Mechanical and Friction Properties of Glass-filled Thermoplastics Modified by Polyethylene Additives

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Synopsis

Temperature and concentration dependences of elasticity modulus, wear and wearability of industrial glass-filled thermoplastics modified by low-density polyethylene were studied. It is shown that polyethylene additive reduces the elasticity modulus in the solid aggregate state of polymer matrix and enhances it in the softening region. For the first time a possibility was found to reduce friction, wear, and wearability of glass-filled thermoplastic materials by incorporating optimum amount of alloying polymer additive thermodynamically incompatible with the polymer matrix.

INTRODUCTION

At present the Soviet domestic industry has adopted production of polymers such as polyolefines, polyamides, polycarbonates, and other thermoplastic materials filled with mineral and glass-fibre fillers. The processing of these materials by extrusion and injection molding leads to drastic wear of equipment. Damage of metal surfaces is observed in transfer zones of solid materials and polymer melt, this resulting in the drop of machinery output and deterioration of product quality.[1-4] The enhancement of wear resistance of the operating members by reinforcing them with coatings on the basis of nickel, cobalt, tungsten and molybdenum involves higher equipment cost.[1] In this connection a necessity arises of creating new compositions of high wear resistance under conditions of processing.

One of the prospective ways of improving the mechanical properties of filled polymers is their modification by polymers of other nature. In the majority of cases the maximum effectiveness of such modification is attained at small dope concentrations.[5-7] Taking into account the interdependence of mechanical and friction properties in solid bodies,[8] an improvement of friction and wear characteristics of a filled polymer may be anticipated as a result of introducing a small quantity of a polymer of other nature. It should be noted that the studies of mechanical and friction properties of polymeric compositions concentrate on either filled polymers or polymer blends. There are but few publications devoted to investigation of more complex systems such as polymer matrix–mineral filler–polymeric modifier.[6,7,9,10] It is this circumstance that calls for studying the mechanical and friction properties of glass-filled thermoplastic materials within a wide range of temperatures and pressures, depending on the content of a mineral filler and polymeric modifier.

Presented in this paper are the results of investigations of temperature and concentration dependences of the elasticity modulus, friction coefficient, wear, and wearability of some industrial glass-filled thermoplastic materials modified by polyethylene.

EXPERIMENTAL

We studied the following systems: polyamide 66 OST 6-06-369-74 (PA 66), polyamide 6 OST 6-06-09-76 (PA 6), polyoxymethylene TU 6-05-211-899-76 (POM), and polycarbonate TU 6-05-1668-80 (PC). Glass roving (brand RBR-13-25220-019, GOST 17139-79) was used as a filler (particle diameter of the order of 13×10^{-6} m, and length about 3×10^{-4} m); low-density polyethylene (brand 15802-020, GOST 16337-77) (PE) was used as a modifier.

PE additive was introduced in the amount of up to 10 mass % relative to the polymer matrix, the content of the glass fiber in all the cases was 30 mass % relative to the polymer constituent. The compounds were prepared in a laboratory extruder at temperatures typical for processing glass-filled thermoplastic materials. Longitudinal moduli of elasticity E were determined from the slope of the initial portions of stress–strain curves, measured on a cylindrical sample under uniaxial compression.

Friction characteristics were measured in a contact with nitrided steel (38 2MYUA, GOST 4543-71), and 08 kp, GOST 1050-74, used now for the manufacture of the operating parts of the processing equipment and employed in laboratory model experiments to estimate the wearability of polymer compounds by a technique described earlier[11] under pressures ranging from 1 to 10 MPa. Temperature dependences of the friction coefficient were investigated at a sliding speed of 3×10^{-3} m/s in the course of continuous heating of a metal sample at the rate of 0.25 K/s. The tests for wear were conducted at a pressure of 7.0 MPa, sliding speed of 0.5 m/s, the friction path being 15×10^3 m at various temperatures. The extent of wear of metal and polymer and polymer samples was determined gravimetrically with the accuracy of weighing 5×10^{-7} kg. The linear wearout rate of the samples was then calculated by a common method.[12] Relative measurement error of the elasticity modulus and the friction coefficient were 5–7%; that of wearout, of the order of 10–15%.

The effect of the filler and modifier on the structure of the crystalline phase of polymers was studied by differential scanning calorimeter (Model DSM-2); the morphology of compositions were studied by means of polarizing microscope MIN-8; the possibility of chemical interaction of composition components was estimated by infrared spectroscopy, TGA and DTA.

RESULTS AND DISCUSSION

Mechanical Properties

The data on temperature dependences of the elasticity modulus given in Figure 1 show that the introduction of polyethylene into filled and unfilled polymers has no essential effect on the pattern of temperature dependence of the elasticity modulus. At the same time, the addition of low-modulus
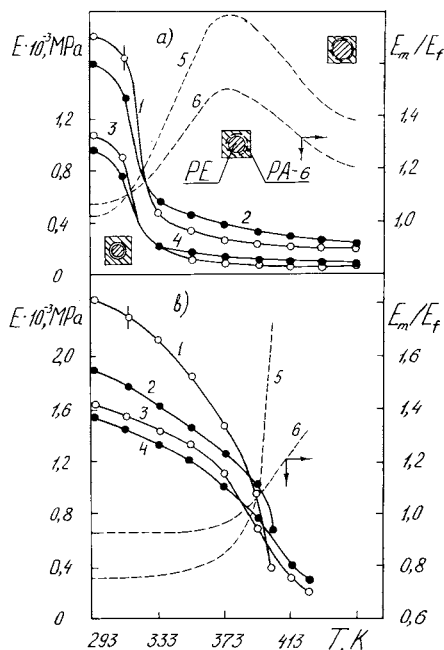
Fig. 1. Temperature dependences of elasticity modulus (1–4) and relative modulus (5,6) of compositions: (a) (1) PA 6 (glass-filled); (2) PA 6 (glass-filled) + 4% PE; (3) PA 6; (4) PA 6 + 4% PE; (b) (1) PC (glass-filled); (2) PC (glass-filled) + 4% PE; (3) POM (glass-filled); (4) POM (glass-filled) + 4% PE; (5) ratio of elasticity modull of compositions 1 and 2; (6) ratio of elasticity moduli of compositions 3 and 4.

polymer, as expected, leads to the drop of E of the composition in the solid aggregate state, while in the softening region of polymer matrix some rise of the modulus is observed. Along with this the relative moduli (E_m/E_f) shown in Figure 1 by dotted lines (where E_m and E_f are the moduli of glass-filled polymers with 4% addition of polyethylene and without additive, respectively) rise sharply. For polyamide-based compositions the maximum rise occurs at temperatures close to polyethylene melting point T_m, or to high-temperature α-relaxation of polyamides.[13,14] For compositions based on polycarbonate (PC) and polyoxymethylene (POM), the rise of modulus is observed, correspondingly, in the glass transition region and at $T \geqslant T_m$, i.e., in the softening region of polymer matrix; here, E_m/E_f rises with temperature. It is interesting to note that in the presence of filler the efficiency of the polyethylene (PE) additive is higher, independent of whether the modulus is decreasing or rising [see Fig. 1(a)].

The microscopic data indicate that in absence of glass fiber the PE particles in the polymer matrix are present in the form of dispersed inclusions differing considerably in size (on the average from 1 to 20 μm, larger particles up to 100 mum also being encountered). Upon introduction of the glass fiber into a polymeric mix no dispersed PE inclusions are observed, which indicates their dispersion to dimensions below the resolving power of the microscope (of the order of 1–2 μm) (compatibility of polymers is ruled out, since the DSC thermograms at 388 K exhibit a PE melting peak,

practically in all compositions). The improvement of the polyethylene dispersion quality due to the presence of the glass fiber results in an increase of its surface area and, consequently, in the rise of its efficiency as a modifier.

To analyze the temperature dependence of the modulus, we shall proceed from the following concepts. Since the polymer modifier (PE) has a lower melting point as compared with the matrix, the PE inclusions, during the cooling process of compositions from the melt, will restrict the growth of structural elements of the basic polymer, playing the part of inert interlayers. It is most probable that the PE will be localized in the least ordered amorphous region between the end faces of crystallites (in crystallizing polymer matrixes), thus changing the mobility of tie macromolecules. In other words, the variation of the modulus of glass-filled modified compositions should be attributed to the structure variation of the amorphous regions of the crystallizing polymer matrix.

On cooling of polymer samples to a temperature below the melting point of polyethylene, crystallization and sharp drop of its specific volume (V) take place. This may result either in delamination of PE inclusions from the matrix and formation of microcavities, or all-around extension of PE inclusions, provided a sufficient adhesion exists between the latter and the polymer matrix (taking into account low cohesion energy of polyethylene, the latter case seems less probably). Evidently, similar effects will lead to composition modulus decrease, this being observed experimentally in the solid aggregate state of polymer matrix. Apart from that, the addition of PE leads to some drop of the degree of crystallinity of polymer matrix (see Table I).

The specific volumes of the matrix and modifier increase with temperature and, according to available data,[15] the increase of polyethylene V on melting is substantially higher than in other polymers investigated by us. The increase of the volume of PE inclusions should lead to the appearance of excessive hydrostatic pressure in the intercrystallite layers of the con-

TABLE I
Thermal and Thermophysical Characteristics of Glass-Filled Polymer Compositions

No.	Polymer composition	T_1 (K)	T_m (K)	T_2 (K)	ΔH (kJ/mol)	X (%)
1	PA 6	481	495	505	49	20
2	PA 6, glass-filled	472	495	511	40	19
3	PA 6, glass-filled + 4% PE	442	493	500	37	17
4	PA 6, glass-filled + 4% PE, anneal.	461	493	505	38	18
5	PA 66	507	533	543	72	24
6	PA 66, glass-filled	494	533	543	65	22
7	PA 66 + 4% PE	—	532	542	42	15
8	PA 66, glass-filled + 4% PE	—	532	540	33	10
9	PA 66, glass-filled + 4% PE, anneal.	493	532	542	47	17
10	POM	412	441	453	160	49
11	POM, glass-filled	412	441	450	141	44
12	POM, glass-filled + 4% PE	408	438	452	122	39

tinuous phase. As a result of this, the distances between the crystallites will increase, thus leading to a specific "self-reinforcement" of the system. In case of the polyethylene trapped in the interphase, there may occur a sort of "self-healing" of structure defects and reduction of internal stresses arising in the interphase region due to a difference in the thermal expansion coefficients of polymer and glass fiber. So, according to the concepts of Paul and Newman,[16] presence of a soft interlayer between the solid fillers and sufficiently rigid polymer matrix has a favorable effect on system properties, with the best effect attainable when the interlayer modulus does not exceed 0.1 of the matrix modulus. In compositions investigated by us this ratio is also rather close to 0.1.

With further rise of temperature, softening of polymer matrix takes place, e.g., in the region of high-temperature α-relaxation. The onset of thermal mobility by the intercrystallite matrix sections which are under the action of excess pressure of polyethylene is accompanied by stress–relaxation and a drop of elastic energy stored up in the tie chains. As a result, the stresses and, consequently, the reinforcing effect should diminish, this being observed experimentally in compositions based on polyamides.

Taking into account the fact that the effect of PE on the modulus of glass-filled polymers is manifested, mainly, due to its action on the structure of amorphous regions, a rise of modification efficiency with drop of crystallinity of the polymer should be expected. In fact, such correlation was established in our studies (see Fig. 2). In solid aggregate state [Fig. 2(a)] the relative modulus of compositions grows with the increase of polymer matrix crystallinity (X) (the crystallinity of the samples was determined, as $X = \Delta H / \Delta H_{cr}$, where ΔH_{cr} is the melting heat of crystalline sample,)[17] with maximum departure of the ratio E_m/E_f from unity being observed in the amorphous polycarbonate (PC). In the softening region of polymer matrix the relative modulus decreases with the rise of X, with the maximum efficiency of reinforcement being also observed in PC [Fig. 2(b) shows maximum values of E_m/E_f obtained from experimental curves of Fig. 1]. In high
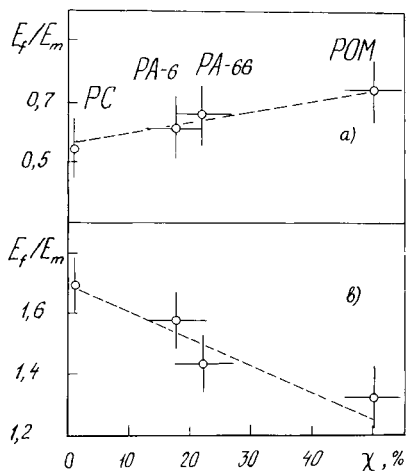

Fig. 2.   Dependence of relative modulus E_m/E_f on crystallinity of glass-filled thermoplastics: (a) T = 293 K; (b) $T > T_g$.

crystalline polyoxymethylene the modulus is determined, mainly, by the elastic properties of the crystalline structure, and the effect of the modifier is, practically, absent. Here, the departure of E_m/E_f from unity is minimal.

Figure 3 shows modulus dependences of glass-filled PA 6 on polyethylene concentration (C). As follows from Figure 3(a), the incorporation of PE leads to a steady decrease of the elasticity modulus in the solid aggregate state of polyamide. In this instance, the calculated curves indicated by dotted lines are in a good agreement with the experiment (the calculation was carried out according to the generalized Nielsen equation,[14] the filler modulus assumed to be zero:

$$\frac{E_m}{E_f} = \frac{1 + AB\Phi_2}{1 - \psi\Phi_2}$$

where Φ_2 is the volume fraction of the filler (polyethylene); A, B, and ψ are the constants, calculated from boundary conditions by means of the well-known formula.[14]

The coincidence of experimental and calculated curves conforms our hypothesis about the appearance of microcavities at temperatures $T < T_m$ of PE. Certain lowering of experimental curves is, probably, caused by polymer amorphization and/or the increase of the number of defective crystals in the presence of filler and modifier (see Fig. 3 and Table I).

Above the polyamide glass-transition point the behavior of the temperature–concentration dependence changes: the curves exhibit a maximum in the region of $C = 2\%$, with the polyamide melting heat dropping sharply [see Fig. 3(b)]. Taking into account that the modification efficiency increases with the decrease of polymer crystallinity, such a pattern of dependence $E(C)$ becomes quite understandable.

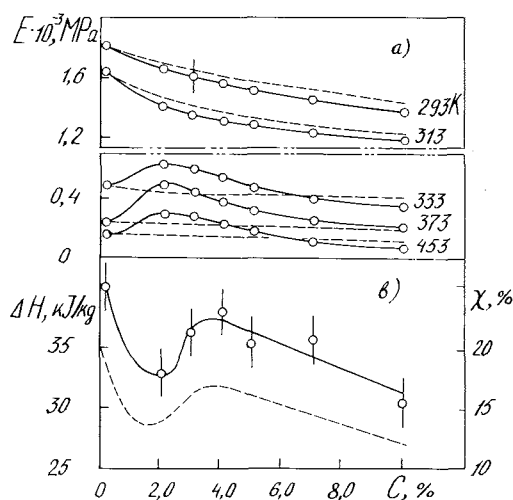Upon introduction of PE into glass-filled PA 6 there occurs a drop of

Fig. 3.   Effect of polyethylene concentration (C) on: (a) elasticity modulus E; (b) melting heat ΔH of glass-filled PA 6. Dashed lines show: (a) calculated concentration dependences, (b) crystallinity of polymer matrix PA 6 (X).

polyamide melting temperatures; i.e., the starting (T_1), maximum (T_m) and the end temperature (T_2) of endotherms (see Figs. 4 and 5). The most substantial drop (by 30–35 K) is observed in T_1 at PE concentration below 4%. Taking into account that PA 6 contains a sufficiently large amount of low-molecular products[18] with lower melting temperatures, it may be supposed that at $C \leqslant 4\%$ the low-molecular products are dissolved in PE. Apparently, this should result in a sharp drop of T_1. It is interesting to note that at $C = 2\%$ the PE melting peak is, practically, not observed. A slight shift of polyamide T_m indicates that the modifier actually does not affect the primary crystalline regions of the polymer. It is worth noting that for compositions PA 6–PE, after the PA 6 melting peak, the DSC curves exibit an exothermic peak with maximum at 505 K (see Fig. 5). Upon annealing above the polyamide T_m this peak does not appear. With the increase of modifier concentration the peak area increases (see Fig. 4), its shift with temperature was not observed. It is likely that the appearance of the exothermic process at 505 K is associated with the dissolution of low-molecular homologues of PE and PA 6. The PE melting maximum, practically, does not depend on the polymer concentration in the polyamide, which indicates that the primary crystalline regions remain intact. Due to a quite rapid melt cooling (exceeding, evidently, the rate of equilibrium structure formation) at first compositions with a structure of overcooled melt are produced, while on repeated heating a phase decomposition takes place in the melt. It should be noted that according to TGA, DTA, and infrared spectroscopy data, no chemical transformation of polymers occur in this temperature range.

With the PE content exceeding 2%, ΔH of polyamide starts to grow. The rise of crystallinity within this range of additive concentrations may be associated with the improvement of structural homogeneity of the polymer matrix due to the localization of low-molecular admixtures on the surface of the polymer modifier.[5,19] With the increase of crystallinity, the effect of
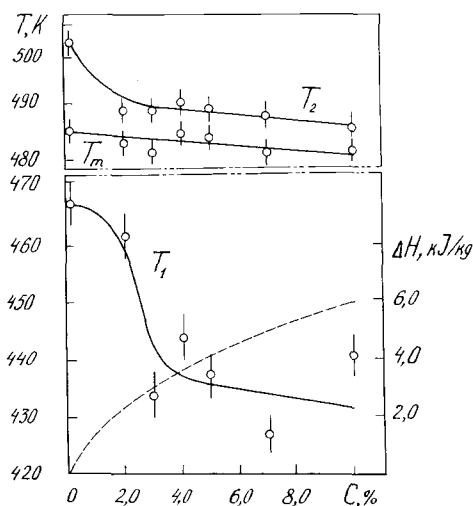

Fig. 4.   Dependece of starting (T_1), maximum (T_m), and end temperatures of compositions based on glass-filled PA 6 on polyethylene concentration (C). Dashed line indicates heat dependence of exothermic effect (ΔH) with maximum at 505 K.
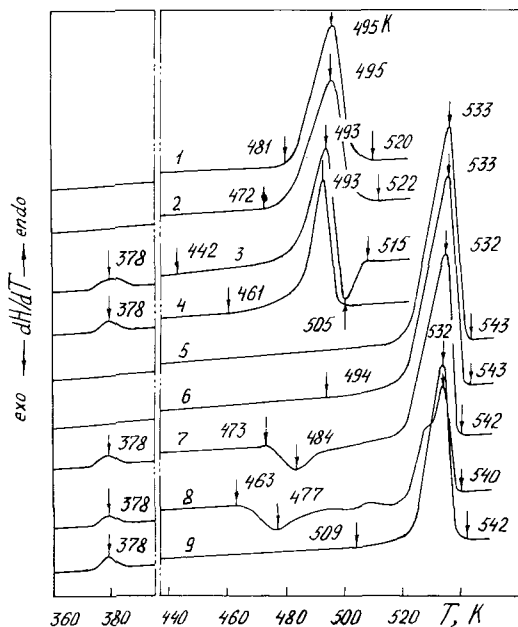
Fig. 5.   DSC curves of compositions based on PA 6 (1–4) and PA 66 (5–9): (1,5) initial polymers; (2,6) glass-filled polymers; (3,8) glass-filled polymers with additive of 4% of polyethylene; (4,9) the same after annealing; (7) PA 66 + 4% PE.

modulus increase by the addition of PE should be diminishing, and this has been observed experimentally [see Fig. 3(a)]. Henceforth, the degree of PA 6 crystallinity decreases monotonically, due, probably, to the increased amount of polymer contained in the interphase layer. The decrease of the elasticity modulus may be caused, for instance, by the fragmentation of crystalline aggregates as a result of the excessive amount of PE penetrating into the intercrystallite side layers.

Calorimetric studies of compositions based on PA 66 containing a small amount of low-molecular homologues have shown that, apart from the decrease of polyamide crystallinity, the introduction of PE leads also to a retardation of the crystallization process. Thus, according to Figure 5, exothermic effect is observed at 60–70 K below the PA 66 melting maximum, the area of this effect being commesurate with the area of the melting peak. After annealing of the samples at $T > T_m$, this effect disappears, whereas the melting heat somewhat rises, but remains considerably lower than ΔH of "pure" and glass-filled polymers (see Fig. 1). In the presence of filler, the exothermic effect is manifested more distinctly, due to the increase of PE surface area. The temperatures T_1 and T_2 of polyamide 66 melting drop with the introduction of a modifier, while T_m remains, practically, constant.

In the study of compositions based on POM, as in the case of PA 6, some drop of T_m is found upon the introduction of PE, but no exothermic effects were observed before and after the melting of the polymer matrix.

Thus, the addition of polyethylene in the amount of up to 10% mass brings about a decrease of the elasticity modulus in glass-filled compositions within the region of solid aggregate state of the polymer binder, and an

increase of E within the softening region. With the introduction of the glass fiber, the modification efficiency rises considerably due to PE dispersion in the presence of filler. The modification efficiency increases also with the decrease of crystallinity degree in the polymer binder, i.e., the effect of polyethylene on the modulus should be attributed, mainly, to its action on the structure of matrix amorphous regions.

Friction Properties

Presented in Figure 6 are temperature dependences of the friction coefficient (f) of investigated polymer compositions. It follows that incorporation of PE into unfilled and glass-filled thermoplastic materials essentially changes the pattern of function $f(T)$. Here, the friction coefficient f changes throughout the entire temperature range. The maximum modification efficiency is attained at temperatures above the polyethylene T_m. Relative friction coefficients (f_m/f_f) are in this case minimal (f_m and f_f being the coefficients of a glass-filled polymer with the addition of 4% of PE and without the additive, respectively). It is worth noting that the maxima of $f(T)$ curves in the region of glass-transition point are also seen upon modifier introduction, but are less pronounced and are shifted toward the region of high temperatures by 10–15 K.

In analyzing the temperature dependences of $f(T)$, we shall proceed from the results obtained in the investigations of the elasticity modulus; viz., at temperatures above the polyethylene melting point T_m excess hydrostatic pressure arises in microcavities containing PE. Evidently, under conditions
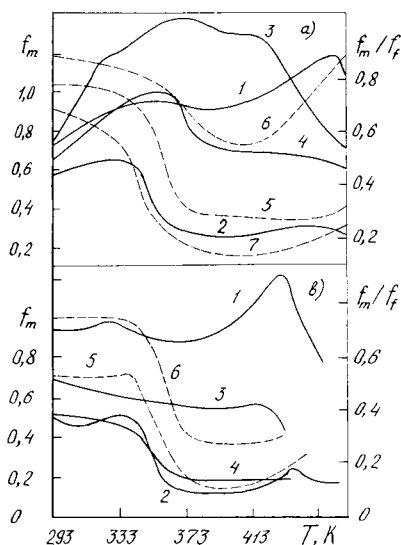

Fig. 6. Temperature dependences of friction coefficient f (1–4) and relative friction coefficient f_m/f_f (5,6) of compositions: (a) (1) PA 6, glass-filled; (2) PA 6, glass-filled + 4% PE; (3) PA 6; (4) PA 6 + 4% PE; (b) (1) PC, glass-filled; (2) POC, glass-filled + 4% PE; (3) POM, glass-filled, (4) POM, glass-filled + 4% PE; (5) ratio of friction coefficients of compositions 1 and 2; (6) ratio of friction coefficients of compositions 3 and 4. Curves 1–6 correspond to pressure 1.0 MPa, curve 7 to 10.0 MPa.

of friction interaction with a metal abradant, microcavities located near the surface will be broken and the molten polymer-modifier will be "squeezed out" into the friction zone, thus forming a lubricating layer.[20] The transfer of polyethylene is also possible due to hydrodynamic pressure arising during melt movement. It should be noted that the rise of temperatures of the maxima on curves $f(T)$ upon the introduction of PE may be explained by impaired heat transfer from the metal sample to the polymer owing to the presence of the separating lubricating layer.

Introduction of polyethylene into unfilled polymers also leads to a decrease of the friction coefficient; yet the modification efficiency is essentially lower. In our opinion, this is caused by a relatively low dispersion level of PE in the polymer matrix and low elasticity modulus of unfilled compositions. It is worth noting that modification efficiency increases considerably with the rise of temperature (see Fig. 6, curve 7).

As can be seen from Figure 7, the most significant decrease of f in glass-filled PA 6 is observed upon introduction of a small amount of polyethylene (up to 4–5%). Presumably, squeezed out by the excessive pressure from the matrix and forming in the contact zone a thin film which acts as a lubricating layer. Evidently, the thickness of PE film in the zone of friction contact in this composition range is close to optimum, which, according to the theory of boundary friction,[21] should not exceed the total height of microroughness of the friction bodies (according to the profilographic data, in this case it is about 10^{-6} m). This assumption is supported by a sharply retarded rate of f decrease with further increase of PE content, which may
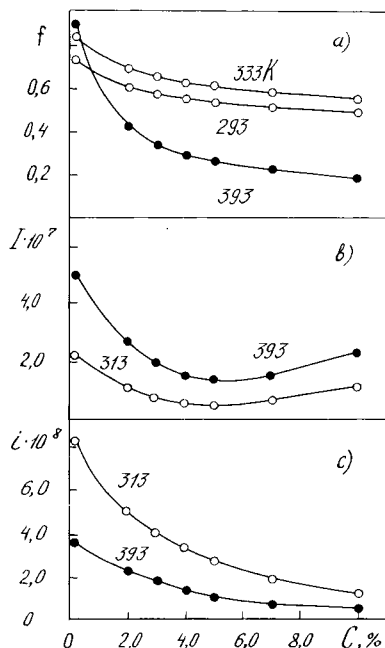

Fig. 7. Effect of polyethylene concentration on: (a) friction coefficient f; (b) wear I; (c) wearability of glass-filled polyamide 6. Pressure in friction contact zone: (a) 1.0 MPa; (b,c) 7.0 MPa. Number at the curves refer to temperature of measurement (K).

be attributed to the transition from boundary to hydrodynamic friction conditions. Dashed lines in Figure 7 show the additivity lines connecting the f of the glass-filled PA 6 and PE (at $T > T_m$ of PE its friction coefficient was assumed to be zero). Experimental lines run considerably lower than the additive ones; at $C = 10\%$ the values of f in the modified compositions are quite close to the polyethylene friction coefficient f. This indicates a dominating effect of PE on the friction coefficient of glass-filled compositions.

The filling of microroughnesses on the surface of the metal abradant by the lubricating layer is equivalent to the increase of distance between the cutting edges of the metal and the polymer sample surface. This should, therefore, lead to wear reduction. Indeed, this is exactly what we observed in our experiments [Fig. 7(b)]. It is remarkable that in this case the sharpest drop of linear wear intensity (I) is in the region of low PE content (up to 4–5%). With the incorporation of more than 4–5% of polyethylene, a gradual increase of polymer sample wear takes place, this being, probably, caused by certain structure disordering and a decrease of polymer matrix crystallinity. In this case dependence of f on C is more pronounced at temperatures above T_m of PE.

The wear of metal abradant (steel 08 kp) also decreases in the presence of PE, although dependence of i on the content of PE is described by a more smooth curve [Fig. 7(c)]. Apparently, the lubricating PE layer deactivates macroradicals formed in the friction zone as a result of mechanical destruction of the polymer modifier. This effect is more pronounced at lower temperatures when the polymer transfer to metal surface is at its minimum. According to microscopic data, the friction transfer is observed in the friction of all compositions (most intensive in PA 66 and PC). This leads to the "screening" of metal surface from the abrasive action of fiber–glass particles and to some drop of polyethylene efficiency. The friction transfer of polymers to the substrate surface grows with temperature.

On the basis of the above data, it may be expected that the content of PE of the order of 4–5% will also prove to be the best for other thermoplastic materials which are thermodynamically incompatible with PE. Should it be supposed that, owing to the presence of the lubricating PE layer, the adhesion component of the friction force will be reduced to a minimum, then the friction characteristics of a polymer composition will, probably, be determined by the deformation component of the friction force, which depends on the mechanical properties of the polymer-matrix.

As follows from Figure 8, the values of f for the glass-filled compositions containing 4% of PE are really decreasing with the growth of sample elasticity modulus. A higher efficiency of PE additives in PA 6 composition as compared to PA 66, both of them being of similar chemical structure, is, apparently, due to a higher content in PA 6 of low-molecular products (monomers and oligomers) capable of penetrating, together with PE, into the friction contact zone and forming the lubricating layer.[22] The introduction of 4% of PE into all studied systems results in the decrease of both I and i [Figs. 8(b) and 8(c)], this effect being most pronounced in the case of glass-filled POM and PA 6, which exhibit maximum wear and wearability in the absence of a modifier.[23]
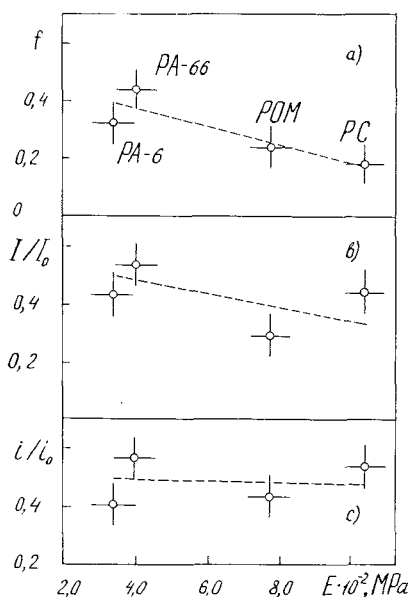
Fig. 8.   Effect of elasticity modulus (E) of glass-filled thermoplastics modified by 4% PE on: (a) friction coefficient f; (b) relative wearability of polymer I/I_0; (c) relative wearability of metal i/i_0, where I, i and I_0, i_0 are the wear and wearability of samples with and without additive, respectively; $T = 393$ K; pressure in friction contact zone: (a) 1.0 MPa; (b,c) 7.0 MPa.

Investigations carried out earlier[23] have shown that in a number of cases the increase of wear resistance of polymer compositions leads to a decrease of metal substrate wear. In this connection it was to be expected that the wear of metal samples would be decreased with the use of certain anti-friction additives in polymers. As modifiers of glass-filled thermoplastic materials we used traditional antifriction additives of inorganic (aluminium powder APS-IA, GOST I0096-76, aluminum oxide of 3–5 μm dispersity, copper powder PMS-2, GOST 4960-75, molybdenum disulfide brand MWChP) and organic (glycerol, GOST 4960-75, cylinder oil 38, GOST 6411-76, silicon oil PFMS-4, GOST 6824-76) origin, as well as polymeric additives, low-density polyethylene, and polytetrafluoroethylene, GOST 10007-72. The concentrations of additives were taken according to published data.[8,22,24]

To estimate reliably the efficiency of modifiers under conditions of processing and operation, comparative tests were conducted on a device specially designed for determination of wearability of polymer melts,[25] and on an experimental testing unit imitating the operation of a metal-and-polymer friction assembly.[23] Figure 9 presents friction characteristics of modified glass-filled polyamide PA 66 ks TU 6-11-15-42-76 containing 30% mass of fiber glass.

From Figure 9 follows that the introduction of aluminum oxide and dispersed metals proved ineffective. So, with their introduction the friction coefficient value remains, practically, unchanged, the contact temperature drop is negligible, and the wear and wearability are higher (except for copper). Organic additives essentially reduce the friction coefficient, the most efficient among them being the cylinder oil. With its use the temperature in the friction contact zone drops by 25–30 K, but the wear and
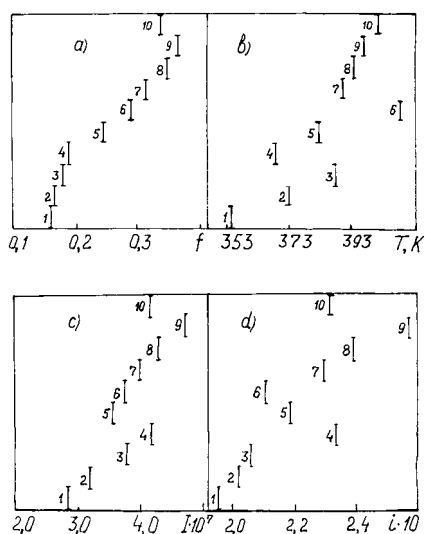
Fig. 9. Relative effect of antifriction additives on friction coefficient (a), temperature in contact zone (b), wear (c), and wearability (d) of glass-filled PA 66. Numbers in the figure denote: glass-filled PA 66 without additive (1), with 3% of aluminium oxide (2), with 3% of aluminium (3), with 3% of copper (4), with 3% of glycerol (5), with 3% of silicon oil (6), with 3% of cylinder oil (7), with 2% of molibdenum disulfide (8), with 10% of Teflon (9), and with 4% of PE (10).

wearability are, practically, not reduced. The glycerin additive reduced considerably the metal wear, while the friction coefficient decreases insignificantly and the contact temperature rises. The additives of molybdenum disulphide and polytetrafluoroethylene proved to be quite efficient, but these materials are costly and require special technological methods for their introduction under conditions of processing. The polyethylene additive produced the effective reduction of the friction coefficient (1.9–2.1-fold), the contact temperature drop by 40–50 K, the decrease of I by a factor of 1.4–1.5 and of i by a factor 1.3–1.4.

The introduction of PE into glass-filled PA 6 proved to be most effective, which should, probably, be attributed to the presence of low-molecular fractions in this latter polymer. So, as compared with the unmodified glass-filled PA 6, the friction coefficient decreased 2–5-fold, composition wear became 5–7-fold lower, and metal abradant wear was 2.0–2.5-fold less.

Presented in Table II are the results of investigations of melt wearability and of the thermal stability of glass-filled polymer compositions on the basis of PA 66 and PA 6 (thermal stability of compositions was estimated from the TGA data as temperatures of 10% and 50% mass loss of the samples T_{10} and T_{50} and as effective activation energy of thermal degradation E_{ef}.[26])

The experimental temperatures T_{10} and T_{50} for compositions based on PA 6 and PA 66 was about 533 and 593 K, respectively; the pressure was of the order of 10–15 MPa, worm speed being 2.5 rps.

The obtained data show that additives of inorganic origin, the molybdenum disulfide inclusive, practically, do not reduce the wearability of polymer melts. At the same time, the metals enhance, to a certain extent, the thermal stability of the compositions. The glycerin and cylinder oil

additives proved to be of little efficiency. The drop of thermal stability of compositions upon their introduction is, evidently, caused by decomposition of these additives in the polymer melt. The additives of thermally stable silicon oil and polyethylene reduce metal wear by a factor of 1.4–1.8. The polytetrafluoroethylene additive proved to be most efficient. Its introduction resulted is a 2.0–2.2-fold wear reduction for compositions on the basis of PA 66. The reduction of metal wear due to the introduction of polymer additives may be due to several causes. The additives of PE and the PTFE are of higher thermal stability than the polyamides, so that their introduction enhances the total thermal stability of the composition. In addition to that, the polyethylene and PTFE, being of higher viscosity than the polyamides,[17] should, due to rheologic peculiarities of the flow, be forced out during extrusion toward the metal surface, thus "screening" the metal against the abrasive action of the fiber glass particles. It is also worth mentioning that the introduction of the polyethylene and PTFE results in a certain increase of extrusion output, which, according to Ref. 27, also promotes reduction of metal wear. Analyzing the results obtained, it should be borne in mind that the efficiency of additives can, probably, be enhanced by selecting their optimal concentrations (except PE, for which we have already found the optimum). However, this requires special investigations and is out of the scope of this paper.

CONCLUSIONS

The polyethylene additive reduces the elasticity modulus in the region of solid aggregate state of polymer matrix and increases it in the region of

TABLE II
Effect of Antifriction Additives on Wearability of Melts and Thermal Stability of Glass-Filled Polyamides

Polyamide	Modifier (% mass)	Wearability i_{p2} (mg/cm)	Extrusion efficiency Q (kg/h)	Thermal stability		
				E_{ef} (kF/mol)	T_{10} (K)	T_{50} (K)
PA 66, glass-filled	—	2.0	2.4	205	633	723
	Aluminum oxide, 3%	2.1	2.6	210	653	723
	Aluminum, 3%	2.05	2.9	215	663	728
	Copper, 3%	1.91	2.6	220	688	743
	Glycerin, 3%	1.82	2.7	200	618	713
	Silicon oil, 3%	1.42	3.0	205	643	743
	Cylinder oil, 3%	1.78	2.8	190	623	718
	MOS_2, 2%	1.85	2.4	210	648	733
	PTFE, 10%	0.95	3.7	225	663	743
	(Polyethylene, 4%)	1.25	3.3	220	643	733
PA 6, glass-filled		1.92	2.6	210	663	728
	Polyethylene, 4%	1.06	3.5	225	673	733

softening; the modification efficiency rises in this case with the decrease of polymer crystallinity. This is indicative of the effect the additive has on the structure of amorphous regions in the polymer matrix.

A possibility is shown of reducing friction, wear, and wearability of glass-filled thermoplastic materials by introduction of optimum amount of an alloying polymer additive which is thermodynamically incompatible with the polymer matrix. As compared to the binary polymer blends, the efficiency of the polymer additive rises in the presence of fiber glass owing to the increase of dispersion degree of the polymer matrix.

High efficiency of polymer modifiers, as compared to traditional inorganic and organic antifriction additives, has been established under conditions of processing and operation of compositions in friction assemblies.

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