COLLOID CHEMICAL CONTROL OF KAOLINITE PROPERTIES RELATED TO CERAMIC PROCESSING

Lyudmyla A. Pavlova[1] and Michael J. Wilson[2]

[1] Institute of Colloid and Water Chemistry, National Academy of Sciences of Ukraine, L. Gavro St. 14, Apt. 104, Kiev-210, 254210, Ukraine

[2] Macaulay Land Use Research Institute, Craigiebuckler, Aberdeen, AB15 8QH, Scotland, United Kingdom

Abstract—Experimental data on structure formation in highly concentrated aqueous dispersions of kaolinite were analyzed using rheological models. The physicochemical properties of the clay mineral surface were studied during heating at a range of temperatures, and correlation of acid-base properties with physicomechanical characteristics of the spatial structures formed during heating was obtained. It was shown that interparticle interactions and plastic yield mechanisms under load are dependent upon interfacial phenomena. A method for estimating optimal structural parameters was developed for semidry dispersions, enabling regulation of physicochemical and mechanical properties of ceramic mixtures during processing.

Key Words—Acid-Base Interfacial Interactions, Ceramic Processing, Electroconductivity, Interparticle Interactions, Kaolinite, Optimal Structures, Silicoorganic Liquids, Surface Modification.

INTRODUCTION

Ceramic processes use various clays and clay minerals. Desirable physicomechanical properties of fired bodies such as high density and strength and, occasionally, high porosity, require control of the spatial arrangement of particles in the unfired clay and of appropriate types of interaction between these particles. The unfired clay must be "structured" and clay particles well arranged (Kruglitskij 1968). Ability to be structured, interparticle interactions in natural aluminosilicate dispersions and their activity in various processes are significantly related to phenomena acting at the interface. These interparticle interactions cannot be quantified at present because of the complicated nature of the interfacial phenomena and their associated forces.

The formation of coagulation structures in highly concentrated mineral dispersions was studied by Kruglitskij et al. (1989), Pavlova et al. (1991) and Taranukhina et al. (1996). They followed fundamental studies of the basic and acidic properties of silicate and oxide surfaces (Bibik et al. 1986). The latter showed that these surfaces were characterized by a definite number of acidic (Bronsted and Lewis) sites, and they further suggested recombination of these sites with similar basic ones. These sites could lead to the formation of interparticle bonds of different strengths.

Our studies demonstrated that the mobility of clay particles is hindered because of coagulation structure formation in the bulk of the dispersion, but that rearrangement of particles and increase of density is possible provided that interparticle contacts in the system are destroyed to a maximum extent (Uriev et al. 1987).

The present paper presents data showing how highly developed coagulation systems can be formed. It discusses the role of clay surface acidic properties in the structure formation and the influence of different chemical substances. The physicochemical properties of concentrated kaolinite dispersions are considered as well as the question of how the structure parameters can be controlled by modifying the kaolinite surface using cations and silicoorganic liquids. The study makes extensive use of concepts and data arising from research in the former Soviet Union that may not be widely known by western clay scientists.

EXPERIMENTAL

Samples of natural Ukrainian kaolinite in cation-substituted forms were prepared by the standard technique (Fripiat and Toussaint 1963). Samples were dried at 373 K. Concentrated dispersions were prepared with distilled water or appropriate solutions by aerosol wetting and with continuous mixing in a laboratory mixer to bring the liquid phase to levels between 0–20% mass.

Infrared (IR) spectroscopy was used to study the nature of the active sites on the kaolinite surface (Zubkov et al. 1994). Adsorbed layers of water on the clay surface were eliminated by preheating during the evacuation procedure and the number of active sites studied using adsorbed molecular probes (Paukshtis and Yurchenko 1983). The kaolinite samples were pressed into tablets and placed in a glass tube that was evacuated at 423, 523 and 673 K for 4 h, after which the tube was soldered and placed in a special vacuum camera. Protonic Bronsted acidity (B) was assessed on the basis of adsorbed pyridine spectra using the 1540-cm^{-1} band characteristic of the pyridinium ion (PyH$^+$). The aprotic Lewis (L) acidic sites were assessed using benzonitrile and the $-C\equiv N$ high intensity oscillation band. The relative concentration of L-sites was deter-
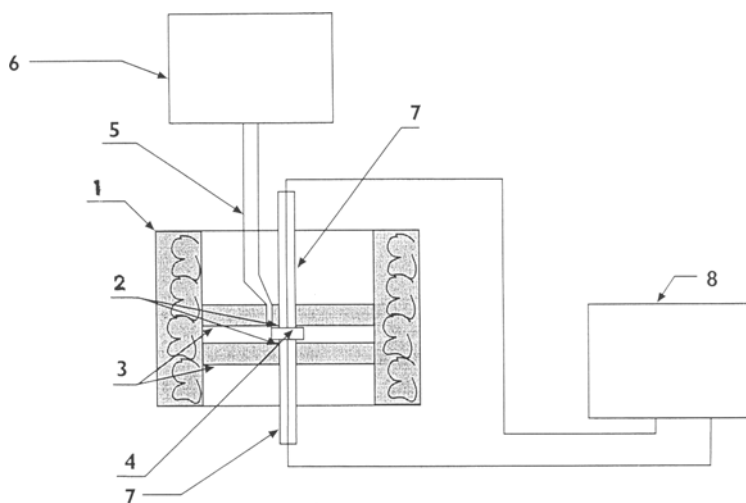
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Figure 1. Scheme of device for measuring surface electroconductivity of the samples during heating: 1—electric furnace, 2—Pt electrodes; 3—insulating ceramic layers, 4—sample under study; 5—thermocouple; 6—regulating device; 7—ceramic tubes; 8—electric signals transformer.

mined on samples exposed at 523 K, a temperature that would remove water molecules coordinated to the exchangeable cations of the kaolinite.

Specific wetting heat was determined by the adiabatic calorimetry method with a Calvet calorimeter after preevacuation at 378 K for 24 h. Adsorption of a monolayer on the preheated samples was calculated to an error of about 5%. Surface area of natural, modified and treated samples was determined by an argon desorption technique (Tarasevich et al. 1983) and by using adsorption of $3.10^{-4}\,M$ solutions of methylene blue (MB) according to the procedure of Hang and Brindley (1970). Chemisorption treatment of the kaolinite surfaces was made according to the method of Bondarenko et al. (1986) using 0.1–0.2 mass% of Na-methylsiliconate and Na-ethylsiliconate aqueous solution as well as polyethylhydridsiloxane (silicoorganic liquids).

The rheological behavior of the wetted samples in a powder-like state was studied using the method of stepwise volume compression under increasing external load (Kruglitskij et al. 1989) and the model for elastic and plastic yield for solid-like systems including a rupture element, as advocated by Regel et al. (1974). Rupture elements reflect contact breakup during plastic deformation.

Curves of specific surface electroconductivity of clay dispersions and calcined samples were obtained as shown in Figure 1 (Pavlova 1988). Wet dispersions of clay were pressed into tablets 1 mm thick and placed into a laboratory electric furnace between 2 Pt electrodes. Electroconductivity registered between 293–1273 K. The method is sensitive and gives results with <1% error. To characterize the parameters of the structures of the disperse system, a model of porous powder-like solids by Rebinder et al. (1964), as improved by Uriev et al. (1987), was used. Total compressive strength and apparent density were used as base values to calculate F, the strength of individual contacts, and χ, the number of contacts per square unit (Pavlova 1997).

RESULTS AND DISCUSSION

Optimal Coagulation Structure Formation; Influence of Water Content

Ceramic pastes and semidry compressed green-bodies maintain their strength through a high number of interparticle contacts forming a continuous network (Yaminskij et al. 1982). Experimental values of F are to a first approximation considered to be proportional to the depth of the first potential minimum of the clay-water interaction curve (Derjaguin and Churaev 1982; Uriev et al. 1987).

Figure 2 demonstrates the relationship between specific external load and the strength and number of individual contacts during compression of kaolinite dispersions with different concentrations of water. The theory of Regel et al. (1974) concerning thermal fluctuations in solids during deformation under load enables a better understanding of interparticle phenomena in the dispersions, particularly with respect to deformation processes occuring during compression, and of the development of possible means of control. Thus, ascending branches of the curves mean plastic deformation of the dispersions, similar to viscous-plastic yield, with increase in contact strength and numbers. Contact strength increases because of a rearrangement of the particles, and numbers of individual contacts increase because of the breakup of old contacts and
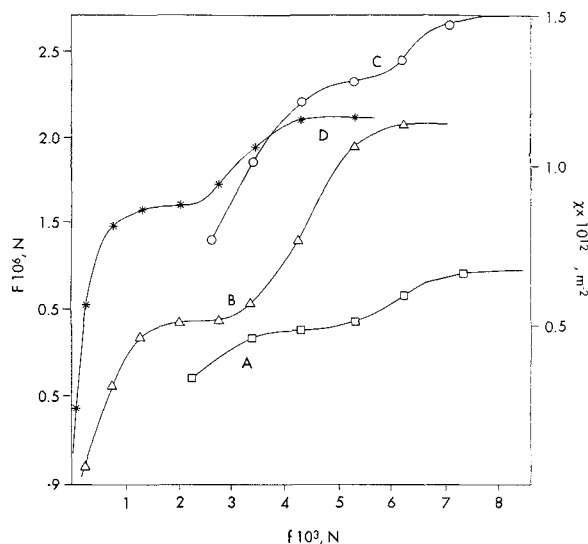
Figure 2. Strength F 10^6 (N) (A, B) and number χ 10^{-12} (m^{-2}) (C, D) of individual contacts, depending on specific external load f (N), for the dispersions with different water content: A = C = 5 mass%; B = D = 10 mass%.

the formation of new stronger ones with greater numbers of neighboring particles; the particles become more perfectly stacked. Where the curves show a horizontal plateau, this indicates that the level of specific compression at contact sites is insufficient for further plastic deformation to occur, or that there is equilibrium between the numbers of breaking and forming contacts. Using this technique, it is possible to obtain so-called "optimal structures" in wet dispersions of clays. Curves B and D (Figure 2), where the dispersions have a water content of 10 mass%, show the variation of structural parameters F and χ of the dispersions with the highest total strength. These dispersions would have a sufficiently high density to provide lower levels of strain and minimum concentrations of fractures during heating (Pavlova 1988).

It is of interest to consider the nature of the optimal coagulation structure formation. The idea that water associated with the surfaces of laminated silicates forms a network of layers with particular properties was developed by Derjaguin and Churaev (1977), Derjaguin et al. (1987), Tarasevich (1988) and Tarasevich and Gribina (1985). The works of Low and coworkers (Oliphant and Low 1983; Sun et al. 1986) showed that water is modified to a depth at least 5 nm from the surface of the clay, leading to a corresponding distance between adjacent surfaces of 10 nm. Taranukhina et al. (1996) estimated the distance between interacting particles in optimal structures having the highest total strength to be 10 nm with values of structural parameters F and χ being intensively increased on account of plastic deformations under load. These studies are consistent with the concept that the clay particles are

surrounded by hydration shells that increase in integrity with proximity to the particle surfaces, so that they become increasingly difficult to displace as the particles approach each other. These interactions appear to be associated with specific surface or ion hydration effects. Hydration forces were found to be the main cause of the deviations from the classical Derjaguin-Landau-Verwey-Overbeek (DLVO) theory in the short-range particle interactions in liquid water (Israelachvili et al. 1978). The significant role of hydration forces in clay-water interactions was demonstrated by the experimental works of Low (1980, 1987) and Viani et al. (1983, 1985) and by Pashley (1980) and Derjaguin et al. (1987) for other silicates. The interaction between water molecules and hydrophilic clay surfaces gives rise to a monotonic repulsion and its strength depends on the magnitude of the hydration energy of the surface. Hydration forces could determine interparticle contact formation through a thin aqueous film (Israelachvili 1985; Israelachvili and Wennerstrom 1992) and, therefore, promote effective particle rearrangement under load.

Acidic Properties and Coagulation Structure Formation

It had been realized for some time (van Oss 1993) that hydration forces can be both attractive and repulsive in aqueous media due to acid-base interactions, and that the attractive acid-base energy of cohesion of water molecules does not disappear when a net hydrophilic repulsion occurs. Table 1 shows data on hydrophilicity and acidic properties of kaolinite samples treated with different cations and silicoorganic liquids as well as a comparison of the structural parameters F and χ for hydrophilic (ion-exchanged) and hydrophobized preparations. It is clearly seen that the values of contact strength for hydrophobized samples are initially significantly lower but increase during the course of heating. With regard to contacts number χ it is higher for practically all the samples of hydrophobized kaolinite.

According to Tarasevich (1988), mineral-water interactions result in the occurrence of mobile protons. This is explained by the strong polarization of O-H bonds of adsorbed water molecules in the oppositely charged fields of oxygen and exchangeable cations. Figure 3 shows that coagulation structure formation as assessed by the parameters F and χ is related to interactions at the Bronsted acid sites. These interactions may take place between polarized water molecules coordinated to B sites on the clay surface, leading to formation of hydrogen bonds (H-bonds) of the donor-acceptor type (Hamilton 1968). It was confirmed by computer simulations (Skipper et al. 1991a, 1991b) that water molecules establish H-bonds to the clay surfaces and to other water molecules in the interlayer space. The strength of the contacts is higher because

Table 1. Physicochemical and structural properties of ion-exchanged and hydrophobized kaolinite showing specific wetting heat q (Jm^{-2}), strength of contacts F (10^{-6} N), individual contacts number χ (10^{12} m^{-2}), concentration of Bronsted B and Lewis L (10^{13} molecules cm^{-2}) surface active sites.

Temper-ature T(K)	Parameter	Natural kaolin	Kaolinite						
			Ion-exchanged				Hydrophobized		
			Al	Mg	Ca	Na	NaES	NaMS	PHES
293	q	1.10	1.02	1.13	1.22	1.16	0.03	0.03	0.03
	F	2.15	0.95	3.75	1.35	0.48	0.23	0.35	0.32
	χ	1.30	1.90	0.95	2.06	3.40	2.90	2.98	2.94
423	q	1.13	—	—	—	—	0.02	0.02	0.02
	F	3.46	1.44	5.13	2.08	0.83	1.61	2.14	1.92
	χ	1.21	2.64	0.88	1.85	3.20	2.71	2.70	2.70
	B	—	1.75	2.20	3.47	—	—	—	—
523	q	0.80	—	—	—	—	0.09	0.12	0.07
	F	2.98	1.28	4.01	2.38	1.23	1.38	2.02	1.76
	χ	1.12	2.57	0.85	1.73	3.05	2.13	2.17	2.15
	B	—	1.32	1.49	2.30	2.05	—	—	—
	L	—	5.45	19.23	32.40	29.41	—	—	—
673	q	0.33	—	—	—	—	0.17	0.19	0.14
	F	6.01	3.74	5.77	2.88	1.96	2.78	3.65	3.04
	χ	1.01	2.63	0.80	1.61	3.25	2.56	2.62	2.55
	B	—	1.42	1.11	1.69	—	—	—	—
	L	—	11.34	27.96	39.64	—	—	—	—

Key: NaES = Na-ethylsiliconate; NaMS = Na-methylsiliconate; PHES = polyethylhydridsiloxane.

their energy is 2 to 3 orders of magnitude higher than that originating from van der Waals bonds. At the same time, the hydrogen bonds represent the energetic barriers for effective particle repacking and the higher density reached under the action of external pressure.
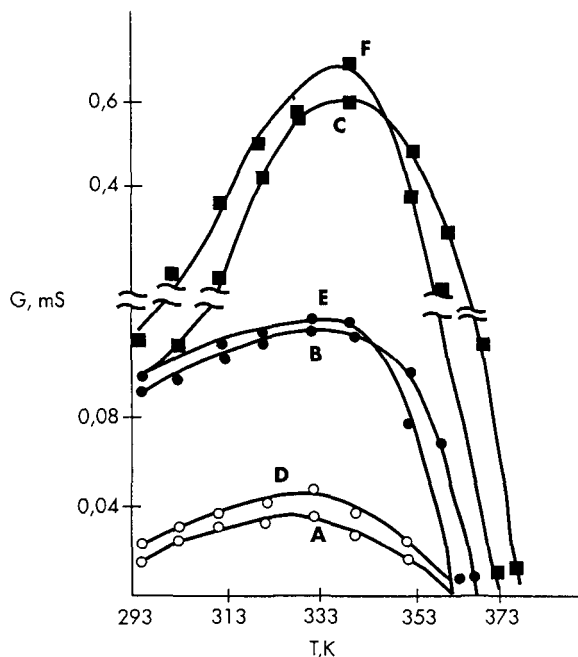

Figure 3. Electroconductivity G (S) curves of Ca-kaolinite (A–C) and Na-kaolinite (D–F) structures in range of temperatures for dispersions having different water content: A = D = 5 mass%; B = E = 10 mass%; C = F = 15 mass%.

Further thickening of the water film and the formation of mobile water may serve as a screen for interacting particles and contacts strength decreases.

Coarse-grained particles of natural well-crystallized kaolinite are not able to form highly developed networks of contacts, whereas highly dispersed particles of Na-kaolinite are able to form numerous contacts (Table 1). Sufficient numbers of these contacts may be maintained during heating when the concentration of B sites decreases and a significant part of the H-bonds between the particles is destroyed. As has been suggested, individual contact values F are integrating various forces between clay particles. Assuming that hydrophobized samples interact only due to van der Waals forces, it may be concluded that the hydrophilic surfaces generate attractive forces capable of keeping the silicate layers together to a greater extent than van der Waals forces.

Effect of Temperature and Different Cations on Conductivity

More detailed characterization of the physicochemical and deformation processes of kaolinite dispersions was achieved by observation of the dependence of surface electroconductivity over a whole range of temperatures (Figures 3 and 4). Curves A and D, B and E, and C and F reflect different states of Na- and Ca-kaolinite structures during heating under the same conditions (Figure 3). The highest values of surface conductivity in the 313–353 K interval correspond to optimal kaolinite structures, and are consistent with a highly developed network of bonds within the structure that provides the best way of carrying the charge
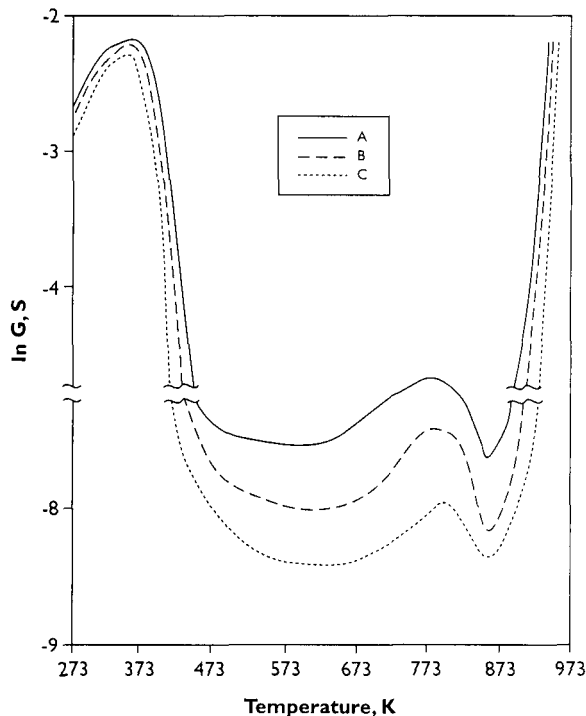
Figure 4. Electroconductivity ln G (S) dependence in the whole range of temperatures of A = Li-, B = Na- and C = K- forms of kaolinite.

bearers. The maximum of the curves in the interval may be due to the destruction of the special structure of boundary layers of water (Derjaguin and Churaev 1977). The 2 to 9 times increase in conductivity values reflects an increase in the mobility of the charge bearers. This could be due to the clay surface water molecules becoming more mobile, or it could be a consequence of the higher solvating ability of water layers having been destructurized during heating. The sharp decrease in conductivity in the 343–373 K range does not mean that the water molecules leave the surface of the clay but that the special water network is destroyed.

The elimination of thermally activated water molecules from the surface of the kaolinite during the dehydration process is reflected by the long descending branches of the electroconductivity curves, G (Figure 4). The values of G decrease more than 4 orders of magnitude. The minimum values for conductivity of kaolinite saturated with different monovalent cations follow the order Li > Na > K. With regard to the monovalent cations, Schramm and Kwak (1982) presented evidence to show that particle thickness of the different cation forms of montmorillonite followed the reverse order, namely K > Na > Li. Results on the relative intensity of light transmission and absolute viscosity showed that the particles of Li-montmorillonite are thinner than those of Na-montmorillonite,

which in turn are thinner than those of the K-form of the clay. If these results could be extrapolated to kaolinite—and it is not certain that they can be, as the layer charge of kaolinite is very much lower than that of montmorillonite—it would mean that Li-kaolinite would be highly dispersed, forming a well-developed network of contacts, which would promote conductivity.

Physicochemical Properties of Kaolinite Dispersions

The general course of the conductivity curves coincides with a stepwise change of physicochemical properties of kaolinite dispersions (Figure 5). Thus, the sharp decrease of specific wetting heat q is proportional to the decrease in conductivity, and loss of hydrophilic properties, which is caused by heating above 700 K, is reflected in the curve of monomolecular adsorption capacity, a. The relationship between conductivity and these physicochemical properties may be useful in the determination of the temperature of fully dehydrated structures of kaolinite in aqueous dispersions or other modified forms.

A vital stage in the transformation of the clay dispersions occurs in the temperature range of dehydration. This is the stage where some part of the Bronsted active sites is destroyed and the number of individual interparticle contacts decreases. It can be seen from Figure 5 that the highest values of the strength of contacts as well as the number of contacts and specific conductivity are associated with dehydrated structures based upon optimal coagulation structures. In this context, it should be noted that the main condition for production of high quality ceramics is to prevent the green-body from fracturing during drying. Recommendations are being developed for users as to acceptable periods of time for maintaining dehydrated structures with the minimum level of microstresses.

The 700–1200 K range is characterized by an increase of almost all parameters of the clay structure as shown in Figure 4. Some decrease in the concentration of the Bronsted active sites is caused by the elimination of OH-groups from the surface of the clay and by the general process of dehydroxylation. At the same time, the best conditions arise for the Lewis acidic and basic active sites to interact, so forming stronger donor-acceptor bonds between the particles (Bibik et al. 1986). At the contacts of particles, electron donor centers may recombine with electron acceptor centers, strengthening the bonds between them. Here, the dehydroxylation process initiates a great number of structural defects which play the role of high strength active sites. This promotes a further increase in strength and number of the individual contacts during the next temperature interval.

The enrichment of the clay surface with exchangeable cations such as Li and Na initiates a sufficient number of structural defects, which behave as active
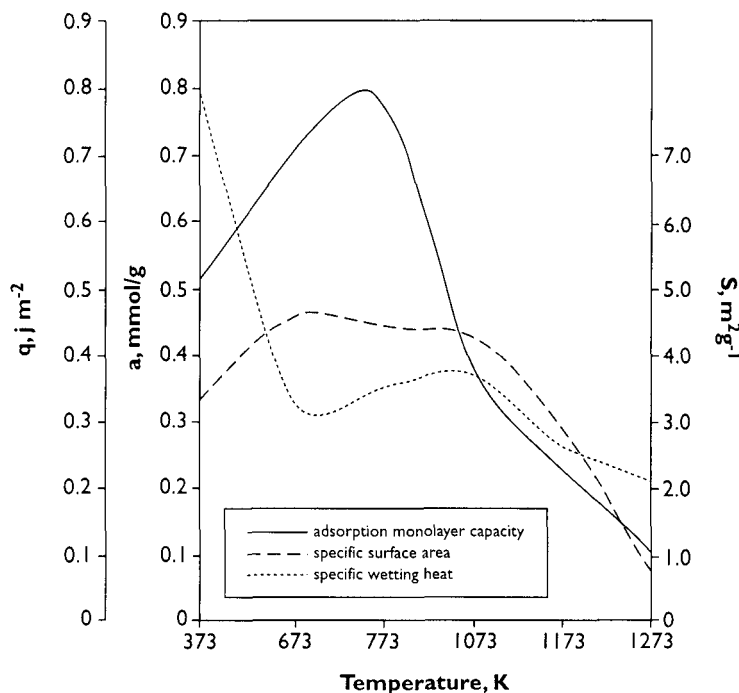
Figure 5.   Physicochemical properties of natural kaolinite dispersions: specific surface area, specific wetting heat; monomolecular adsorption capacity in dependence on temperature of preheating.
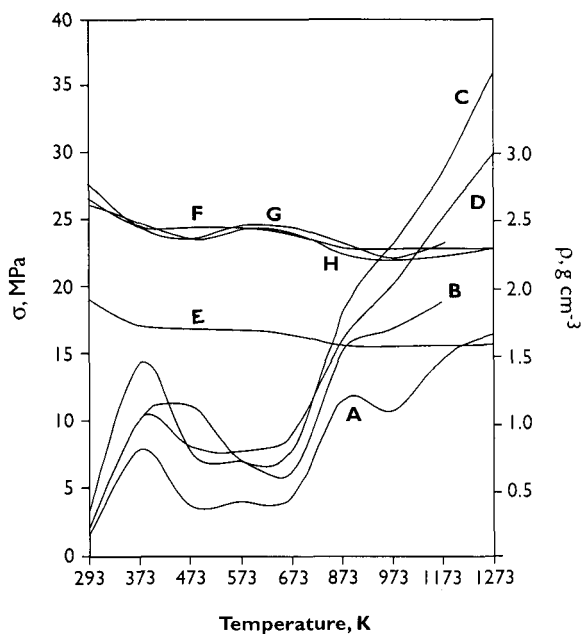

Figure 6.   Physicomechanical properties of natural and modified kaolinite: A = total strength σ (MPa), E = apparent density ρ (g.cm^{-3}) of natural kaolinite structures; B, C, D = values of total strength σ (MPa) and F, G, H = apparent densities ρ (g.cm^{-3}) of kaolinite structures premodified by Na-methylsiliconate, Na-ethylsiliconate and polyethylhydridsiloxane, correspondingly.

centers at the surface to promote the process of diffusion sintering at lower temperatures. This involves the creation of amorphous-like, "quasi-liquid" interlayers on particle surfaces, which is a condition for the rheological process of sintering at higher temperature (Skorokhod 1981).

Physicochemical Properties of Modified Kaolinites

The chemisorption of molecules of silicoorganic liquids onto the surface of kaolinite blocks the greater portion of active sites and specific wetting heat decreases up to 0.03 Jm^{-2}. The strength of contacts of unheated clay is significantly reduced. Interparticle interactions occur according to hydrophobic mechanisms because the silicoorganic film formation at the kaolinite surface leads to the loss of hydrophilic properties (Pavlova and Taranukhina 1995). As a result, the ceramic body has higher strength and density than a ceramic body made from natural kaolinite even in the initial, optimal state. The density of the samples under the same conditions increases significantly, as seen in Figure 6. Due to the highly developed network of interparticle contacts, the total strength of the modified structures, σ, after heating is between 1.1 and 2.5 times higher. Thermal treatment of the dispersions in the 473–673 K range results in the thermodestruction of alkylsiliconate groups, which promotes the unblocking of the active sites and leads to intensive donor-acceptor interaction at the contact sites.

CONCLUSIONS

Experimental data on rheological behavior and physicochemical properties of highly concentrated kaolinite dispersions show that, under load, these dispersions deform plastically, leading to the rearrangement of the particles in a more perfectly stacked way. Optimal conditions provide formation of highly developed coagulation structures. These structures involve effective action of hydration forces and hydrogen bond formation. Sufficient number of individual contacts form to promote a lower level of microstresses during heating. Possible means of controlling coagulation structures, both in their formation and reformation, are 1) modification of the kaolinite surfaces by deflocculating cations and 2) chemisorption using silicoorganic liquids.

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