lubricants	−60÷+150
Lubricating greases	up to +180
Polytetrafluoroethylene lubricant	up to +220
ASP plastic	−100÷+300

A distinguishing feature of ASP plastics is their low coefficient of friction and its constancy with variation in temperature. The dependence of the coefficient on the rate of slippage and on the pressure is governed by the ambient temperature. Up to 100°C the permissible loads on these plastics in bearing contact are 100–150 kgf cm^{-2}. The ASP plastics are resistant to benzene, oils, and vibration, are unaffected by moisture, and can be stored for long periods.

The principal use of ASP plastics is as self-lubricating retainers in antifriction bearings, and also as linears in friction bearings. Several standard sizes of ball-bearings with ASP plastic retainers have been designed in the Soviet Union, and introduced into the national economy. The use of such plastics at high temperatures is especially promising. Thus ball-bearings with ASP plastic cages remain in a working state at 250°C after 1000 h operation. These plastics can be used in bearing contact units in which high rates (up to 16 000 rev/min) or high loadings (up to 150–200 kgf cm^{-2}) are required with small rates of displacement of the shaft, and also in cases in which translational motion must be realised after prolonged stationary contact[211]. It is possible to make also ASP plastics pinions bearing a low load, which may ensure high rates of rotation of the shaft.

The superiority of ASP plastics is especially noticeable when they are used in friction units in which other lubricating materials cannot be applied because of high temperatures, radiation effects, or other conditions.

* * *

Thus the above survey makes clear how complicated is the problem of designing antifriction plastics. However, several relations have already been established between the chemical structure of thermostable polymers and the frictional properties of filled polymer systems. This offers wide opportunities for obtaining new materials with specified properties by controlled variation of the chemical structure of the polymer binder.

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