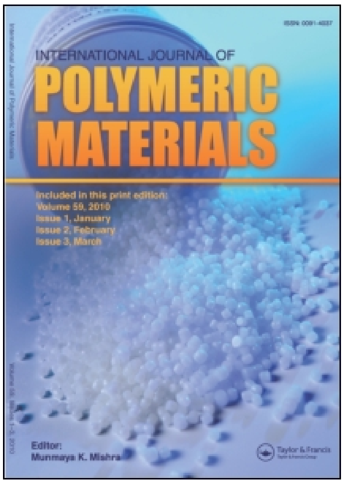

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On the Mechanism of Thermoplasts Modification by Ultradispersed Inorganic Fillers

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The polarizing mechanism enhancing service characteristics of thermoplasts filled with ultradispersed inorganic compounds (SiMeON) obtained by plasma-chemical synthesis has been studied. The results of examining spectra of thermostimulated currents and polarizing charge surface density of filled polyethylene, polyvinyl butyral and polytetrafluoroethylene have proved the presence of a spontaneous electric charge in the filler. Experiments have been conducted to simulate the effect of the filler particle electric field on the strength and permolecular structure of contacting surface layer of the polymer. Recrystallization of the binder in electric field of the filler particles is shown to result in varying crystalline structure and phase transition temperature as well as increased strength of the polymer surface layers at the filler particle boundary. The formation of filled by ultradispersed particles polymer material is accompanied by generation of the polarizing charge in the binder. The mechanism of polarization complements traditional ideas on physico-chemical nature of polymer filling.

Keywords: Thermoplastics; filled charge density; polyethylene; polyvinyl butyral; polytetrafluoroethylene; particle electric field

INTRODUCTION

Ultradispersed (with about 0.01 – 0.10 μm particle size) inorganic high-melting fillers on silicon nitride base have a structure of solid solutions

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where nitrogen atoms are partially substituted by oxygen while silicon atoms by aluminum, boron and yttrium ones [1]. Polymers filled by these substances display extraordinary properties which surpass the traditional plastics in wear resistance and deformation characteristics [2, 3]. This is attributed to high defectiveness of their crystalline structure as well as high specific surface and low particle size of the filler [1]. If to reduce filler particle size the share of the binder decreases and it transforms into the state of a surface layer with special properties [4]. There are grounds to presume that the technique of producing ultra-dispersed fillers involving high-frequency plasma assists electric polarization of the filler. The particle charge state plays an essential role in shaping the filled polymer properties.

The present work object is to investigate the mechanism of improving service indices of polymers filled by ultra-dispersed particles of inorganic refractory substances, to study such fillers charge state and its effect on physico-chemical processes of filled plastics formation.

EXPERIMENTAL

Ultradispersed inorganic compounds of sialon type (US) were obtained by a plasma-chemical method [2]. Powders of Si, Al, Y and B oxides were introduced into a flow of nitrogenous high-frequency plasma. The mean mass temperature of the flow in the zone of powder feeding was 5600 – 6200 K. To cool the plasma down to a temperature of stable behavior of nitrogen-containing Si products (2300 K) and to increase active nitrogen content ammonia was supplied to the reaction zone. Due to full evaporation of the solid material the reaction of synthesis proceeded in a vapor-gas phase and their products condensed as US powder:

$$\mathrm{Si} + \mathrm{Me\ oxide} + \mathrm{N_2} \xrightarrow{\text{nitrogen HF-plasma}} \mathrm{SiMeON}$$

Electrophysical parameters of US and filled by them polymer samples were determined using an automatically controlled measuring system 31/53 of Tektronix Co.

The samples as 0.1 to 0.5 mm thick polymer coatings on Al were electrically polarized in corona discharge using a high-voltage source ≪Razryad-1≫, thus producing corona-electrets (CE); or in the field of electrodes contacting (through a dielectric film) the sample and accepting a constant voltage from a source of current B5-50, thus producing thermoelectrets (TE).

In order to simulate physico-chemical processes taking place in polymers when filled with US, TE were formed in PTFE samples as discs cut from the rod. The disc was brought into contact with the polarizing electrode (U = 300 V) and subject to thermal treatment under the following conditions: i) heating to 200°C at velocity v = 180 degree/h, from 200 to 340°C at v = 70 degree/h; ii) endurance under 340°C for 1 h; *iii*) cooling from 340 to 20°C during 5 h.

Current spectra of thermally stimulated depolarization (TSD) were obtained by the electret-thermal analysis and surface density of polarizing charges was measured by the induction-compensation method following State Standard 25209-82. When determining TSD currents a dielectric lining was placed between the sample and electrode. So, the induced current was recorded which sign is opposite to that of the charge being measured.

The deformation and strength characteristics of TE were estimated adhering to State Standard 11262-80 (listed in the paper data are average values from not less than 20 tests). Temperatures of endothermal peaks on DTA curves were determined using Derivatograph Q-1500. The relation of crystalline phase *versus* noncrystalline one was checked by X-ray spectrometer Dron-3,0. Separation of lines and crystalline phase identification was performed using *Cor* and *Background* programs.

RESULTS AND DISCUSSION

Investigations of the charge state of US-filled polymers were undertaken with three binders differed in their polarizability and time of the polarizing charge life, namely LDPE, polyvinyl butyral (PVB) and PTFE. The study of filled PTFE is of an individual applied importance, that's why it was continued on models simulating the polymer-US particle system.

LDPE

Table I shows electrophysical parameters of US-filled LDPE samples. It is evident that electric conductance of the samples rises abruptly at filling, thus bringing LDPE dielectric close to a semiconductor state. This is also proved by kinetic dependencies of TE and CE charge relaxation of these materials (Fig. 1), *i.e.*, the higher degree of filling the lower polarizability of the samples and closer to null (under all other conditions being equal) surface density of σ_{ef} charge.

Spectra of TSD current of nonpolarized samples show that the initial LDPE does not have the polarizing charge but if filled with 0.5% of US its temperature dependence displays flash-ups of current. At 2% and above US concentration a stable current arises in the samples like that of conductivity, though its stable direction and noticeable magnitude make it possible to consider it a TSD current of some accumulated in the samples charge. Since the samples were not subject to electric polarization, most probable nature of the current is liberation of the polarizing charge at heating which is intrinsic for US. This is confirmed by the TSD current spectra of a tablet obtained by US powder compression. The spectrum was taken by a set-up intended for polymer TSD with 300°C upper temperature limit. In Figure 2 stable peaks evidence that high-temperature traps for charge carriers are present in US. They are more numerous on US spectrum in the up to 2000°C temperature range and charge carriers entrapped on them are preserved more stable than on low-temperature traps peculiar for polymers.

If so, then spontaneous polarizing charge of US exerts an effect on polarization of filled polymers as well as on US particles adhesion to the binder (electrostatic component of adhesion) and on polymer crystallization in the particle vicinity thus governing structure and properties of filled plastics.

TABLE I Electric properties of LDPE-based samples

US filling mass%	*Dielectric permeability*	*Specific conductance*
0	1.56	10^{-15}–10^{-16}
0.5	1.66	$1.5.10^{-8}$
2.0	1.86	$1.7.10^{-6}$
10	1.99	$2.5.10^{-6}$
20	2.26	$3.1.10^{-6}$

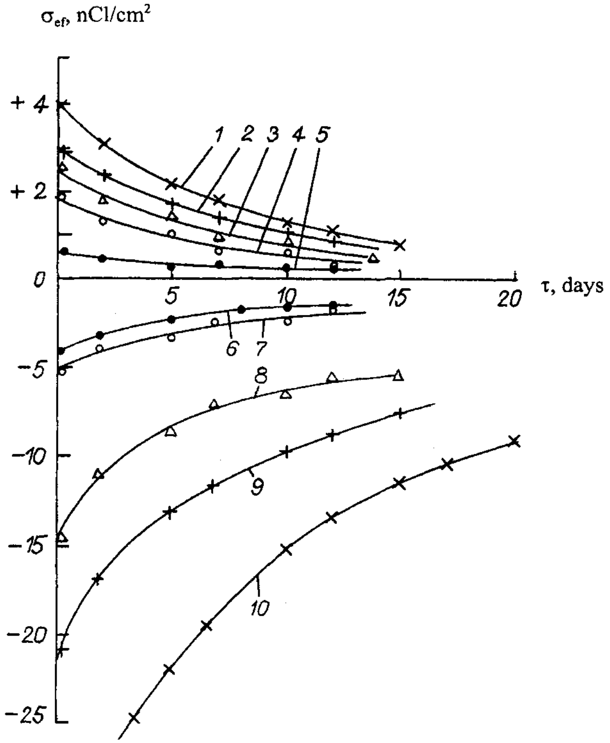

FIGURE 1 Kinetic dependencies of surface charge state for TE (1 – 5) and CE (6 – 10) based on LDPE. US concentration (mass%): 0 (1, 10); 0.5 (2, 9); 2 (3, 8); 10 (4, 7); 20 (5, 6). Electric polarization regimes: for TE field intensity is $E = 20$ kV/cm; for CE intensity is $U = 25$ kV; time of charging $t = 10$ min and temperature $T = 60°C$ are similar for all samples.

Interaction of the outer electric field E and intrinsic for US field E_c and E_c with polymer electret field formed under E action was studied on filled and electrically polarized samples.

In Figures 3a – c spectra of CE TSD currents are shown. A stable peak of the negative charge relaxation is peculiar for the initial LDPE (located above zero line). It corresponds to the homocharge and has the same sign with the polarizing corona discharge. At LDPE melting point the curve of discharge current passes zero and the peak transforms into a halo which corresponds to generation of conductivity current in the sample. Introduction of 0.5% of US reduces

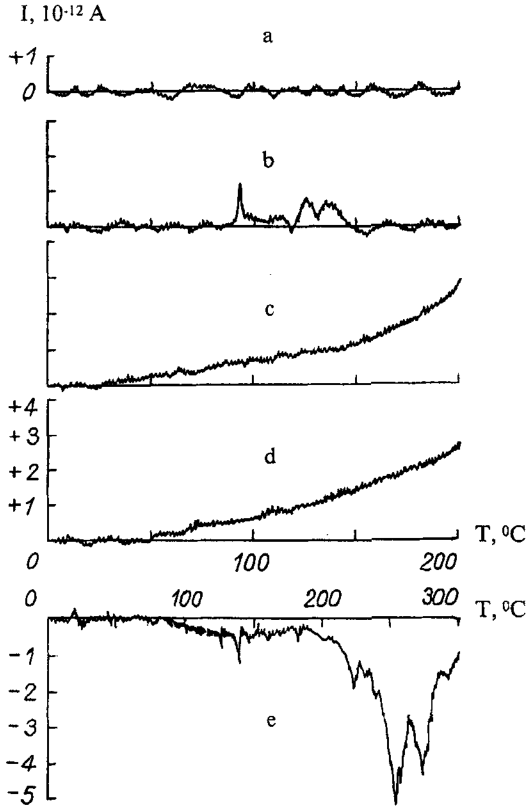

FIGURE 2 TSD currents of LDPE-based nonpolarized samples: a – initial, b – filled by 0.5% US, c – 2, d – 20% of US, e US without LDPE.

homocharge and increases conductivity current. With enlarging filling content those effect intensify.

Embed (immured) in LDPE semiconducting US particles participate in distributing injected into CE charges by creating conductivity chains. So, σ_{ef} dependence on E in CE varies with filler content (Fig. 4, curves 9 – 12) passing the maximum. This occurs due to competing effect of two processes intensifying with E augment: i) rising number of injected into the sample charge carriers and ii) charge draining from out-of-round US particles [2] as a result of gaining local intensity of the field on sharp faces of particles.

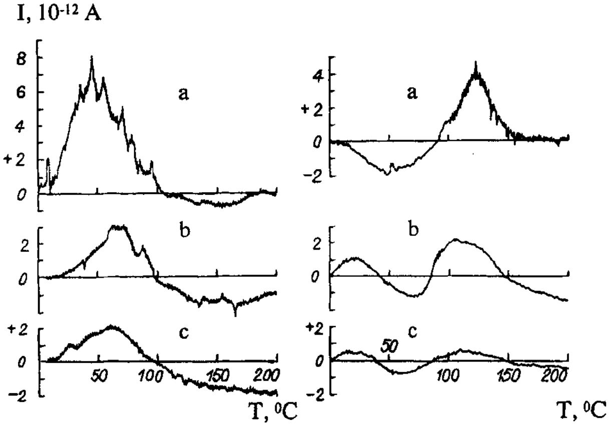

FIGURE 3 TSD currents of CE (a–c) and TE (d–f) on LDPE base: a and d of the initial, b and e of filled by 0.5% of US, c–f – filled with 20% US. Regimes of electric polarization similar with Figure 1.

One can see the curve of discharge current on TSD current spectrum of the initial LDPE TE (Fig. 3d) which is below zero line and corresponds to a positive heterocharge. It arises following the mechanism analogous with double electric layer formation, that is, the polarizing electrode acquires the negative potential and a positive charge is formed on contacting the electrode surface layer of the sample predominantly by the mechanism of relaxation polarization as a result of orientation or shift of ≪inherent≫ polymer dipoles and ions [5]. Above zero line there is TSD current curve of the negative charge. It corresponds to relaxation of the volume charge formed in the heterocharge field.

At 0.5% of US filling a new peak of the negative charge forms in the low-temperature part (20–50°C) of TE spectrum. Heterocharge peak reduces its area and high-temperature peak shifts to the area of lower temperatures (from 110–120°C to 100°C). Filling increment leads to the reduction of all peaks areas. The emergence of a new peak in filled TE is probably connected with Maxwell-Vagner's polarization (M-V). This is polarization of filled dielectrics occurring from free charge carriers shift to the boundaries of the dielectric-filler particle interface [5]. It is obvious that M-V polarizing charge acquires the negative charge, *i.e.*, it is formed due to electron migration from US to LDPE. This agrees well with conclusion derived from analyzing Table I

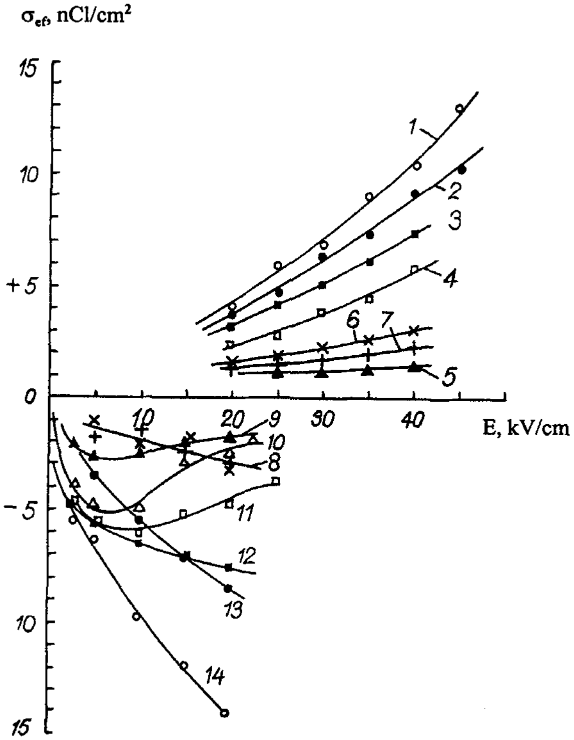

FIGURE 4 Surface charge density of TE (1–7) and CE (8–14) *versus* polarizing field intensity. Polymers: PVB – 1, 2, 13, 14; LDPE – 3–5, 9–12; PTFE – 6–8. US concentration (mass%): 0 (1, 3, 6, 8, 12, 14); 0.5 (4, 11); 2(1, 7, 10, 13); 10(5, 9). Regimes of polarization: t = 10 min, T = 60°C.

confirming that US occupies an intermediate place between dielectrics and semiconductors and it possesses more free electrons than the typical dielectric LDPE has. M-V peak area reduces with filling content since the polarizing charge relaxation runs more intensely at increased sample conductivity.

The analysis of diagrams 3–4 in Figure 4 discloses that TE charge increases in response to gaining intensity of the polarizing field. During TE formation the upper electrode contacted the sample through the dielectric lining. This obviously ensures a more uniform charge distribution among structural elements of the filled LDPE as compared with the sample subject to corona discharge which initiates charge draining from US particles. When filled to 10% σ_{ef} does not practically depend on E. In this case sample polarization is governed by autoelectronic emission and breakdown of the binder [6].

It's to be noted that marked changes in the charge state of filled LDPE take place at 0.5% of US concentration. This complies with described in [2, 3] peculiarity of US-filled plastics: threshold concentration of US beginning with which a considerable enhancement of physical, mechanical, tribological and physico-chemical characteristics of plastics is observed does not surpass 1%. The polarizing charge arising on US particles during their formation contributes to this effect.

PVB

Electrets on PVB base outdo many other polymer electrets by the value and stability of their polarizing charge.

On TSD current spectrum of CE from initial PVB (Fig. 5a, curve 1) two peaks are seen corresponding to negative homocharge relaxation under 30–50 and 60–80°C. Filling (2) reduces polarizing charge in the samples. This mainly effects the magnitude of the first peak. At 130–150°C discharge current of the filled CE passes zero and a current onsets in the sample like that of conductivity. It would be logical to suppose that the current direction obeys the field of US inherent charge.

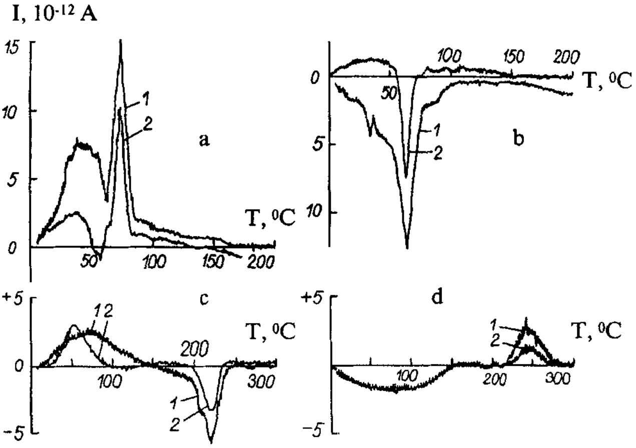

FIGURE 5 TSD currents of CE (a, c) and TE (b, d): 1 – from initial polymer, 2 – from filled by 0.5% of US. Regimes of electric polarization the same as in Figure 1.

Peaks corresponding to heterocharge are typical for PVB-based TE (Fig. 5b, curve 1). When US is introduced, first, heterocharge reduces and second, negative charge relaxation currents appear on low- (20–60°C) and high-temperature (80–140°C) traps. Most probable reasons of their appearance are M-V and volume polarizations of the sample in the field of inherent US charge [6].

At rising polarizing intensity the charge of PVB-based TE and CE increases (Fig. 4, curves 1, 2 and 13, 14). Difference in LDPE and PVB polarization is evident at comparing diagrams 1 and 3, the former being close to proportionality, the latter to parabolic dependence. US filling reduces charge of PVB electrets under all studied intensities of polarizing field.

So, in spite of the presence of inherent polarizing charge in US, filling doesn't result in growth of recorded parameters of polymer electrets charge state. There are at least three reasons: (1) US polarizing charge is concentrated on high-temperature traps and relaxes negligibly at polymer samples TSD; (2) US standing between a poor dielectric and semiconductor assists draining of the polymer binder polarizing charge; (3) interaction between the fields of spontaneous US charge and induced by outer field polarizing charge of the binder do not always lead to increase in TSD currents and σ_{ef}. Apparently, most noticeable effect of US spontaneous charge on the structure and properties of filled plastics consists in the fact that the formation of transition layers at the polymer-US particle boundary occurs in US charge field.

PTFE

At low filling degree (below 20%) US particles are isolated from each other by interlayers from PTFE being one of the best polymer dielectrics. This actually eliminates draining of PTFE polarizing charge along conductivity chains formed by the filler particles.

On TSD current spectrum of CE from initial PTFE (Fig. 5c, curve 1) a vast halo is observed which corresponds to negative homocharge relaxation at 50–150°C asymmetric peak of the volume positive charge (200–230°C). Spectrum of PTFE filled by US differs radically: at 20–90°C a strong peak of M-V polarization arises and homocharge halo disappears; the distinct peak of the volume charge degenerates into a halo (180–260°C). At a slight increase of polarizing intensity the halo acquires again the form of a peak and the filled sample spectrum becomes similar with the initial PTFE one, *i.e.*, US filling does not change in principle PTFE polarization.

TSD current spectrum of TE from initial PTFE (Fig. 5d, curve 1) contains a halo (50–120°C) conforming to positive heterocharge relaxation and an oppositely directed peak of the volume negative charge (220–270°C). The latter, as compared to analogous CE peak, is shifted to the side of high temperatures (maximums at 240 and 220°C, correspondingly) and is symmetric. The spectrum of filled samples is almost the same, though having a somewhat lower peak height. By increasing E it is possible to make the initial and filled PTFE spectra to become similar.

The dependencies $\sigma_{ef}=f(E)$ for PTFE-based electrets are given in Figure 4 (6–8). In all cases σ_{ef} grows with E rise. Those dependencies for CE from the initial and filled by 2% of US PTFE almost coincide.

It turns that the charge state of electrets on PTFE base changes little at filling. US polarizing charge exerts a more appreciable effect on physico-chemical processes accompanying filled polymers formation.

A model for filling with US

When modeling physico-chemical processes occurring in PTFE at filling the structural, deformation and strength parameters of formed in electric field and without samples were compared.

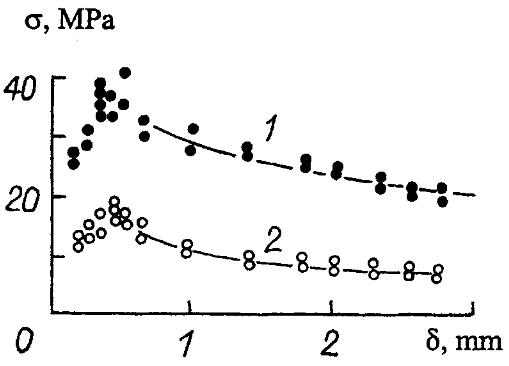

FIGURE 6 Ultimate strength (1) and yield point (2) of electrically polarized PTFE *versus* sample thickness.

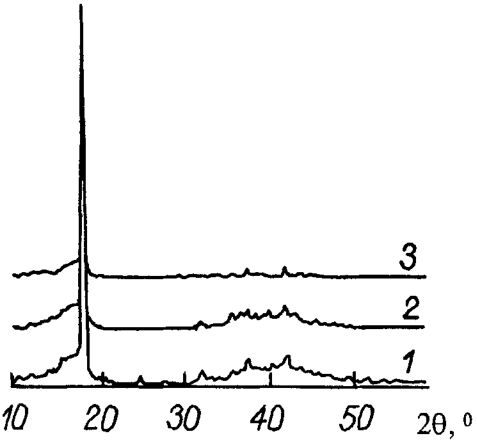

FIGURE 7 Roentgenograms of PTFE samples: 1 – initial, 2 – upon thermal treatment, 3 – subject to thermal treatment and electric polarization.

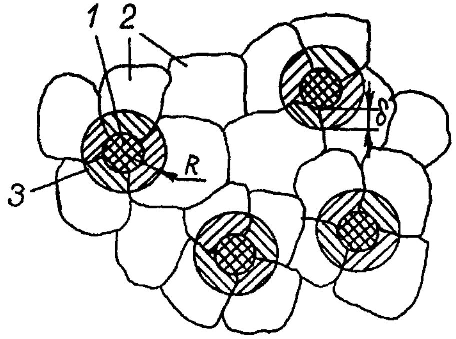

FIGURE 8 A schematic of US-filled PTFE formation. 1 – US particle, 2 – PTFE particle, 3 – PTFE surface layer at US boundary.

During mechanical tests ultimate strength (σ_v), yield point (σ_T) at tension and relative elongation (ε) at breakage were recorded. The results are presented in Table II. Their analysis shows that: (1) recrystallization of PTFE in electric field provides strengthening of the samples in contrast to reference ones; (2) thermal treatment impairs slightly strength of initial samples due to, probably, destruction of oriented permolecular structures in fluoroplastic rods at annealing; (3) relative elongation of all samples is actually similar.

TABLE II The dependence of deformation and strength characteristics as well as temperatures of endothermal peaks of PTFE melting *versus* type of treatment

Type of sample treatment	σ_v *MPa*	σ_T *MPa*	ε *%*	*Temperatures, °C*		
Thermal treatment + electric polarization	32.49	14.25	214	305	310	317
Thermal treatment only	29.10	11.73	203	314	320	328
Without any treatment	30.33	13.93	216	311	318	325

The dependence of strength *versus* thickness of polarized samples was recorded (Fig. 6). This can apparently be attributed to formation of surface layers in the contact with electrodes whose strength is higher than that of PTFE in the bulk. Maximum on diagrams at $\delta = 400 \div 500\,\mu m$ evidences that the hardened layer thickness equals $\delta/2$, that is, $200 \div 250\,\mu m$.

Strengthening of samples subject to recrystallization in electric field is accompanied by rearrangement of PTFE permolecular structure. Table II lists temperatures of characteristic points of endothermal peak of PTFE crystalline phase melting on the curves for DTA samples. It is seen that melting temperature (T_m) depends on the charge state of the samples. Lowered T_m of electret sample confirms that mobility of macromolecules in PTFE crystalline lattice increases which is equivalent to increase in their flexibility due to conformation or weakening of intermolecular bonds [7]. This is the result of crystallization of electrically polarized macromolecules.

Roentgenograms presented in Figure 7 have a typical for PTFE crystalline peak ($2\theta \sim 18°$) and a halo of crystalline phase (30 – 60°). The initial samples have the most prominent halo reducing upon thermal treatment and disappearing at polarizing. This displays that characteristic for PTFE pseudo-structures transform into standard-type crystalline lattices and technological additions having noncrystalline structure are removed from the polymer. The results of X-ray phase analysis are cited in Table III. The following notations are used here: θ – is Bragg angle, d – period of crystalline lattice, I and B – intensity (pulses per second) and half-width of crystallization peak, K – the ratio of crystalline to noncrystalline areas in a spectrum. The analysis of data

TABLE III Results of X-ray phase analysis of PTFE samples

Type of sample treatment	*2θ*	*d, Å*	*I, I/s*	*V degree s*	*K*
Thermal treatment + electric polarization	18° 16.4	4.885	40921	0.103	4.27
Thermal treatment only	18° 14.4	4.890	13108	0.294	1.46
Without any treatment	18° 10.4	4.901	11375	0.303	0.98

from the Table proves that as a result of polarization the location of crystallization peak and PTFE crystalline lattice period vary within the variation error, crystalline phase content in the samples increases, while that of noncrystalline reduces.

The mentioned information makes it possible to present the mechanism of enhancing service characteristics of PTFE at US filling as follows. The formation of filled PTFE takes place at compaction where its particles and those of US are brought into contact (Fig. 8). Due to difference in their melting temperatures (~2000°C) relaxation of US electret charge during filled plastics formation is practically absent. In the vicinity of US particle PTFE melt is effected by electric field of the particle polarizing charge. Radius of the field effective action is R. If distance between the particles less than $2R$, then actually all polymer binder concentrates in the field of the filler electret charge.

US field effects mainly binder surface layers (of δ thickness) at the boundary with the particle. Its electric polarization could take M-V mechanism or charge carrier injection from US, or relaxation polarization with heterocharge formation [4, 5]. This leads to next consequences. Crystalline structure changes and the strength of the binder surface layer increases at US particle boundary. This influences to a more degree tribological and engineering characteristics of filled plastics since they are structurally sensitive parameters of materials.

CONCLUSIONS

Obtained by plasma-chemical synthesis ultradispersed fillers based on SiMeON compounds carry a polarizing charge whose carriers are captured by high-temperature traps. In the process of filled plastics formation an electric polarization of the binder surface layers takes place at the particles boundaries under the charge field effect. This results in increased crystallinity degree, changed temperature of the state, improved strength of the surface layers and raised filler adhesion to the binder. The mechanism of polarization supplements traditional notions on physico-chemical nature of polymers filling and helps to explain high efficiency of ultradispersed nonmetallic fillers.

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