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TECHNOLOGICAL FEATURES OF OBTAINING AND PROPERTIES OF GRAFTED POLYVINYLPYRROLIDONE COPOLYMERS

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The impact of the vinyl monomers nature, concentration, and temperature on the kinetics of dispersion polymerization in the presence of polyvinylpyrrolidone was studied. The optimal technological parameters of the copolymer synthesis process are determined. It is defined that the properties of dispersion polymerization depend on the process conditions. Such conditions are temperature, monomer and aqueous phase ratio, monomer and initiator concentrations and as well as the amount of polyvinylpyrrolidone. Presented materials derived on the ground of the developed compositions are characterized by principally high working and physical-mechanical properties.

Key words: aqueous phase, methylmethacrylate, copolymer, polyvinylpyrrolidone, dispersion polymerization, vinyl monomers.

Introduction

The current scientific and technological progress requires the new polymer materials creation with respective special properties. Such properties are the next: high adhesion to supports of various nature, high physical, mechanical and thermophysical as well as selective-sorption properties. Above mentioned includes low-toxic adhesive polymer-monomer compositions of medical and technical purpose.

Within the methods applied for the preparation of materials are those based on the known industrial polymers modification in process of polymerization. These methods provide obtaining of polymer materials with preferable collection of the technological and working properties. The main factor for the most of technologies based on preparation of modified polymer materials is a modifier. Such polymers which possess the high surface activity, good solubility in water and other organic media, high ability to complex formation as well as high sorption characteristics are applied as modifiers [1, 2].

Polyvinylpyrrolidone and its copolymers are the polymers with specific properties which allow to obtain new functionalized modern materials [3, 4] as well as expand the areas of their application [5,6].

The composition containing polymer and monomer are widely applied in the different manufacturing fields, mainly as a basis for preparing materials with increased adhesion properties.

Acrylates belong to such special materials. Foremost the increased interest in acrylates-containing adhesive materials is caused by their high working properties, for instance, cure velocity, adhesion to different materials, fastness and durability of adhesive compounds and its low toxicity. In this manner, mentioned materials are widely applied in a variety of industries, for instance, in medicine, dentistry, construction, engineering, automotive as well as electrical and textile industries. It needs to be emphasized that the use of (meth) acrylic compositions is now being designed a number of technological issues [7].

The elementary components of (meth)acrylic glues are (meth)acrylic monomers or polymers, initiating systems, hardeners, stabilizers as well as modifiers. Methyl methacrylate (MMA) is frequently applied as the basic monomer in the (meth) acrylic glues. It supports the high sticky strength and demonstrate itself as a good diluent for a significant part of the polymers. At the combining with oils, MMA allows to stick together untreated surfaces.

Mentioned monomer possesses of the several disadvantages, for instance high volatility, pungent odor and fire risk. MMA is being applied in impurity with the high boiling monomers which is hydroxyalkylmethacrylate, glycidyl methacrylate, methacrylates of higher alcohols (tetrahydro tetrahydrofurfuryl-, diethylaminoethyl-, 2-oxopropylneopentyl- and other glycol methacrylates) and styrene [7,8].

The purpose of this work: to investigate the influence of nature, concentration, temperature and mixing rate of vinyl monomers on the kinetics of dispersion polymerization in the presence of polyvinylpyrrolidone.

Materials and methods

Copolymers has been synthesized via the dispersion polymerization of vinyl monomers in the presence of PVP, potassium persulfate or hydrogel peroxide at 60–70 °C as well as the ratio of monomer to aqueous phase of 1:3.

The kinetics of the dispersion polymerization of the test compositions was researched through dilatometric method via fixing the volume change of the reaction blend at the polymerization.

The glue compositions were synthesized through the MMA polymerization or its blend with other monomers in the presence of synthesized copolymers at the room temperature.

The set temperature of the experiment was set in the thermostat. The tube filled with the polymerization mixture was placed in a thermostat with organosilicon liquid so that the upper level of the composition was below the liquid level in the thermostat. Simultaneously with the immersion of the tube in the thermostat, a millivoltmeter was connected to which a thermocouple was connected to measure the temperature change in the test composition.

After completion of the esoteric curing process (temperature drops to bath temperature), the millivoltmeter and thermostat were turned off, and the sample tube was removed from the thermostat.

The surface hardness of the samples at the conical flow point was determined on a Heppler consistometer at a temperature of 293 K, pressing into the polymer sample a steel cone with a sharpening angle of 580 08 'under a load of 5.0 kg for 60 s;

Vicat softening point of the templates were measured applying the Heppler consistometer.

Adhesion was identified according to ISO 527-5:2009.

Results and discussion

Our polymers are synthesized on the ground of PVP and vinyl monomers (MMA, vinyl acetate (VA), styrene) through the dispersion polymerization. Mentioned polymerization of vinyl monomers is mostly conducted in the presence of substances which are surfactants of the different nature [7–10].

The nature of mentioned substances and its concentration in the reaction medium significantly impacts the mechanism and kinetics of the polymerization and consequently the technological features of the process and its efficiency. Described impact is caused by the changes in interphase features of the polymerization system, adsorption phenomena at the phase boundary, also by the changes in monomers dissolubility at the dispersion medium with an active part of the dispersants. Mentioned substances have to correspond a certain requirements [9, 10] in particular, high surface activity, ability to micellization and non-toxicity.

Owing to its properties and structure the PVP can serve as the dispersant in the processes of polymerization and also to play a role of polymer matrix, which actively participates directly in the polymerization. It need to be emphasized that the impact of the dispersant on the peculiarities of the dispersion polymerization of vinyl monomers is firstly resulted in the interphase characteristics change of the polymerization system and the monomers solubility in the reaction medium.

On the ground of previous research, it was determined that PVP macromolecules show the high surface activity on interphase surface of water-vinyl monomer. Described activity rises with the reducing within the monomer polarity in VA–MMA–styrene series.

It is proceeds due to the nature of the interphase tension isotherms in vinyl monomer-aqueous PVP solution system. It has been showed applying the PVP adsorption dependences in the coordinates of the Langmuir equation, the maximum values of the Gibbs adsorption (G_m = $2.14 \cdot 10^{-6}$ mol/m^2) and work of adsorption (W_{ad} = $48.8 \cdot 10^{-3}$ J/m^2) for styrene. PVP has various influence on the total (true and colloidal) solubility of vinyl monomers in the water solution [11].

With an increase of the PVP up to 0.2 mol/L the monomer concentration and solubility of MMA increases from 0.15 to 0.22 mol/L and it decreases from 0.33 to 0.18 in case of VA, that it is almost constant in the case of styrene. Certainly, this is a consequence of the specific intermolecular interactions that will impact the polymerization processes in the mentioned systems. High surface activity and solubilization ability of PVP focuses on high efficiency as dispersant in the processes of dispersion polymerization of vinyl monomers (KKM PVP: 0.09–0.11 mol/L monomer concentration).

The imoact of the monomer nature (VA, MMA, styrene), concentration factors, temperature and mixing velocity on the kinetic features of the dispersion polymerization of vinyl monomers in the presence of PVP is studied.

The dispersion polymerization of vinyl monomers in the presence of PVP is noted by various rate depending on the nature of the monomer (Tabel 1).

Table 1

Time dependence on the degree of vinyl monomers conversion

Conversion time τ, s	Conversion degree A, %		
	vinyl acetate (VA)	styrene	methyl methacrylate(MMA)
2000	20	2	3
4000	88	5	8
6000	–	10	20
8000	–	15	60
8500	–	18	73

It was found that the polymerization velocity of all the studied vinyl monomers rises with an increase in the ratio of the monomer phase to water phase as well as the concentration of the initiator and the temperature.

Grounded on the defined kinetic characteristics of the dispersion polymerization of vinyl monomers in the PVP presence, the well-founded technological parameters of the polymerization process are determined depending on the nature of the monomer (Table 2).

Table 2

The principal features of dispersion polymerization depending on the monomer nature

Parameter	styrene	vinyl acetate	methyl methacrylate
Temperature of polymerization, K	343	323–333	323–333
Mixing velocity, rpm	140–160		
Time of polymerization, hour	6.0–6.3	2.5–2.7	3.8–4.0
PVP concentration, mol/L	$(9.0–9.5) \cdot 10^{-2}$		
Initiator concentration, mol/L	$(2.6–3.0) \cdot 10^{-3}$		
Correlation of monomer phase to aqueous phase	1:(2–3)	(0.88–1):1	1:3
Permanent content of monomer, %	0.7–0.9	1.0–1.2	0.05–0.8

The consistency of the process technological stages for derivation of synthesized copolymers in the form of finely dispersed powders is defined as following: sedimentation with potassium alum (C_{pa} = 1 %), centrifugation ($v_{centrif}$ =1700 rpm, $\tau_{centrif}$ = 20–30 min), washing with demineralized water and drying (T_d = 313–343 K, τ_d = 150–200 min) [12].

Due to the polymerization, the graft copolymers of PVP are formed in the systems under study. The physical and chemical researches are confirmed above mentioned.

Effectiveness and degree of grafting depend remarkably on the conditions of the process, namely the PVP concentration in the water medium and the process temperature.

It has been determined that the properties of latexes derived by dispersion polymerization (surface tension, pH, particle radius etc.) depend on the conditions of the process, such as the ratio between the monomer and aqueous phases, the temperature, the concentration of the monomer and initiator and the PVP quantity. With the increasing concentration of the initiator the temperature of the process decreases also the latex particles size and the pH decrease (Tabel 3).

Table 3

The effect of initiator concentration on the pH medium and particle size

Initiator content, %	Parameters of dispersion polymerization	
	pH medium	Size of latex particles *r*, nm
0.5	3.42 / 3.45	68 / 100
0.8	3.26 / 3.33	63 / 101
1.1	3.19 / 3.33	61 / 99
1.4	3.13 / 3.33	59 / 98

at the temperature 323K / 333K

The components ratio of the polymerization system and the mixing speed also has a considerable effect on the size of latex particles. The polymerized graft copolymers of PVP were applied as a polymer matrix for the MMA copolymer compositions cured through the block polymerization.

It should be noted that the MMA polymerization in the presence of PVP copolymers is an exothermic reaction with substantive thermal effect. Consequently, thermometric study was carried out aimed to determine the temperature change of polymer-monomer compositions during polymerization (Fig. 1).

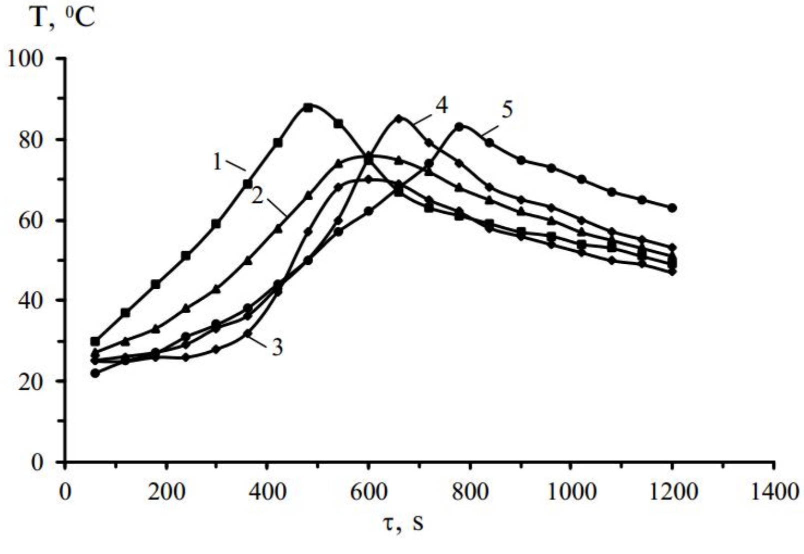

Fig. 1. Thermometric polymerization curves for the polymer-monomer compositions. Polymer matrix (PM):PVP-gr-PMMA (1, 4, 5); PVP-gr-PS (2); PMMA (3). Monomer phase (MPh): MMA (1–3); MMA:HEMA=8:2 (4); MMA:GMA=8:2 (5). PM:MPh=2:1

During the blending of a finely dispersed polymer with a monomer phase, a homogeneous composition is being formed. Such polymerization is characterized by the presence of an induction period.

During the induction, the composition possess plasticity and the temperature does not rise. The induction period duration and the maximum of the heating temperature of the composition substantially depend on the nature of monomer and polymer phases. The duration of the induction increases with the co-monomer addition. This is obviously regards to the effect of the HEMA and GMA co-monomers on the MMA activity in the direction of a charge-transfer complex formation between the double bond of the monomer and copolymer carbamate group. As a consequence, the temperature is being increased during the polymerization and the monomer can be evaporated.

As the result, the co-monomer and water content in the monomer phase impact the evaporation process.

The derived modified materials which based on the developed MMA-copolymer compositions have a intensified working properties, such as Vicat softening point, surface hardness, as well as adhesive bond strength to supports of the different nature.

The surface hardness and Vicat softening point depend on the nature and synthesis conditions of polymer matrix as well as on the co-monomer nature. The adding of bifunctional GMA to the composition causes considerably increase in surface firmness and heat resistance. The above described is explained by the formation of more structured materials. Vinylpyrrolidone rises mentioned values, probably as a result of the more uniform structure formation due to the rather swelling of the copolymer containing PVP units in the monomer phase. The adding of the co-monomers containing the polar groups into the composition causes the increase strength of the adhesive compound of polymethylmethacrylate materials. The filler content has a essential influence on the surface firmness and Vicat softening point (Fig. 2, 3).

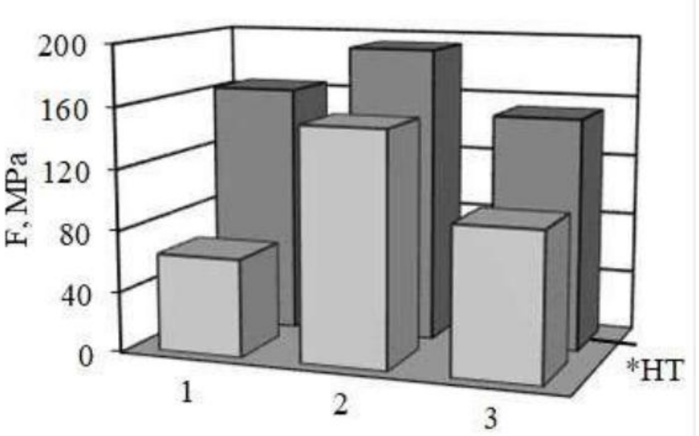

*Fig. 2. Surface firmness of materials based on MMA and PVP-gr-PMMA as a function of the nature of the filler: 1 – without filler; 2 – SiO_2; 3 – Al_2O_3. The filler content is 10 wt.%. *HT – heat-treated samples*

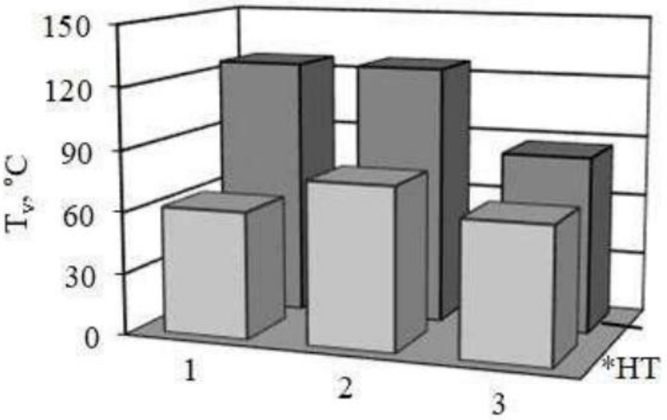

*Fig. 3. Vicat softening point of materials grounded on MMA and PVP-gr-PMMA as a function of the filler nature: 1 – filler free; 2 – SiO_2; 3 – Al_2O_3. The filler content is 10 wt.%. *HT – heat-treated samples*

It can be observed that the adding of SiO_2 and the heat treatment at 333 K causes an increase in the surface firmness and Vicat softening point [13].

It should be emphasized that the presented materials possess high strength of the adhesive bond, in spite of the substrate nature. The highest glue bond strength is demonstrated during sticking together of PMMA materials (35–37 MPa). Apparently, it is caused by their fractional swelling due to the MMA diffusion from the monomer-polymer composition.

Conclusions

Monomer-polymer compositions grounded on MMA and graft copolymers of PVP-gr-PMMA or PVP-gr-PS possess a high reactivity at the room temperature. It can be regulated through the nature of the polymer matrix, the adding of co-monomers and the fillers due to influence of physical and chemical factors on the polymerization process.

Materials based on the described compositions possess low content of the residual monomer and enhanced working properties, such as heat resistance, surface hardness as well as adhesion to supports of the various nature.

Te addition of different fillers, that is, silicon (IV) oxide and aluminum oxide, leads to the polymerization velocity decrease of MMA and the marginal degree of polymerization.

According to the nature of polymer matrix and monomer phase, the correlation between phases and the filler presence during polymerization under the researched conditions, a number of parameters can be distinguished in sence of physical and chemical properties: gritty, sticky, dough-like, viscous, and fully cured.

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ТЕХНОЛОГІЧНІ ОСОБЛИВОСТІ ОТРИМАННЯ ТА ВЛАСТИВОСТІ ПРИЩЕПЛЕНИХ ПОЛІВІНІЛПІРРОЛІДОНОВИХ КОПОЛІМЕРІВ

Досліджено вплив природи, концентрації та температури на кінетику дисперсійної полімеризації у присутності полівінілпіролідону. Визначено оптимальні технологічні параметри процесу синтезу кополімеру. Визначено, що властивості дисперсійної полімеризації залежать від умов процесу. Такими умовами є температура, співвідношення мономеру та водної фази, концентрації мономеру та ініціатора, а також кількість полівінілпіролідону. Наведені матеріали, отримані на основі розроблених композицій, характеризуються принципово високими робочими та фізико-механічними властивостями.

Ключові слова: водна фаза, метилметакрилат, кополімер, полівінілпіролідон, дисперсійна полімеризація, вінілові мономери.