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Hybrid Polymer Inorganic Materials Prepared from Ternary Microemulsions

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Summary: The microemulsion system containing vinyl acetate (Vac), silane derivatives tetraethoxysilane (TEOS), methacryloxypropyltrimethoxysilane (MPTS), vinyltriethoxysilane (VTES), methyltriethoxysilane (MeTES), octyltriethoxysilane (OTES), nonylphenol etoxylated with 25 mol of ethylene oxyde ($NPEO_{25}$) and water was studied. It was established that the probability of microemulsion formation increases with surfactant concentration. The microenviroment of the solubilization of the VAc and of silane derivatives in the aggregates of $NPEO_{25}$ was affected by their polarity. Hybrid materials were obtained by sol-gel reaction of silane derivatives combined with free-radical polymerization of VAc. The change of the glass transition temperature and of thermal stability of the polymer chains in the presence of the inorganic one proved the formation of simultaneous polymer inorganic hybrids.

Introduction

The interest in hybrid polymer-inorganic materials [1-3] as well as that in dispersion of inorganic in fluids lead to an increasing number of studies combining these fields [4-6]. It emerged in getting hybrid polymer-inorganics as particles dispersed in organic solvents [7,8] polar solvents-water mixtures [9-11] or even in water [12-19].

The present paper describes the obtainment of vinylacetate (VAc) polymer-silica hybrids.

All literature data were referred to these inorganic materials in the analyzed litterature studies. The silica was either commercially available as different sorts [7,8, 12-18] or it could be prepared from sol-gel processes [9-11,15,20].

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The bonds between the polymer and the inorganic component may be formed by the copolymerization of the unsaturated monomers on the surface of silica particles. These reactive bonds can form by the reaction of the silica OH groups with metacryloyl propyltrimethoxysilane derivatives (MPTS) [10, 11, 14-18] or vinyltriethoxysilane. (VTES) [20, 22]. There are studies in which it is shown that initiator groups are fixed silica particles allowing thus the grafting of the polymer chain [7, 14].

For the polar polymers, there is evidence for interactions between hydroxyl groups of silica and the polar groups of polymers[21]. For nonpolar polymers, some interactions between alkyl or aryl groups from the modified silica and polymer chains were put in evidence [22,23].

In most cases, the polymer and the inorganic component are obtained successively. The hybrids may be generated by getting silica (trough sol-gel process), in the presence of polymers [9], or by performing the polymerization of monomers in the presence of performed silica [7,8,10-19].

The polymer types for obtaining the hybrids as dispersed particles [7,8,10-19] in fluid media, studied still now are: poly(vinyl acetate) (PVAc) [12,14], poly(methyl methacrylate) (PMMA) [13-15], poly(ethyl acrylate), [15-17] copolymer (vinyl acetate-ethyl-acrylate) [15], copolymer (styrene-butylacrylate) [14,15], polystyrene [7,10,11], poli(vinyl pyrolidone), poly(2-ethyloxazoline) [9], polymers obtained by the spontaneous polymerization of cationic surfactant monomers [8].

The polymers were synthesized by the polymerization in the presence of silica in solution [7, 8], in dispersion [9-11] or emulsion [12-19]. To our knowledges no attempts have been reported to obtain hybrid polymer-inorganic particles in ternary microemulsions.

There are studies in which silica particles were obtained in inverse microemulsions [24-27]. Studies performed by the authors concerning the microemulsion polymerization [28,29] demonstrated that due to the nanostructuration ability of short chain alcohols (C2-C4)-water mixtures microemulsions of the W/O, O/W, bi-continous type were obtained.

From this point of view, the classic syntheses initiated by Stober [30] may be regarded as microemulsion reactions. The analysis of used reaction medium composition [31] showed that the synthesis of the monodispersed particles of silica occur in a bi-continuous microemulsion.

If the ternary systems formed by tetraethoxysilane (TEOS), surfactant and water [32, 33] would be transparent, they might be considered ternary microemulsions. A recently published review shows the huge interest in ternary microemulsions for the preparation of polymeric microparticles [34].

The fact that ternary systems consisting of surfactant-water-VAc monomer and surfactant-water-alcoxysilanes are known to be reactive independently under similar conditions was a good premise for succesfully crossing the polymerization and silica formation. The goal is to find conditions for the radical polymerization of VAc and the sol-gel process of some alcoxysilane derivatives.

Experimental Part

Materials

Vinyl acetate, styrene (ST), butyl acrylate (BuA), commercial product, were purified by rectification. Tetraethoxysilane (Merck-Schuchard), methyltriethoxysilane (MeTES) (Merck-Schuchard), vinyltriethoxysilane (VTES) (Merck-Schuchard), octyltriethoxysilane (OTES) (Merck-Schuchard), metacryloyl propyltrimethoxysilane (MPTS) (Fluka) were used without supplementary purifications. Nonylphenol ethoxylated with 25 moles of ethyleneoxide ($NPEO_{25}$) commercial product was used without any purification. The ethoxylation degree was determined by NMR. Nonylphenol ethoxylated with 25 moles of ethylenoxide sulphosuccynate ($NPEO_{25}SS$) was synthesized like in [35]. Sodium dodecyl sulphate (SDS) (Merck) was used without any further purification. Ammonium persulphate (APS) (Loba-Feincheime) was used without any further purification.

Procedure

VAc and silica derivatives were solubilized by adding the components under stirring to the surfactant solution. The solubilization limit is observed when the ternary mixture became turbid. The solubilization process was performed at 25°C.

The polymerization were performed in the glass reactor, equipped with an anchor stirrer, having 150 rot/min. The surfactant solution, the monomer and if it is the case, the silica derivative are successively introduced in the reactor. Under stirring at room temperature, it is purged with argon for one hour.

The reaction mixture is then heated, under stirring, to 65°C and under argon. APS is added under stirring. The total quantity of reactants was 400 g or 200 g and the quantity of APS was of 1 g, respectively 0.5 g.

Analysis

The quantity of polymer formed was gravimetrically established. The polymerization rate was estimated from polymer-time curves for 400 g reaction mixture. The undecomposed initiator quantity was determined ceriometrically [36].

The size of latex particles was determined with a Nicomp 270 instrument. After polymerization, the stable latexes or the deposits of the separated ones, were subjected to dialysis to eliminate the surfactant and low molecular weight products.

The thermal analyses of polymers and hybrids were performed with a Dupont 2000 instrument. The samples were heated in air with a rate of 20°C/min for TGA and 10°C/min for DSC. ^{1}H-NMR spectra were recorded with a Bruker Avance DRX 400 instrument at 400 MHz. The signals of α vinyl protons for the monomers were determined in $CDCl_3$ solutions (10%-δI) and in $NPEO_{25}$ solutions (10%-δII). The signals for surfactants were determined in the same conditions. The differences between the chemical shifts were calculated for the surfactants solution in water, in the presence and the absence of monomers.

The fluorescence measurements were recorded with a Shimadzu RF-5001 PC instrument, using pyrene ($5*10^{-6}$M) as reference. The fluorescence spectra were recorded for alcoxysilane derivatives and their mixtures in $NPEO_{25}$ 10% solution, at the solubility limit concentration. The ratios I_1/I_3 are presented in Table 1.

Table 1. Parameters of the fluorescence spectra of the pyrene in the presence of the alcoxysilanes and of the solutions of surfactants.

	I_1/I_3					
	Surfactant	TEOS	MeTES	VTES	MPTS	OTES
		0.909	0.829	0.855	1.298	0.921
SDS – 15%	1.067	0.975	1.019	0.992	0.989	0.991
$NPEO_{25}$ – 15%	1.222	1.227	1.203	1.236	1.212	1.225

Results and Discussions

The solubility domain of VAc in $NPEO_{25}$ and $NPEO_{25}SS$ solutions is mentioned in Fig. 1. Because of the excessive increase of surfactant solution viscosity, its maximum concentration was 50% weight. These diagrams are very similar to the ternary diagrams published before [37, 38]. The VAc solubility increases with the increase of surfactant concentration and temperature.

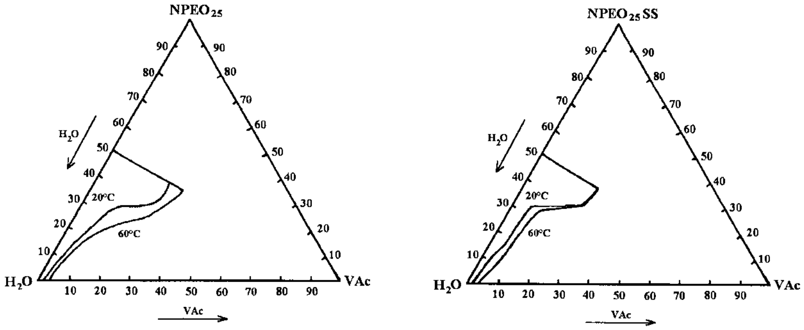

Figure 1. Phase diagrams for NPEO25, NPEO25SS, VAc, water (max. NPEO25 (NPEO25SS) / water = 50/50).

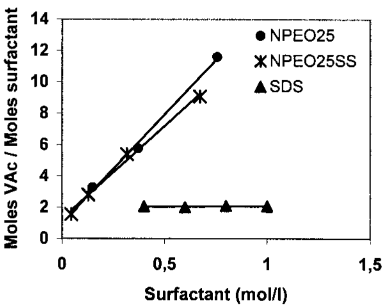

Figure 2. The modification of the VAc solubilization versus surfactant concentration.

The quantity of solubilized monomer, the ratio moles VAc/ moles of surfactant, was calculated in water with the increasing the surfactant concentration (Fig. 2). The results are very interesting. The VAc solublized by 1 mole of surfactant increases proportionally with its concentration in water. The specific solubilization of VAc by NPEO25, nonionic surfactant, is greater than in the case of NPEO25SS, anionic surfactant, but with a similar structure. For comparison, the solubility of VAc by SDS is given too [39]. In the case of this surfactant the specific solubilization of VAc does not change with its concentration in water. These differences demonstrate the complexity of the solubility phenomenon. Studied published before [40, 41] showed that depending of their the polarity monomer can mainly interact with the hydrophilic or the hydrophobic part of the surfactant. The results in the Fig. 2 demonstrate that this solubilization depends also on the structure of the surfactant. Our previous RES studies [42] showed that the solubility of VAc in $NPEO_{25}$ solutions takes place mostly on the polyethyleneoxide groups, meaning the hydrophilic part. NMR studies showed that in aqueous solutions of SDS, VAc interacts with both the hydrophilic and the hydrophobic part [39].

In this work we measured the change of the chemical shifts of the α vinyl protons or VAc, BuA, ST in surfactant solutions (δ II) with respect to those in $CDCl_3$ (δI). The results are presented in Fig. 3. It was observed that the changes of these chemical shifts depend on the nature of monomers. This information indicate a change of the domain in which monomers are soluble in micellar aggregates of $NPEO_{25}$.

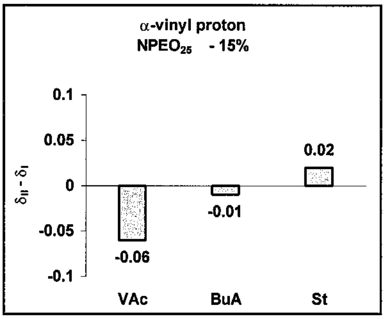

Figure 3. The differences (δ_{II}-δ_I) for monomers solubilized in $NPEO_{25}$ solutions (δ_{II}) and in $CDCl_3$ (δ_I).

Supplementary information about solubilization zones was obtained following the modification of the chemical shifts of phenyl and ethyleneoxide protons in the hydrophobic and hydrophylic zone.

In agreement with the previous results [39-41] it was shown there was a change both of the phenyl protons from the hydrophobic zone and of the protons of the ethyleneoxide units. The ratio of the calculated differences for phenyl and ethylenoxide protons is presented in Fig 4. These results showed that although the monomers are distributed both in the hydrophilic and in the hydrophobic zone. Styrene, a more hydrophobic monomer, modifies mostly in the phenyl zone, and vinyl acetate more hydrophylic modifies in the ethylenoxide protons zone.

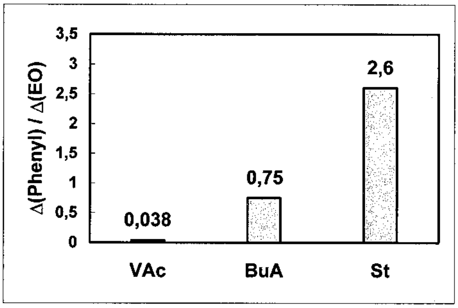

Figure 4. The variation of the ratio Δ('HΦ)/Δ('HEO).

We consider that these results demonstrate for the first time the way of solubilization of the monomers in nonionic surfactant ternary microemulsion. The monomers interact mostly either in the hydrophobic or hydrophilic zone depending on their polarity.

Studies regarding the factors which affect the polymerization rate of VAc and the cleavage rate of APS were recorded in $NPEO_{25}$, surfactant with the highest solubilization capacity.

For the start, the influence of monomer concentration was studied (Fig. 3). The polymerization rate increases nonlinear with the monomer concentration. Then is a larger polymerization rate above VAc/ $NPEO_{25}$ = 0.4. The ratio corresponds to the limit of solubility of the monomer. These results, similar with those obtained for anionic surfactants [43], indicated that over the solubility limit, in emulsion polymerization conditions, the increases in polymerization rate is due to the appearance of monomer droplets.

The productivity of the initiator decomposition (grams of polymerized monomer for a gram of decomposed APS) increases with the increase of monomer concentration (decrease of the VAc/ $NPEO_{25}$ ratio). This phenomenon, observed also in other cases of VAc polymerization [35, 43] suggest the existence of a strong initiator-surfactant interaction. A part of initiator is inefficiently consumed with $NPEO_{25}$.

The effect of the changes in surfactant concentration is presented in Fig. 6. In this case, the polymerization occurs only in microemulsions. The polymerization rate increases with the increase the VAc/ $NPEO_{25}$ ratio (Fig. 6). The decrease of the polymerization rate with the increase of surfactant concentration (the decrease of the VAc/ $NPEO_{25}$ ratio) suggests an inefficient initiator consumption, in the reaction with the surfactant, reaction which decreases the number of active radicals for initiation. Like in the Fig. 5, the increase of the VAc/ $NPEO_{25}$ ratio, increases the initiator productivity (Fig. 6).

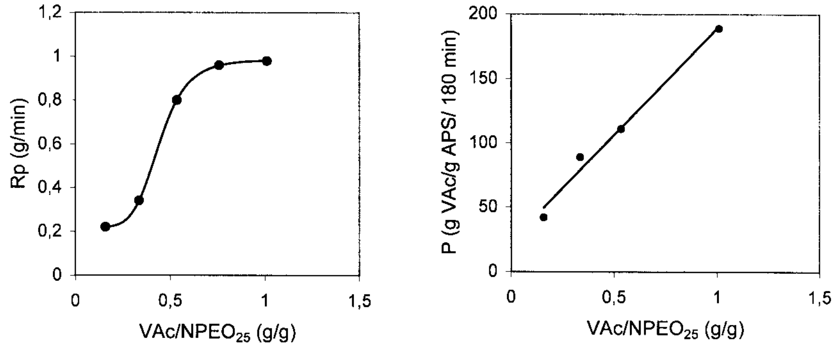

Figure 5. The influence of VAc concentration on the polymerization rate (Rp) and on the productivity of APS (P); ($[NPEO_{25}]_0$ = 33%, $[VAc]_0$ = 5-25%, 65°C, 3h).

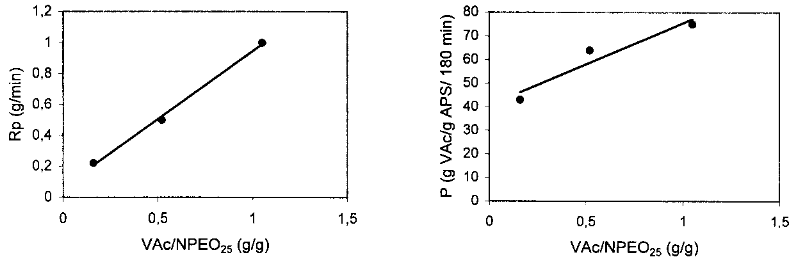

Figure 6. The effect of surfactant concentration on the polymerization rate (Rp) and on the productivity of APS (P); ($[NPEO_{25}]_0$ = 5-33%, $[VAc]_0$ = 5%, 65°C, 3h).

A very important aspect for obtaining hybrids as dispersed particles in water, is that stable latexes were obtained only at surfactant concentrations in $NPEO_{25}$, under 10%. The increase of solubilization of VAc over this concentration (Fig. 1) may be due to formation of supramolecular aggregates, which determine the agglomeration of particles in latex.

The study of the conditions for PVAc-silica hybrids started with the determination of the solubilization capacity of alcoxysilane derivatives when 15% wt surfactant solutions were used (Fig. 7). The calculated quantity of the solubilized alcoxysilane derivatives by $NPEO_{25}$ or $NPEO_{25}SS$ shows that the maximum is obtained for MeTES. The minimum quantity was obtained for OTES which was not used for subsequent syntheses. It was demonstrated again that the solubilization of alcoxysilane derivatives depends on the nature of the product. The presence of a methyl group in MeTES induces a higher solubility, probably due to its interaction also with a part the hydrophobic chain. SDS presents a modified solubilization capacity as in the case of VAc. (Fig. 2). In this case the maximum solubilization is for MPTS. The presence of ester and those of methyl or methylen groups give a better solubility. The solubilization of alcoxysilane derivatives is smaller (Fig. 2, 7) compared to the solubilization of VAc.

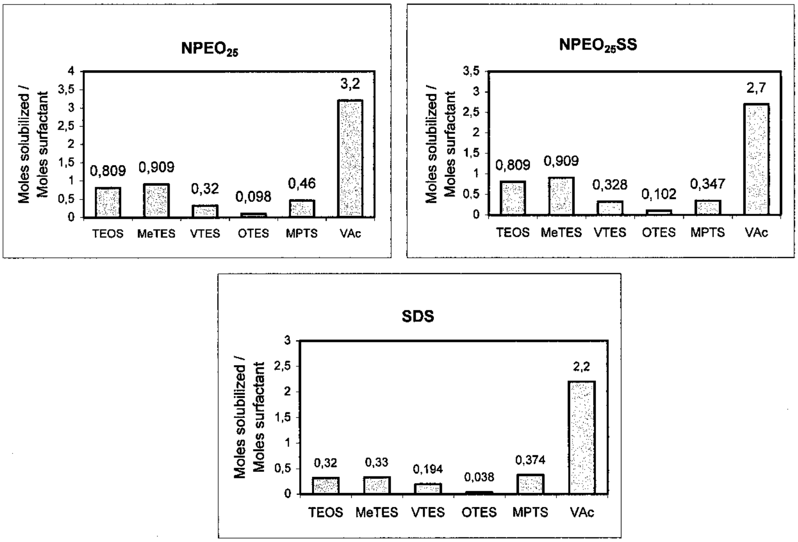

Figure 7. The solubilization of alcoxisilanes in water solutions of surfactants ([surfactant] = 15%).

In order to obtain information regarding solubilization zone of alcoxysilane derivatives, fluorescence measurements were performed using pyrene as reference.

Previously published data [44] showed the solubilization of pyrene in SDS micellar aggregates in the hydrophilic polar zone, and in nonionic surfactant aggregates, $NPEO_{25}$ in the aromatic ring, hydrophobic zone.

The I_1/I_3 ratio is a measure of the polarity of pyrene microenviroment [27, 39]. The order of the modification of this ratio for the SDS micellar solutions and for alcoxy derivatives microemulsions is:

MPTS<OTES<VTES<MeTES<TEOS<SDS

This change is a indication of the solubilization of the most polar derivative of TEOS toward the hydrated polar zone, and those nonpolar MPTS, OTES to the nonpolar zone. In the case of $NPEO_{25}$ micellar aggregates the changes of I_1/I_3 ratio are not so large. The order of these changes is:

MeTES<MPTS<$NPEO_{25}$≤OTES<VTES

Even if the changes are not significant they may suggest the fact that MeTES, MPTS are solubilized mainly at the nonpolar aliphatic chain, and the polar TEOS (VTES) to the polar zone.

A first test of the reactivity of alcoxysilane derivatives in microemulsions was performed on the micro emulsions obtained after the solubilization tests. In most of the cases, after 52 hours of reaction at 65°C, the final mixtures remain homogeneous. The opalescence, due to the formation of particles, was observed in the TEOS-$NPEO_{25}$, MPTS- $NPEO_{25}$, SDS-VTES systems.

Table 2. Conditions of polymerization of VAc and of the sol-gel process (190g sol $NPEO_{25}$, 10g VAc, 0.5 g APS, 3h, 65°C).

No.	Conc. $NPEO_{25}$	RTES	pH	Solids	Medium diameter of particles(nm)		D_v/D_n	Final appearance
	(%)	(g)		(%)	D_n	D_v		
1284	4.9		3	8.08	10.1	21.9	2.1	
1285	5.2	TEOS/1.26	3	9.6	9.2	19.7	2.14	
1286	5.27	MeTES/1.1	5	10.8				
1287	5.0	VTES/1.15	5	7.66				separated
1288	5.1	MPTS/1.5	5	7.93				separated
1289	5.12		5	8.82	8	17.2	2.15	
1290	5.17	TEOS/1.26	5	9.13	7.9	16.3	2.06	
1295	5.5	MPTS/1.5;24h	3	8.6				separated
			without VAc					
1291	5.42	TEOS/1.26	5	5.86				transparent
1292	5.13	MeTES/1.1	5	5.65				opaque
1293	5.35	VTES/1.15	5	5.81				transparent
1294	5.13	MPTS/1.5	5	6.52				separated

The reaction conditions for obtaining PVAc-SiO_2 hybrids are presented in Table 2.

Some of the syntheses were performed with an aqueous phase with pH =3, obtained by adding HCl. This path was used because, it is known that, the hydrolysis of RTES derivatives of type occurs with maximum rate at acid or basic pH [45]. Because after polymerization, the aqueous phase has eventually pH = 3, some syntheses were performed without correcting the initial pH.

A first observation from the data presented in Table 2 is the fact that the conversion of VAc is not total.

An agglomeration of particles and their separation from the aqueous medium was discovered also in the case of presence of mixed monomers, MPTS, VTES, which react both radically, and in sol-gel processes. Probably their presence in the polymeric particles will determine a lower stabilization of the surfactant. In the case of MPTS polymerization without VAc (s. 1294) large agglomerated particles were obtained. If only MeTES was used large particles were also obtained (Dn = 1200 nm) which sediment slowlier (s. 1292). When TEOS or VTES were used without monomer the final system is homogenous, and transparent. Probably in the case of these derivatives the rate of the sol-gel process is lower.

The stable latex particles obtained in the presence of VAc and its alcoxysilane derivatives have smaller medium diameters than those obtained only with VAc. From the distribution of particle diameters one can see that this result was obtained due to the decrease of number of agglomerated particles. It is an interesting stabilization phenomenon by the products of the sol-gel process, effect observed in the emulsion polymerization in the presence of silica [13].

In order to reveal the formation of PVAc-SiO_2 hybrids the behaviour at programmed heating the process (20°C/min) was studied for the obtained products (Fig. 8, Tab. 3). The elimination of surfactant from the sample was done by dialysis until the exterior water of membranes, containing the sample, did not show the presence of surfactant by UV. The value of the inorganic residue corresponds to a product without the surfactant (Tab. 3). By heating PVAc (s. 1284, 1289) two main steps of thermal decomposition were observed: one appeared until 400°C, and the other until 600°C.

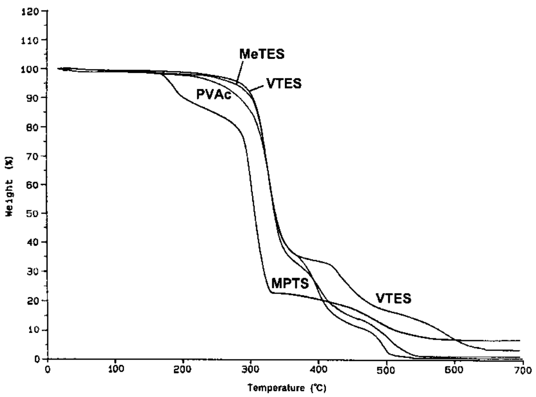

Figure 8. TGA curves for some hybrides (Tab. 3).

Table 3. The influence polymer and hybrid compositions on thermal stability.

No.	RTES	Solides	Loss of weight (%) / T_{max}						Theoretical residue	$RSiO_{1.5}$
	g	%	<100 °C	<200 °C	<300 °C	<400 °C	<500 °C	<600 °C	%PVAc %PVAc+NF	g
1285	TEOS 1.26 pH=3	8.79	1.22	2.64	11.21	68.38 320	90.9 410; 446	99.4 520		--
1286	MeTES 1.1 pH=5	10.83	0.85	1.88	9.9	75.34 333	92.35 405; 500	98.12	4.4 2.1	0.436
1287	VTES 1.15 pH=5	7.66	0.5	0.94	8.76	66.22 323	82.8 433	92.6 586	5.0 2.2	0.49
1288	MPTS 1.5 pH=5	7.93	0.13	9.64 180	31.3	79.22 307; 400	88.4 480	92.8	7.9 3.9	0.803
1289	-- pH=5	8.82	0.6	2.05	14.07	76.7 330	96.96 490	99.2	0 0	0
1290	TEOS 1.26 pH=5	9.13	0.66	2.25	11	72.7 340	91.3 410	97.5 510	3.7 2.5	0.3614

In agreement with the previous published results [21, 46-48] the first step corresponds to the elimination of acetate side groups, and the second step to the thermooxidative decomposition of the left polymeric chain. From the differential curves the temperatures at which these two steps have a maximum rate were measured. The temperature at which the first step has a maximum rate was considered a parameter for the estimation of the thermal stability [48].

Except for the hybrid obtained in the presence of MPTS (s. 1288) all the other hybrid materials have an enhanced thermal stability compared to the PVAc (Tab. 3). In agreement with the previous published papers [21, 46, 47] the inorganic lattice of SiO_2 in PVAc has as effect the increase of thermal stability. The decrease of the thermal stability in the case of formed VAc-MPTS copolymers (s. 1288) was due to the fact that metacryl, structural units, induce a lower thermal stability than PVAc [48].

The inorganic network of a hybrid material attenuates the transition in the glass phase (T_g) and it shifts to the higher temperature domain [46, 47]. The same effect was observed also in the case of the analyzed samples in Fig. 9. The DSC curves for the samples obtained from latexes (1286, 1289, 1290) have a different aspect compared to those obtained from compact materials during synthesis (1287, 1288). The last two samples are hybrids, strong crosslinked through organic and inorganic chains. In the case of the first two samples, due to the high T_g of PVAc no homogeneous films could be obtained, but only tensioned friable materials. Due to these differences behaviour a similar phenomenon with those mentioned before is observed [21, 46, 47, 49].

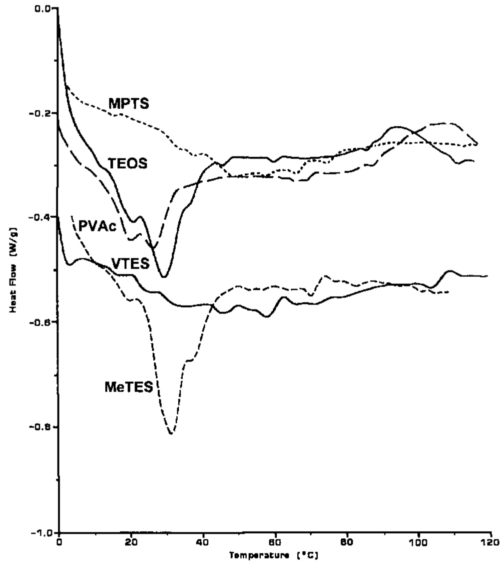

Figure 9. DSC curves for some hybrides (Tab. 3)

The temperature domain at which the modification of the thermal properties starts is minimum for PVAc (s1289).

The increase of the temperature domain at which the transition in the glass phase occurs, the increase of thermal stability, the existence of an inorganic residue when the samples are heated at 700°C (Tab. 3) demonstrate the presence of polymer-inorganic hybrids.

Conclusions

The solubilization of vinyl acetate in aqueous surfactant solutions depends on the nature of the surfactant. It increases with the concentration of the surfactant. Specific solubilization, moles of VAc/moles of surfactant increases with the concentration of surfactant in the case of $NPEO_{25}$, $NPEO_{25}SS$, long hydrophilic chain derivatives.

At the same surfactant concentration the solubilization of TEOS, MeTES, VTES, MPTS is lower than in the case of VAc.

Polymerization rate of VAc in ternary microemulsions increases with the increase of the $VAc/NPEO_{25}$ ratio. This phenomenon as well as the increase of the initiator productivity with the mentioned ratio, demonstrate the existence of initiator-surfactant secondary reactions.

The latexes obtained in the presence of TEOS and MeTES are stable and present a mean diameter of particles smaller than in the case of the homopolymer. It was demonstrated the stability effect of particles induced by the products of the sol-gel process.

The presence of silica and of the modified silica increase the thermal stability of hybrids and the glass transition temperature in comparison with PVAc.

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