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COLLOIDAL SYSTEMS CONTAINING FREE RADICAL-FORMING PARTICLES AND COMPOSITES ON THEIR BASIS

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SUMMARY: Controlled surface activity and reactivity of new carbon-chain functional surface-active oligoperoxides (FSAP) and derived metal complexes (OMC) with side and end di-tertiary and tert-alkyl (aryl) peroxidic, respectively, and other active functional groups cause the possibility of their tailored utilization as emulsifiers, surface-active initiators and modifiers of the phase boundaries of liquid, solid and mixed phases in different colloidal systems in a wide temperature range. New materials can be developed such as water and hydrocarbon polymer dispersions, artificial water dispersions of unsaturated polyesters and alkyd resins, polymer/polymeric blends, active glass and carbon fibers, dispersed fillers, reinforced and filled polymer composites with the definite special properties. Methods for the obtaining and the application of these materials are described.

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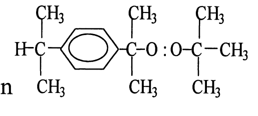
INTRODUCTION

To obtain polymer composites with special properties (such as filled and reinforced ones with controlled adhesion, corrosion and impact resistance) tailored modifications of phase boundaries are necessary. These should offer the needed amounts of reactive fragments and provide a high dispersity level, aggregational and sedimentational stability, and chemical reactivity of formed polymer colloidal systems (PCS).

The Elaboration of theoretical and practical bases of the controlled synthesis of surface-active heterofunctional oligomers based on peroxy-containing and other functional monomers and chain-transfer agents has caused (i) the development of new reactive emulsifiers and stabilizers and of technologies for obtaining a wide assortment of active PCS[1-3]. Among these are, first of all, artificial and synthetic water dispersion filmformers[4, 5] including ones filled by electro-conductive and magnetic fillers, and polymer/polymeric blends.

The concise consideration of the basic principles of the synthesis, structures and properties of carbon-chain functional surface-active oligoperoxides (FSAP), and polymer colloidal systems modified by them is the main aim of this report.

EXPERIMENTAL PART

The peroxidic monomers (PM) VEP $CH_2{=}CH\text{-}C{\equiv}C\text{-}C(CH_3)_2\text{-}O{:}O\text{-}C(CH_3)_3$ and VEH $CH_2{=}CH\text{-}C{\equiv}C\text{-}C(CH_3)_2\text{-}O{:}O\text{-}H$ described in the literature[6] were synthesized from vinylacetylenic alcohol $CH_2{=}CH\text{-}C{\equiv}C\text{-}C(CH_3)_2\text{-}OH$. They show the following characteristics after vacuum distillation: d_4^{20}= 0.867 (refer.0.867); n_D^{20}=1.4480 (refer. 1.4482); active oxygen content was 8,79% (Calcd. 8.75%) and d_4^{20}= 0.964 (refer.0.964); n_D^{20}=1.4772 (refer. 1.4780); active oxygen content was 12.60% (Calcd. 12.68%), respectively. The peroxidic telogen  $H\text{-}C(CH_3)_2\text{-}C_6H_4\text{-}C(CH_3)_2\text{-}O{:}O\text{-}C(CH_3)_3$ MP was used as a mixture of m- and p-isomers. After vacuum distillation its characteristics were as follows: d_4^{20}= 0.921, n_D^{20}=1.1.4821, T_b =345K/0.1mm.

Vinylacetate (VA) was purified by double column distillation at atmospheric pressure, butylacrylate (BA) and acrylic acid (AA) were purified by distillation under vacuum. After that, their constants agreed with reference data[7]. MA was purified by vacuum sublimation and after purification its melting point was 325K (literature data: 325.9K[8]). Benzoyl peroxide

(BP) and azobisisobutyronitrile (AIBN) were purified by recrystallization from ethanol. Dimethyl formamide (DMF) and other solvents were dried and purified by the ordinary techniques[9].

Copolymerizations to prepare FSAP were carried out in an argon atmosphere at 333-353K. The conversion was monitored by dilatometric and gravimetric methods. FSAP were purified by two precipitations from acetone solution to light petroleum and were dried under vacuum to constant weight. FSAP modified by fatty acid, polyethyleneglycole and others were synthesized by polymer-analogous transformations of initial FSAP with active anhydride fragments. The synthesis of FSAP-metal complexes (OMC) was carried out as follows: to a 10% solution of the FSAP a solution of the metal salt in ethanol was added in a three-necked flask equipped with a stirrer and a condenser. After stirring at 298K for some time the reaction mixture was precipitated into distilled water. OMC were carefully washed from metal cations by water and dried under vacuum to a constant weight. The content of metal was determined using elemental analysis and controlled by atom-adsorption spectroscopy. The average deviation was about 3 – 5 % which does not exceed the systematic error of both methods. The OMC structures were confirmed by UV - spectroscopy of FSAP and OMC in ethanol and ethyl acetate on a “Specord 40” device. Voltammetric characteristics of FSAP and OMC were investigated on a ECL device for electrochemilumenecsence and electrochemical investigations using glass-carbon and copper electrodes for measurement and AgCl electrode for comparison in 0.03 M solution of $(C_4H_9)_4NClO_4$ in DMF. The MA and AA unit contents in FSAP and OMC were determined by potentiometric titration of carboxylic groups; the VA unit content was determined by alkaline hydrolysis method[10]. Peroxidic fragment contents (VEP units) were determined via the thermal decomposition of FSAP at 483K followed by gas chromatographic analysis of the final product decomposition[11]. The error of functional groups determination did not exceed 7%.

MWD parameters were studied by a GPC method using a “Waters Co.” gas-liquid chromatograph[12]. THF was the eluent and its flow rate was 1.2 mL/min at a temperature of 298K. The column calibration technique and the calculation of M_N ,M_W , M_Z values and their ratios were described previously work[13].

The surface tension (σ) of water-alkaline solutions of FSAP and OMCs was determined by the measurement of maximum bulb pressure after achievement of equilibrium state by technique described in ref[14]. The amounts of FSAP and OMC adsorption at aqueous solution-air phase boundary as well as the values of their surface activity ($G = -d\sigma/dC$ at their concentration in solution $C \to 0$) were calculated from the experimental σ vs. C isotherms using Gibbs equation[15]. The values of $d\sigma/dC$ were determined from the slope angles of tangents to σ - C isotherm curves at $C \to 0$. Then the values of adsorption (A) at the phase boundary can be calculated by the substitution of known values of C and $d\sigma/dC$ in Gibbs equation. The content of FSAP and OMC sorbed on the γ-Fe_2O_3 or copper particle surface as well as peroxidic fragment content in particle shells were determined via the thermal decomposition of peroxide containing fillers at 483K under argon, followed by gas chromatographic analysis of the decomposition final products as described above. The samples were previously treated with solvent for FSAP and OMC. Colloidal copper particles were obtained by chemical reduction of complexes of Cu^{2+} ions and citric acid (potassium salt) with formaldehyde as reducing agent in alkaline medium (12% solution of caustic potash was used for obtaining alkaline water medium) at 298K; then the powder was separated from the reaction mixture, carefully washed with distilled water, and dried till constant weight under vacuum. Metal particles containing oligoperoxide shell were obtained in the presence of surface-active oligoperoxides in solution being reduced[16]. The contents of copper oxides and Cu^0 in metal polymeric particles were determined by the method of added standards using an X-ray structure analysis with a diffractometer DRON-30 (CuK_α - radiation). The content of zero valent copper was 99.5 ± 0.1 %. The particle size was determined using scanning electronic microscopy with further statistical treatment of micrographs.

Water-dispersion polymerizations in the presence of CCP or FSAP (no conventional radical initiator for polymerization initiation was used) were carried out in aqueous alkaline media at 273 - 353K and at pH 10. Monomer to water phase ratio was 1:3 (v/v). Polymerization kinetics was studied by both the dilatometric methods described in the literature[17]: collapsible emulsion dilatometers with magnetic stirrer and gravimetric method in three-necked vessel for additional checking. The polymerization rate was determined from the section of the kinetic curves with the stationary rate when the amount of growing polymer-monomer particles (PMP) was constant. The overall initiation rates were determined from the induction periods observed in the presence of different amounts of oil-soluble inhibitor diphenylverdazyl (DPV).

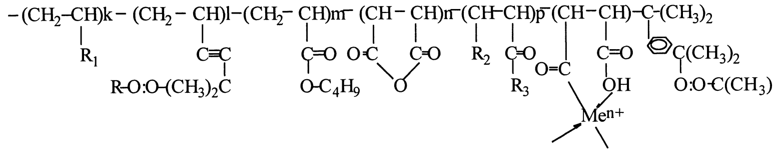
Sodium pentadecyl sulfonate (SPS) was used as emulsifier. The water phase for emulsion polymerization was boiled for 4 hours in the presence of ammonium bicarbonate, after which the pH reached value 10, and then it was carefully purged with argon before charge. No additional alkaline agent was used. After completion of water-dispersion polymerization in the presence of CCP pH of reaction medium was of 9.5-9.7.

Molecular weights (M_η) of polystyrene were determined from intrinsic viscosity's of their solutions using the values $K=2.7 \bullet 10^{-4}$ and $\alpha = 0.66$ (benzene, 298K) [18]. The polymer-monomer particle size (r_{PMP}) was determined by light-scattering method at wavelengths from 420nm to 620nm.

RESULTS AND DISCUSSION

1. THE BASIC PRINCIPLES OF DESIGNED FSAP SYNTHESIS

The structures of bifunctional peroxidic monomers VEH and VEP prove that the presence of two reactive centers in their molecules causes their participation in all elementary reactions accompanying radical polymerization. However, an ineffective consumption of peroxidic groups in reactions of decay, initiation and transfer of chain equals about 3-5%, approximately[19].



$R = -H ; -C(CH_3)_3$

$R_1 = -O-COCH_3$, $-OH$, $-C{\equiv}N$, $Me^{n+} = Cu^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Al^{3+}$

$R_2 = -H, -\overset{O}{\overset{\|}{C}}-OH,$

PEG STX FAlk

$R_3 = -OH$, $-(OC_2H_4)yOH$, $-(OC_2H_4)_6\,O-\overset{O}{\overset{\|}{C}}-C_{17}H_{35}$, $-O-C_zH_{2z+1}$, $-O-CH_2-CH{=}CH$

$\underset{\diagdown O \diagup}{H_2C-CH}-CH_2-O-$, $-NH-C_3H_6-Si(OC_2H_5)_3$

$k = 11,5 \div 41,4\,\%;$

$1 = 0 \div 54,3\%;\ m = 0 \div 41,0\%;\ n = 0 \div 28,0\%;\ y = 12, 35, 115;\ z = 6 \div 9;\ M_N = \approx 1000 \div 4000$

on the basis of peroxidic monomers VEP and VEH and telogen MP.

The participation of peroxidic monomers (PM) mainly in reactions of chain propagation defines their significance as comonomers, first of all. That provides entering of reactive peroxide fragments into oligomeric molecules and permits the use of well-known equations for the description of copolymerizaton kinetics and copolymer structures[20, 21]. The PM are active comonomers and cause the formation of oligomers enriched by their links with high rates and yields. Macro- and microstructures of such oligomers (Tables 1, 2) can be controlled by varying the initial monomer mixture composition and the conditions of conversion and synthesis. This is important for controlling their solubility, surface activity and cooperative interactions in solutions.

Table 1: VA, VEP and AA terpolymerization and FSAP characteristics

Initial monomer mixture composition, M/o			Polymerization time, h	Conversion M/o	FSAP composition M/o					
					Calculated			Experimental		
VA	VEP	AA								
I_1	I_2	I_3			m_{1i}	m_{2i}	m_{1i}	m_{3i}	m_{2i}	m_{3i}
40,00	50,00	10,00	8.5	51,0	9,20	79,50	11,30	10,30	79,80	9,90
53,33	33,34	13,33	8.5	38,1	14,00	67,40	18,60	13,10	69,01	17,80
64,00	20,00	16,00	8.5	30,0	22,44	51,17	26,39	17,90	55,10	27,0
60,00	33,33	6,63	8.5	36,0	17,50	71,50	11,00	14,30	76,10	9,60
40,00	33,33	26,67	8.0	57,3	13,00	56,00	31,00	8,20	58,80	33,00
72,00	10,00	18,00	8.0	37,0	38,50	26,00	35,50	35,20	35,00	29,80

Table 2: The average lengths (l) and number (R) of the same monomer link blocks per 100 links of FSAP

Conversion M/o	Current composition of monomer mixture , M/o			Comonomers mole ratio in initial monomer mixture		l_1 (VA)	l_2 (VEP)	l_3 (AA)	R
	VA	VEP	AA	[AA]/[VA]	[VEP]/[AA+[VA]				
10	49,28	45,75	4,97	0.11	1.0	1.08	7.31	1.02	23.9
30	60,85	34,45	4,70			1.12	5.35	1.02	31.6
50	78,92	17,43	3,65			1.29	3.04	1.03	48.6
10	43,44	16,53	40,03	1.00	0.25	1.07	1.52	1.37	71.6
30	52,24	8,96	38,80			1.10	1.28	1.53	74.0
50	64,24	2,36	33,40			1.18	1.08	1.75	70.4

Satisfactory agreement of calculated and experimentally determined FSAP compositions proves the PM participation mainly in chain propagation reactions and the possibility of using the effective constant values for prognozing of FSAP composition and structure. At the same time the PM participation in chain transfer reactions (when less active radicals are formed) causes the termination of kinetic and material chains and provides the possibility of controlling the molecular weight characteristics of peroxide-containing FSAP, even with formation of very narrow molecular-weight distribution (see Table 2, Fig. 1).

Table 3: FSAP molecular-weight characteristics (conversion - 70%)*.

Components mole ratio		Parameters of molecular weight distribution				
$\frac{[AA]}{[VA]}$	$\frac{[VEP]}{[AA]+[VA]}$	M_N	M_W	M_Z	$\frac{M_W}{M_N}$	$\frac{M_Z}{M_W}$
0.11	0.67	750	1030	1410	1.35	1.37
0.11	0.25	650	950	1410	1.46	1.48
0.25	0.67	870	1300	1950	1.49	1.50
0.25	0.25	770	1180	1760	1.53	1.49

*353K, DMF, [BP] = 3×10^{-2} kmole/m^3, V_M/V_{DMF} = 0.33.

The basic methods of obtaining FSAP are: the initiated radical copolymerization of peroxide monomers in hydrocarbon solutions and in water dispersion, telomerization of functional monomers in the presence of peroxide telogen in different, including aqueous, media, and emulsifier-free water dispersion polymerization with peroxide monomer or telogen participation. Realization of the telomerization of polar monomers (or their mixtures in the presence of peroxide-containing chain transfer telogen–MP) is a prospective method to obtain the FSAP of intentional nature and composition. For this purpose such polar monomers as VA and MA, which form reactive growing radicals, are especially interesting. FSAP formation with controlled content of the end hydrophobic peroxide fragments and with hydrophilic backbone is provided by the presence of a movable hydrogen atom situated in P-position to a thermostable tert-butyl (aryl) peroxidic fragment.

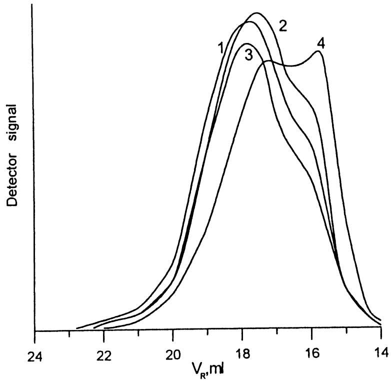


Fig. 1: MWD function of FSAP obtained at initial mole ratio [VEP]/([VA]+[BA]) = 1.0 and [BA/[VA]=0.33 (1), 3.0 (2); [VEP]/([VA]+[BA]) = 0.25 and [BA]/[VA] = 0.33 (3), 3.0 (4).

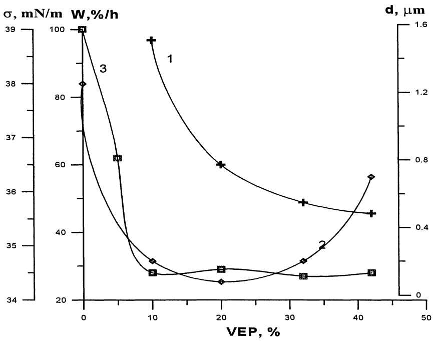


Fig. 2: The dependence of surface tension (σ) (1), polymer particle size (2) and polymerization rate (3) on VEP concentration in initial monomer mixture at water dispersion emulsifier-free polymerization.

It is obvious that the variation of peroxide telogen concentration permits also regulating molecular weight values and FSAP hydrophilic-lipophilic balance (HLB).

The emulsifier-free copolymerization of functional polar and hydrophobic monomers with the participation of PM or MP in aqueous medium is an especially prospective method for obtaining FSAP or PCS on their basis for practical purposes. This method ensures high process rate and yield of FSAP in the form of transparent or colloidal solutions as well as the possibility of its further utilization without a preliminary extraction and purification. The retarding influence of the peroxide component on the polymerization rate is indicated by the dependences of emulsifier-free water dispersion polymerization kinetics upon its concentration in the reaction mixture. The colloidal-chemical characteristics of peroxide-containing dispersions formed with the peroxide monomer or telogen participation depend on the concentration of the peroxide component in an analogous manner. It is shown in Fig.2 that the polymerization rate does not depend on VEP concentration after the definite peroxide content in initial mixture is achieved. That can be explained by achieving maximal surface activity of watersoluble peroxide-containing oligomer formed in water solution during emulsifier-free water dispersion polymerization at this mixture composition. The further increasing of the VEP concentration enhances only the VEP content in the hydrophobic core of micelles or of latex colloidal particles formed with oligomeric surface-active substance participation. The amount of the latter is determined by the content and surface activity of watersoluble FSAP formed at this monomer mixture composition. The amount of colloidal particles is constant after attainment of the definite VEP concentration and this only defines the total rate of water dispersion polymerization as it is known[22].

The decrease of surface tension and dispersion particle size with the increase of peroxide monomer content (Fig.2) proves, in our opinion, the formation of watersoluble surface-active oligomers enriched by hydrophobic peroxidic fragments on the first stage in water phase and at interface predominantly. The extremities on the both dependences of latex's surface tension and dispersion particle size on VEP concentration are explained by the attainment of the maximum surface activity of FSAP caused by their specific macro- and microstructure, which are achieved at this VEP concentration.

2. SURFACE-ACTIVE AND COLLOIDAL-CHEMICAL CHARACTERISTICS OF PEROXIDE-CONTAINING FSAP.

Synthesized peroxy-containing FSAP are soluble in nonpolar and/or polar organic media and in water in a wide range of pH depending on their nature and composition. Such biphilic oligomers decrease the surface tension (σ) of their water solutions at the interfaces with air and styrene (St), respectively. They form hydrophobic colloidal structures in volume analogous to the micelles of low-molecular weight semicolloidal surface-active substances as revealed by Fig.3. Critical values of concentrations (CCS), at which hydrophobic colloidal structures arise, depend on the oligomer nature, on molecular weight, and on pH values of the solution. This is especially typical for the FSAP, which are oligoelectrolytes and capable of conformation changes at different pH values due to their chain nature. The dependences presented on Fig. 4-6 confirm the general character of the regularities peculiar to FSAP of different nature, which can change conformation structures in aqueous solution.

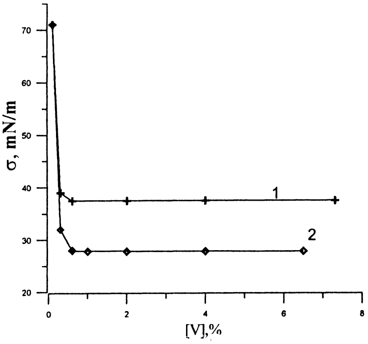


Fig. 3: Isotherms of surface tension of VA-VEP-AA FSAP water solutions at interface water-air (1) and St (2).

The tendency to form associates for FSAP containing hydrophobic ditert. -Alkyl (aryl)-peroxidic fragments is explained by their hydrophobic interactions and for FSAP containing hydrophilic hydroperoxy or carboxyl (hydroxyl) groups by their intermolecular hydrogen bond formation in organic media and hydrophobic interactions in water. Formation of hydrophobic structures in water solutions by FSAP molecules is confirmed by titration with pinacyanol iodide solution as well as by their ability to solubilize water-nonsoluble liquids and substances (Table 4). The modification of initial FSAP by PEG or STX hydrophilic fragments decreases their surface activity and shifts CCS values in water to higher concentrations. On the contrary, the introduction of fatty alcohol hydrophobic fragments in their structures induces a considerable increase of the surface activity and a decrease of the concentration necessary to form colloidal micelle-like structures in solution. The presence of straight parts in the surface tension isotherms (Figs. 4,5; characterizing adsorption from solution onto the phase boundary) is caused, in our opinion, by the existence of compactly packed FSAP molecules or associates of them in solution.

Table 4:CCS values of oligoperoxidic FSAP

CCS values, kg/m^3	
Measurement of surface tension	Titration by solution of Pinacianole Iodide
6.03	6.89
4.47	4.83
5.24	4.89
4.37	4.21

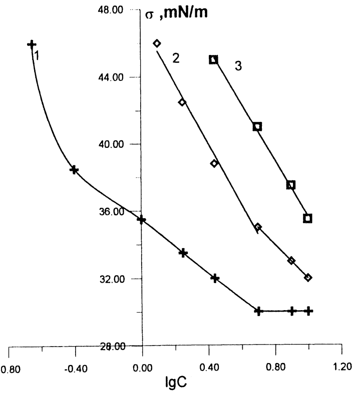


Fig. 4: Isotherms of surface tension of FSAP (N-VP-VEP-MA-VA 30:10:20:40) at: 1 – pH=3.2; 2 – pH = 6.96; 3 – pH=10.5.

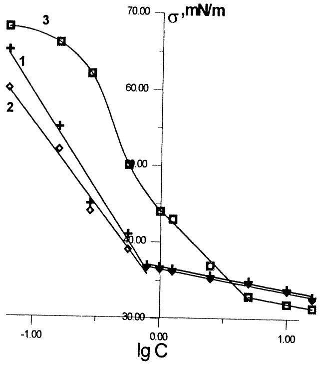


Fig. 5: Isotherms of surface tension: 1 – FSAP VAL-MP-MA 66.7:4.8:28.5 modified by PEG-13 at pH=7; 2- FSAP VAL-MP-MA 66.7:4.8:28.5 modified by PEG-13 at pH=10; 3- FSAP VAL-MP-MA 66.7:4.8:28.5 at pH=10.

It follows from the plots in Fig. 4 that a different character of surface tension isotherms of aqueous solutions of polyampholytic FSAP at different pH values exists. All of them witness about high surface activity and significant difference of CCS values, evidently due to different solubilities and hydrophobic-hydrophilic balances as a result of different carboxyl ionization at different pH values. The existence of compactly packed structures of the FSAP molecules in water is evident from both the coincidence of the CCS and surface tension values of the solutions of FSAP modified by fragments of polyetheleneglykole in a wide range of pH as well as the linear dependences on the plots of surface tension isotherms characterizing process of these FSAP adsorption onto interface. The contribution of nonionic fragments of PEG-13 to hydrophilic-lipophilic balance of initial oligomeric molecules, which are polyelectrolytes of anionic type, is so considerable that colloidal-chemical characteristics of modified FSAP don't depend on medium pH (Fig.5).

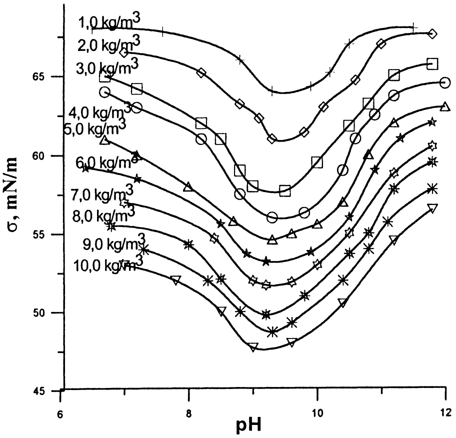


Fig. 6: The dependence of surface tension on pH of colloidal solution of FSAP (VA-AA-VEP-BA 30:15:20:35) peroxide-containing dispersions obtained by emulsifier-free copolymerization method.

The extrema found in the dependences of surface tension of FSAP solutions obtained by emulsifier-free water dispersion polymerization on pH (Fig. 6) indicate different degrees of carboxyl groups neutralization, which cause not only HLB changes but also simultaneous changes of the conformation structures of oligomer molecules in solutions influencing their surface-activity. The extreme dependences of the surface tension of such FSAP solutions on their concentration (Fig.7) are, in our opinion, due to wide molecular weight and functionality distributions of the oligomeric products formed during emulsifier-free water dispersion polymerization which cause significant differences in surface activity of FSAP molecules in the system.

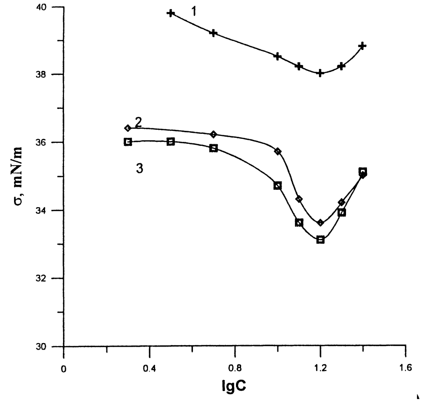


Fig. 7: The dependence of surface tension (σ) of water dispersion obtained by emulsifier-free polymerization at VEP content 6.7% (1); 11% (2); 20%(3) in initial monomer mixture on lg of water dispersion concentration.

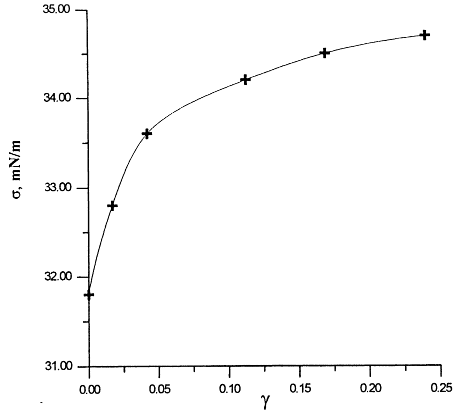


Fig. 8: Surface tension (σ) dependence vs stable OMC mole fraction (γ).

The investigations of colloidal-chemical properties of OMC aqueous solutions showed that the formation of coordinated bonds of copper cations with the FSAP ligands leads to the enhancement of their surface tension (σ) and to its increase with the increase of OMC mole fraction (Fig.8). Surface activity values of these substances calculated from experimental σ vs. C isotherms witness yet that they do not depend on Me^{n+} cation content. The surface activity value for FSAP and derived OMC in the investigated range of OMC mole fraction from 0 to 0.25 is - 0.003 J·m/mole. It is evident that this value is too small. It is characteristic for molecules with high content of polar groups. This phenomenon is explained by decrease of adsorbed OMC molecule size, which results in the distribution of their higher quantity at the interface due to their compactly packed conformations in comparison with conformations of initial FSAP. However, it is known[23, 24] that the more quantity of the lesser molecules at the interface is necessary for the achievement of the same surface tension lowering, which is attained by bigger ones. The decrease of adsorbed OMC molecule mobility due to their more compact packing, which restricts their phase-boundary change, is also the possible reason of such surface tension increase as it was shown by Abramzon[24]. This assumption is inferred by the increase of OMC maximum adsorption at water solution - air interface as well as onto the surface of dispersed γ-Fe_2O_3 fillers with the enhancement of stable OMC mole fraction (Figs.9, 10).

Using maximum values of adsorption of FSAP and OMC at water-air interface we have calculated approximate average surface (S_n) areas per adsorbed oligomeric molecule. From Inspection of Fig. 11 it fiollows that these values diminish with the increase of content of Cu^{2+} cation containing molecules in solution. This is due to their more compact packing and suggests a conformational structure for adsorbed molecules close to the completely extended conformation at the interface.

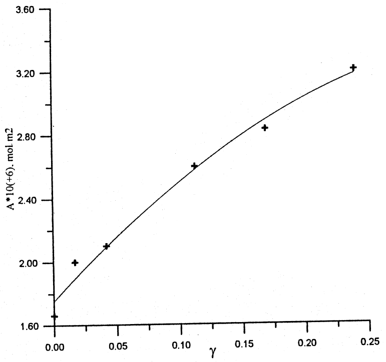


Fig. 9: OMC maximal sorption on water-air phase boundary vs stable OMC mole fraction (γ).

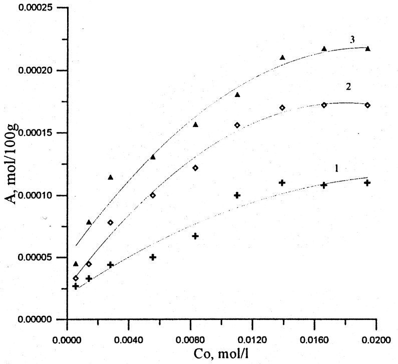


Fig. 10: The dependence of FSAP (1) and OMC (2,3) irreversible sorption on surface of dispersed γ-Fe_2O_3 fillers on their concentration in initial solution at OMC mole fraction γ 0.11 (2) and 0.17 (3).

The irreversible adsorption of oligomeric molecules on the surfaces of different nature causes the formation of solid adsorption layers from them. Varying of the FSAP nature, of the FSAP concentration, and of the adsorption conditions (first of all, pH and solvent polarity) permits to influence the hydrophobity, charge sign, its magnitude and reactivity of mineral or polymeric colloidal particles (Fig.11, 12). Surface controlled functionalization as the result of FSAP adsorption providing definite polarity and thickness of adsorption shell is possible as proved by applying the method of dynamic viscosity measurement of modified colloidal systems at low shear stresses (Fig.11).

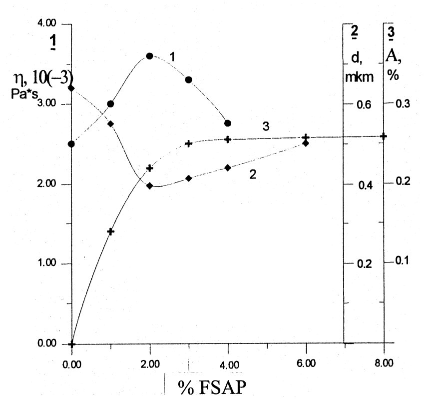


Fig. 11: Dependence of the maximum dynamic viscosity (1) particle size (2) and maximum irreversible sorption of FSAP (3) for ferrous oxide suspension synthesized and modified with FSAP vs. its concentration (solid phase content - 10%).

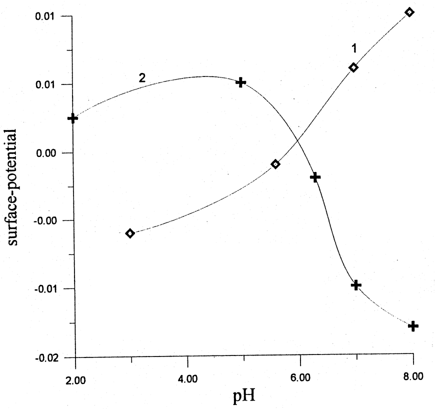


Fig. 12: Dependence of surface-bound charge for ferrous oxide particles, nonmodified (1) and modified (2) by FSAP (copolymer N-vinyl-2-pyrrolidone-VEP-maleic acid) vs pH.

Thus, the tailored irreversible functionalization of interfaces and particle surfaces as a result of FSAP adsorption is a prospective method for formation and modification of PCS of different nature by realization of radical reactions initiated by FSAP molecules immobilized in interfacial or surface layers.

3. FSAP APPLICATION FOR PCS FORMATION, STABILIZATION AND MODIFICATION

Combining of hydrophilic and hydrophobic fragments and reactive (first of all radical-forming) functional groups in water and oil-soluble FSAP structures permits to use them intentionally as active emulsifiers and stabilizers to form, stabilize and activate various PCS.

3.1. OBTAINING OF REACTIVE SYNTHETIC POLYMER WATER DISPERSIONS.

FSAP stabilize water emulsions of monomers nonsoluble in water (St, methylmethacrylate and others). They initiate the water- and organic dispersion polymerization in a temperature range of 273-358K due to thermal or catalytical homolysis of hydroperoxide or ditert.alkylperoxide groups. The localization of initiating radical centers in adsorption layers of phase boundaries provides diffusion and steric control of chain propagation and termination reactions. Thereby high polymerization rates and greater molecular weights of latex's polymers are achieved. Entering of FSAP surface-active fragments into the structure of latex polymer provides a higher latex stability and its irreversible modification. Electron microscopic investigations of latexes obtained in the presence of peroxidic emulsifiers-initiators prove the tendency to form particles with a narrow size distribution. The maximum of the size distribution of particles obtained and stabilized employing FSAP is in the range of 2200-3000A and their polydispersity coefficient is 0.91 (Fig.13).

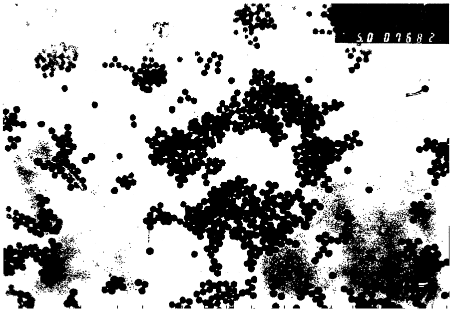


Fig. 13: Micrograph of polySt latex obtained with participation of FSAP VAl-VEP-MA based as emulsifier and initiator (enhancement 5000, [FSAP]=2%, 343K, phase ratio = 1:6).

Kinetic curves as shown in Fig.14 reveal that different mechanisms are active in high temperature polymerization and in polymerization initiated at 298K by OMC when St water dispersion polymerization is initiated by FSAP. This is caused, in our opinion, not only by rapid exhaustion of peroxidic groups during high temperature polymerization but also by different topochemistry of elementary stages of these polymerization processes. The kinetics of low-temperature polymerization initiated by oligoperoxidic metal complexes proves autocatalytical character of the process due to the diffusion control of chain propagation and termination reactions in hydrophobic colloidal structures formed by closely packed oligoperoxidic molecules containing metal cations. That causes also the higher process rates, molecular weights of polymerization products and grafting efficiency in comparison with polymerization initiated by initial FSAP (Table 5).

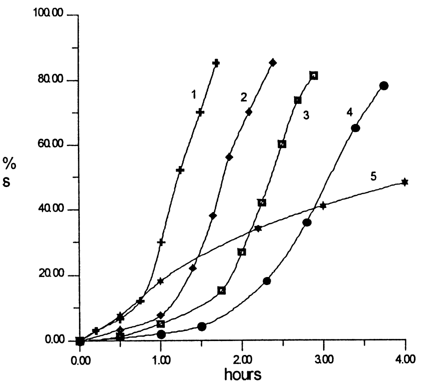


Fig. 14: Kinetic curves of St water emulsion polymerization initiated at 298K by Cu^{2+}-containing peroxide FSAP (pH=10)-1,2,3,4 and at 353K - FSAP (copolymer VA-VEP- maleic acid, without Cu^{2+}-cations) - 5: 1 - 2,5%; 2 - 1,0%; 3 - 0,5%; 4 - 0,25% of FSAP per H_2O-phase; St: H_2O-phase ratio equal 1:3.

Table 5: Comparative analysis of polystyrene obtained by initiation from the surface of Fe_2O_3 dispersed fillers modified by oligoperoxidic initiators (1%)

Initiator sorbed on surface of Fe_2O_3 particles	T, K	Conversion (8 hours), %	Content of polySt grafted to surface of Fe_2O_3, % to total amount of polySt
Oligoperoxidic metal complex with $[Cu^{2+}]$=1.4%, ligand VA-VEP-MA.	298	70	70
Oligoperoxide VA-VEP-MA.	353	89	30

3.2. OBTAINING OF WATER DISPERSIONS AND SUSPENSIONS BY POLYMERIZATION INITIATED FROM SURFACE OF COLLOIDAL PARTICLES MODIFIED BY FSAP

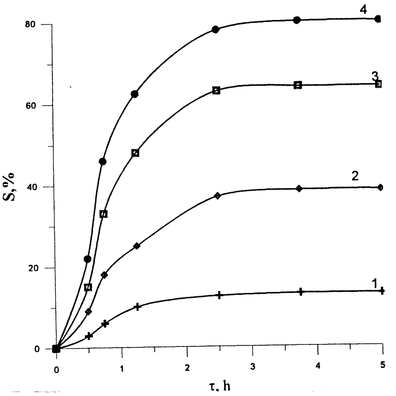


Fig. 15: Kinetic curves of seedea water dispersion polymerization of styrene stabilized and initiated by emulsifier-free water dispersion at its concentration 1.0% (1); 2.5% (2); 5.0% (3); 10.0% (4).

The possibilities of control of particle size and functionality of the latexes (obtained with the FSAP as a surface-active initiator, stabilizer and modifier) ensures the necessary colloidal-chemical (e.g. rheological) characteristics of dispersions, and their aggregational and sedimentational stability. The presence of the radical-forming centers on the surface of polymer or mineral particles modified by FSAP provides the possibility to realize that polymerization processes are initiated from the surface. In the case of peroxy-containing latexes this leads to theformation of new latexes with a particle structure named "core-shell" (Table 6), and in the case of mineral particles the formation of stable suspensions is ensured such as in magnetic liquids. The presence of radical-forming groups in the shell of colloidal particles provides repeated initiation from the surface, and thereby formation of composite polymer particles, which are highly dispersed and stable polymer/polymeric blends with the pre-definite properties. In our opinion, the localization of the radical formation reactions by peroxide fragments predominatly immobilized on the particle surface is proved by the dependences of the polymerization rates and yields on the content of the particles initiating seeded St polymerization from their surface in emulsifier-free water dispersions (Fig. 15). The leveling off of the kinetic curves for the high temperature seeded polymerization initiated from the particle surface indicates that radical-forming peroxidic fragments capable to initiate are alomost exhausted.

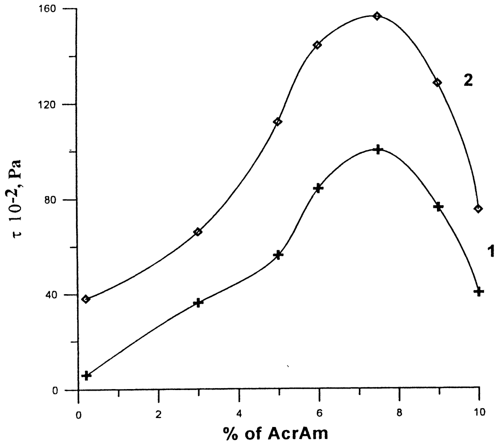


Fig. 16: Dependence of shear stress (at the rate of shear – 90 rotations per second (RPS)) on amount of acrylamide, which was used for modification by method of graft-copolymerization of water dispersions on the basis of: 1- drying oil (in the presence of FSAP (VA-VEP-BA-MA; 16.7:25:41.6:16.7) and 2 – alkyd resin of American production (in the presence of ricinoxe, FSAP (VA-VEP-BA-MA; 16.7:25:41.6:16.7).

The variety of approaches for obtaining different polymer colloidal systems with the composite "core-shell" structure is demonstrated by (i) the extreme dependences on the curves of dynamic viscosity of artificial water dispersions stabilized by FSAP molecules (Fig.16), (ii) the enhancement of the particle size of Polyvinylacetate and Polystyrene synthetic water dispersions (obtained and modified with metal-containing oligoperoxidic complexes (Table 6) after seeded polymerization initiated from their particle surface), and (iii) results presented above for seeded polymerization from the surface of peroxy-containing emulsifier-free water dispersions.

Table 6. The characteristics of water emulsion polymerization initiated from the surface of peroxide containing latex's (298 K, monomer: initial latex ratio 1:9)

Initial latex	Grafted monomer	Initial latex polymer : monomer ratio	Conversion max %	Polymerization rate × 10^4 mole/l×s	Particle size, μm	
					initial latex	latex with particle structure ''core-shell''
polyVA	St	1 : 1	97,0	1,4	0,2	0,8
polyVA	St	2 : 1	98,0	1,2	0,2	0,7
poly St	VA	1 : 1	93,5	1,0	0,1	0,5
poly St	VA	2 : 1	91,0	1,3	0,1	0,5

3.3. OBTAINING OF REACTIVE ARTIFICIAL POLYMER WATER DISPERSIONS

The artificial peroxy-containing waterborne film-formers were obtained by a mechanical dispersion of hot melts of unsaturated polyester, alkyd, epoxide, and silicone resins in the presence of FSAP as dispersers, stabilizers and modifiers, simultaneously. The FSAP surface activity causes the formation of stable water polymer dispersions containing controlled particle size and rheological characteristics (Table 7).

Table 7: The characteristics of the artificial unsaturated polyester resin water dispersions and films on their basis.

FSAP oncentration, % (to otal residue f polyester resin	Surface tension, mN/m	Particle size, μm	Kinematic viscosity, cSt, 298K	Electrolyte resistance, max vol. of 30% NaCl solution for coagulation	Gel-fraction,% (after thermo-curing at 418K, acetone)	Pendulum hardness
0	39,0	0,5	0,036	0,010	2,3	0,06
2,5	36,5	0,2	0,025	0,020	38,7	0,45
5	34,5	0,1	0,027	0,035	78,5	0,60
10	29,1	0,3	0,110	0,040	84,6	0,62

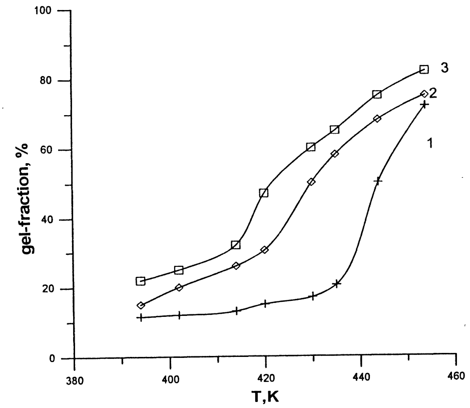


Fig. 17: The dependence of gel-fraction of reinforced composite on the basis of unsaturated polyester and glass fabric modified by artificial water dispersion of polyester resin with content5% (1), 10% (2) and 20% (3) of FSAP VA-VEP-BA-MA based on curing temperature (treatment during 10 minutes).

At the same time the presence of peroxide and other active groups in the adsorption shells of latex particles provides the possibility to thermal, catalytic or oxidation polymerization curing of films and coatings with a improved hardness, water, impact resistance, and adhesion activity. These peroxy-containing artificial dispersions can be successfully used as coupling agents for activation of the surface of carbon or glass fibers and fabrics. The application of them provides the participation of peroxidic fragments immobilized on the filler surface in radical processes of polymerization and curing of reinforced composites (Fig.17). It is evident that the increase of FSAP contents in the composition of the coupling agent shifts the point of acceleration of the reinforced composite curing to lower temperatures (Fig.17). The application of active peroxy-containing coupling agent causes an enhanced impact and corrosion resistance of reinforced polymer composites.

The oxidation-induced curing of the films on the basis of artificial water dispersions of alkyd resins formed and stabilized with FSAP as emulsifier and modifier simultaneously demonstrated the consumption of the ditertiary peroxide fragments in FSAP molecules even at 298K. This clearly shows the participation of the latter in radical curing reactions leading to the formation of –C – C – bonds providing the enhancement of thermostability of cured alkyd coatings.

3.3. OBTAINING OF PEROXY-CONTAINING METAL POLYMERIC AND FILLED COMPOSITE MATERIALS

Metal polymeric particles with controlled shape, size and functionality have been obtained by the method of homogeneous nucleation from solutions of copper, nickel, ferrous salts (including industrial wastes) in the presence of peroxide containing FSAP. The dependence of process rate effective constant on FSAP concentration confirms its participation in particle formation. The existence of high local concentrations of cations in colloidal structures formed by FSAP provokes the formation of particle preliminary nucleus on the juvenile surface, on which FSAP are adsorbed irreversibly. The particles are reliably protected from oxidation and a hydrophobic polymer shell provides their specified polymerophily (Table 8). The presence of radical-forming centers on the surface, which cause initiation and formation of stable filled liquids or solid composites with electroconductive or magnetic properties was proved by the spin-label method.

Table 8: Characteristics of ferrous oxide suspensions formed from the salt solution with participation using FSAP as desperser and modifier

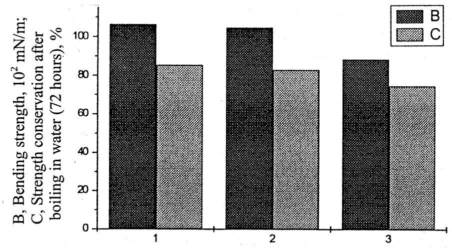
FSAP concentration, % to total residue	Maximal irreversible FSAP sorption on ferrous oxide particle surface,%	Surface hydrophobity, weight of sorbed water to weight ferrous oxide	Particle size, μm	Sedimentation stability 1/tgα*
0.5	0.07	0.17	0.60	4.8
1.0	0.19	0.05	0.72	5.2
2.0	0.36	0	0.53	6.3
5.0	0.39	0	0.54	8.0

- - 1/tgα is value directly proportional to suspensions sedimentation rate.

3.5. OBTAINING OF POLYMER COMPOSITES ON THE BASIS OF POLYMER/POLYMERIC BLENDS AND FILLED OR REINFORCED COLLOIDAL SYSTEMS ACTIVATED BY FSAP.

Oil-soluble FSAP provoke dispersion, stabilization and curing of mixtures of thermodynamically incompatible polymers, such as, for example, castable oligodieneurethanes and oligoesteracrylates. The localization of FSAP in the knots of such heterogeneous systems causes the formation of transitional interface layers and of controlled networks as the result of thermal or catalytic homolysis of peroxide fragments. The use of such oligoperoxides as curing agents provides synthesis and modification of castable rubbers on the basis of oligodieneurethane elastomer (Table 9). Rubbers modified by oligoesteracrylate (OAE) with FSAP as curing agent have higher breaking strength and thermo-resistance at high fatigue strength retention in comparison with those modified only by oligoesteracrylate.

FSAP adsorption on the surface allows the localization of reactive (including radical-forming) groups on it. Ionic, condensation, and radical reactions of functional fragments in the adsorption shell provide the formation of controlled complex of bonds between the phases in PCS within the interval 273-433K and allow the regulation of cohesion and adhesion properties of polymer composites (Fig. 18, 19).



1, peroxide-containing dispersion
(dried over 24 hours at 293 K and 4 hours at 383 K);
2, preroxide-containing dispersion
(dried over 24 hours at 293 K and 4 hours at 323 K);
3, industrial standard.

Fig. 18: Bending strength of lengthways directioned glass-plastic pivots produced with the use of keying agents on the basis of peroxide-containing emulsifier-free dispersion.

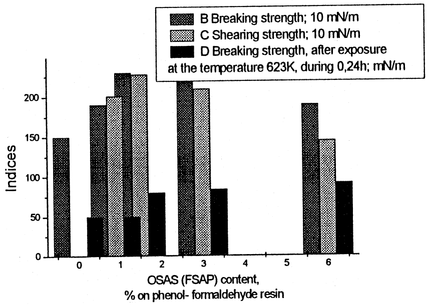


Fig. 19: Characteristics of the properties of composite* phenol-formaldehyde resin - carbon fiber modified by FSAP.

Table 9: Comparative characteristics of castable compositions on the basis of oligodienediol modified by oligoesteracrylate and peroxide-containing FSAP

Obtaining conditions and properties of the resins	Modifier	
	oligoesteracrylate + dicumyl peroxide	oligoesteracrylate + FSAP
Vulcanization parameters, curing in two stages (K/hour)	353/3 433/1,5	353/3 433/1,5
Fracture strength, MPa	17,4/6,0*	30,0/8,0*
Relative lengthening, %	810/660*	780/560*
Residual lengthening, %	15/95*	25/40*
Sol-fraction content, % (chloroform)	3,0	1,7
equilibrium swelling, % (chloroform)	1200	900
Resistance to crack formation (to 50 mm) at multiple bend of samples with zigzag ditch, cycles (10^3)	165	300
Endurance at symmetrical variable bend with rotation (deformation 20%), cycles (10^3)	2500	10000

- \- Numerator - value at 293K, denominator - value at 343K

CONCLUSIONS

We have shown a variety of possibilities of using FSAP for the formation of active interfacial adsorptive layers. In a wide temperature range the layers provide radical and non-radical reactions within themselves for obtaining polymer colloidal systems and composites. The comparison of these polymer composites with analogous ones obtained without FSAP testify (i) an increase of stability and dispersity of polymer colloidal systems, (ii) an increase of strength and dynamic characteristics, fatigue strength, thermal and chemical stability, and adhesive strength of compounds as a result of reactions in the interfacial adsorption layers. These are provided by the formation of controlled complexes via physical and chemical bonds between continuous and dispersed phases independent of their nature.

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