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U.V. Khromyak^a, *V.Ye. Levytskyi*^b, *K.V. Stepova*^a, *V.Y. Skorokhoda*^b**SYNTHESIS AND PROPERTIES OF COMPOSITES BASED ON COPOLYMERS OF POLYVINYLPIRROLIDONE AND METHYL METHACRYLATE**^a Lviv State University of Life Safety, Lviv, Ukraine^b Lviv Polytechnic National University, Lviv, Ukraine

The influence of monomer nature (vinyl acetate, methyl methacrylate and styrene), concentration factors, temperature and mixing rate on the kinetics of the emulsion polymerization of vinyl monomers in the presence of polyvinylpyrrolidone has been investigated. The rational technological parameters of copolymer synthesis have been established. It has been determined that the properties of emulsion polymerization of latexes (surface tension, pH and particle radius) depend on the conditions of the process; the ratio of monomer to aqueous phase, temperature, concentration of monomer and initiator, and also the amount of polyvinylpyrrolidone. The polyvinylpyrrolidone-grafted copolymers that have been synthesized by emulsion polymerization have been used as a polymer matrix for the preparation of methyl methacrylate-copolymer compositions. Block polymerization of methyl methacrylate in the presence of polyvinylpyrrolidone copolymers occurs at a high rate and, depending on the nature of the polymer matrix, the monomer conversion rate of 70–90% is achieved within 10–15 minutes. The highest polymerization rate and the maximum degree of conversion are observed when using a grafted copolymer of polyvinylpyrrolidone with methyl methacrylate. The modified materials obtained on the basis of the developed compositions are characterized by sufficiently high operational properties, such as surface hardness, heat resistance and strength of adhesive bonds to supports of different nature.

Keywords: methyl methacrylate, polyvinylpyrrolidone, copolymer, emulsion polymerization, casting polymerization.

Introduction

The contemporary development of science and technology requires the creation of new polymer materials with corresponding special properties: high adhesion to supports of different nature, high physical-mechanical, thermophysical and selective-sorption properties. This includes low-toxic adhesive polymer-monomer compositions of medical and general technical purposes.

Among the methods for the preparation of materials with the necessary properties, the most interesting materials are those based on the modification of known industrial polymers in polymerization processes. These methods allow obtaining polymer materials with a preferable collection of technological and operational properties and with rather low costs of materials and energy.

The determining factor for the most of the technologies based on the preparation of modified polymeric materials is a modifier. Polymers with high

surface activity, good solubility in water and many aqueous organic media, high ability to complex formation, high sorption characteristics are used as modifiers [1,2].

Polyvinylpyrrolidone (PVP) and its copolymers belong to such polymers. Due to their specific properties, they can provide additional opportunities for improving modern technologies [3,4], obtaining of new functionalized materials [5,6] and expanding the branches of their application.

Monomer-polymer compositions are widely used in a variety of industries especially as a basis for preparing materials with enhanced adhesion properties. Among such materials, acrylates based adhesives occupy a special place. First of all, the increased interest in acrylates-containing glues is caused by their high operational properties, such as cure speed, adhesion to a variety of materials, strength and durability of adhesive compounds and their low toxicity. In this regard, these materials are widely

used in a variety of industries, namely, in medicine, dentistry, construction, engineering, automotive, electrical and textile industries. It should be noted that the use of (meth) acrylic adhesives is now in progress to solve a number of technological tasks [7].

The main components of (meth) acrylic adhesives are (meth) acrylic monomers or polymers, initiating systems, hardeners, stabilizers and modifiers. Methyl methacrylate (MMA) is often used as the main monomer in the (meth) acrylic adhesives. It provides high adhesive strength and is a good solvent for a number of polymers. When combined with oils, MMA allows gluing untreated surfaces. MMA has several disadvantages, in particular high volatility, pungent odor and fire risk. It is used in admixture with high boiling monomers such as hydroxyalkyl methacrylate, glycidyl methacrylate, methacrylates of higher alcohols (tetrahydro tetrahydrofurfuryl-, diethylaminoethyl-, 2-oxopropyl neopentyl- and other glycol methacrylates) and styrene [7,8].

Materials and methods

Copolymers were synthesized by emulsion polymerization of vinyl monomers in the presence of PVP, potassium persulfate or hydrogen peroxide at 60–70°C and the ratio of monomer to aqueous phase of 1:3.

The kinetics of the emulsion polymerization of the test compositions was studied by dilatometric method by measuring the volume change of the reaction mixture during polymerization.

IR spectroscopic analysis was carried out using a spectrograph «Specord-75IR» at room temperature. The spectra were recorded at the same intensity and the same scan rate in the wave range of 400 to 4000 cm^{-1} .

The adhesive compositions were synthesized by the polymerization of MMA or a mixture thereof with other monomers in the presence of synthesized copolymers at room temperature.

The conversion degree of the monomer was determined by the bromide-bromate method. The surface hardness and Vicat softening temperature of the samples were measured by means of the Heppler consistometer. Adhesion was determined according to ISO 527-5:2009.

Results and discussion

Copolymers were synthesized on the basis of PVP and vinyl monomers (MMA, vinyl acetate (VA), styrene) by emulsion polymerization. The emulsion polymerization of vinyl monomers is mostly carried out in the presence of emulsifiers that are surfactants of different nature [7–10]. The nature of the

emulsifier and its concentration in the reaction medium greatly influence the mechanism and kinetics of the polymerization and therefore the technological features of the process and its productivity. This influence is caused by changes in the interphase characteristics of the polymerization system, adsorption phenomena at the phase boundary, as well as by changes in the solubility of monomers in the dispersion medium with the active participation of the emulsifier. Emulsifiers have to meet a number of requirements [9,10] such as high surface activity, ability to micellization and non-toxicity.

Due to its properties and structure, PVP can serve as an emulsifier in the processes of emulsion polymerization and also be an effective polymer matrix, which actively participates directly in the polymerization processes. It should be noted that the influence of the emulsifier on the features of the emulsion polymerization of vinyl monomers is primarily resulted in change in the interphase characteristics of the polymerization system and the solubility of the monomers in the reaction medium. On the basis of the previous studies, it has been established that PVP macromolecules exhibit high surface activity on the interphase surface of water-vinyl monomer. This activity increases with a decrease in the polarity of the monomer in the VA–MMA–styrene series. This is evidenced by the nature of the interphase tension isotherms in the vinyl monomer-aqueous PVP solution system, the PVP adsorption dependences in the coordinates of the Langmuir equation, the maximum values of the Gibbs adsorption ($G_m=2.14 \cdot 10^{-6} \text{ mol/m}^2$) and work of adsorption ($W_{ad}=48.8 \cdot 10^{-3} \text{ J/m}^2$) for styrene. PVP has different effects on the total (true and colloidal) solubility of vinyl monomers in aqueous solution.

At an increase in the PVP concentration up to 0.2 mol/L monomer concentration, the solubility of MMA increases from 0.15 to 0.22 mol/L, it decreases from 0.33 to 0.18 in case of VA, and it is almost unchangeable in case of styrene. Obviously, this is a consequence of specific intermolecular interactions that will affect the polymerization processes in these systems.

High surface activity and solubilization ability of PVP indicate its high efficiency as an emulsifier in the processes of emulsion polymerization of vinyl monomers (KKM PVP: 0.09–0.11 mol/L monomer concentration).

The effect of the monomer nature (VA, MMA, styrene), concentration factors, temperature and stirring rate on the kinetic features of the emulsion polymerization process of vinyl monomers in the presence of PVP is studied. The emulsion

polymerization of vinyl monomers in the presence of PVP is characterized by different rates depending on the nature of the monomer (Fig. 1).

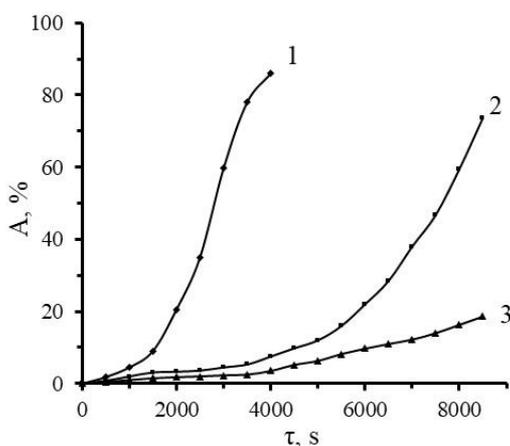


Fig. 1. Dependence of vinyl monomers conversion degree on time: 1 – VA; 2 – MMA; 3 – styrene. $C_{\text{mon}}=0.99$ mol/L; $C_{\text{in}}=2.81 \cdot 10^{-3}$ mol/L; $C_{\text{PVP}}=0.09$ mol/L; $M_{\text{PVP}}=28000$; $T=323$ K

It was found that the polymerization rate of all the investigated vinyl monomers increases with an increase in the ratio of the monomeric phase to aqueous phase, the concentration of the initiator and the temperature.

Based on the revealed kinetic characteristics of the emulsion polymerization process of vinyl monomers in the presence of PVP, the advisable technological parameters of the polymerization process are established depending on the nature of the monomer (Table).

The sequence of technological stages of the process for obtaining of synthesized copolymers in the form of finely dispersed powders is determined as follows: precipitation with potassium alum ($C_{\text{pa}}=1\%$), centrifugation ($v_{\text{centrif}}=1700$ rpm, $\tau_{\text{centrif}}=20-30$ min), washing with demineralized water and drying ($T_{\text{d}}=313-343$ K, $\tau_{\text{d}}=150-200$ min).

As a result of polymerization, the graft copolymers of PVP are formed in the systems under

study. This is confirmed by the results of physicochemical and IR spectroscopic studies. The IR spectra of synthesized methyl methacrylic copolymers have characteristic bands that are related to both the PVP links (1300 cm^{-1} , 1450 cm^{-1} , 1470 cm^{-1} , 1500 cm^{-1}) and PMMA (1140 cm^{-1} , 1160 cm^{-1} , 1180 cm^{-1} , 1200 cm^{-1} , 1220 cm^{-1}).

The degree and effectiveness of grafting depend significantly on the conditions of the process, in particular the PVP concentration in the aqueous medium and the temperature of the process.

It has been established that the properties of latexes obtained by emulsion polymerization (surface tension, pH, particle radius etc.) depend on the conditions of the process: the ratio between the monomeric and aqueous phases, the temperature, the concentration of the monomer and initiator and the amount of PVP. As the concentration of the initiator increases and the temperature of the process decreases, the size of the latex particles and the pH decrease (Fig. 2).

The ratio between the components of the polymerization system and the mixing rate also has a significant effect on the size of latex particles.

The emulsion polymerized graft copolymers of PVP were used as a polymer matrix for the preparation of MMA copolymer compositions cured by block polymerization.

The results of kinetic studies of MMA polymerization in the presence of finely dispersed PVP copolymers depending on the nature of the polymer matrix (PM) and the conditions of its synthesis are shown in Fig. 3.

The rate of polymerization and the degree of monomer conversion largely depend on the nature of the polymer matrix (Fig. 3). Polymerization of MMA occurs at a high rate and, depending on the nature of the polymer matrix, the monomer conversion rate of 70–90% is achieved in 10–15 minutes. The highest polymerization rate and the maximum degree of conversion are observed when using the PVP-gr-PMMA copolymer.

Technological parameters of the emulsion polymerization process of vinyl monomers in the presence of PVP

Parameter	VA	MMA	Styrene
Polymerization temperature, K	323–333	323–333	343
Stirring speed, rpm	140–160		
Polymerization time, hour	2.5–2.7	3.8–4.0	6.0–6.3
Concentration of PVP, mol/L	$(9.0-9.5) \cdot 10^{-2}$		
Concentration of initiator, mol/L	$(2.6-3.0) \cdot 10^{-3}$		
Ratio of monomeric phase to aqueous phase	$(0.88-1):1$	1:3	1:(2–3)
Residual monomer content, %	1.0–1.2	0.05–0.8	0.7–0.9

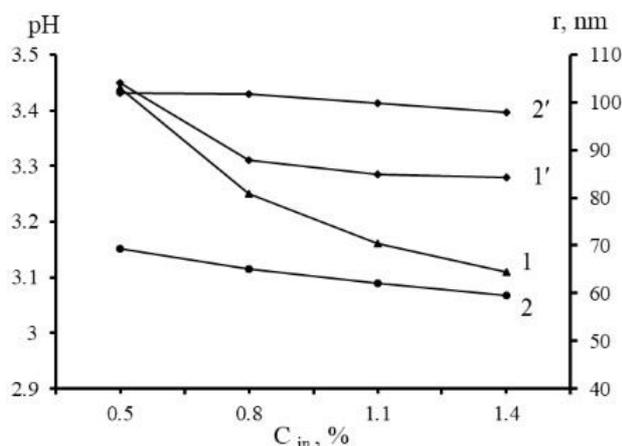


Fig. 2. Effect of synthesis conditions on the properties of copolymer latexes: 1, 1' – pH; 2, 2' – r . 1, 2 – 323 K; 1', 2' – 333 K

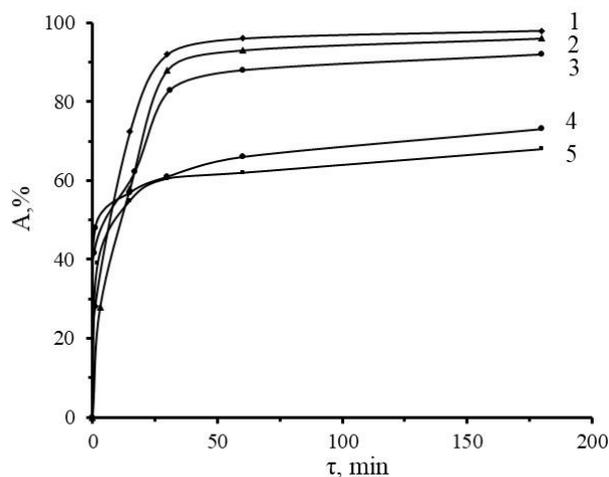


Fig. 3. Kinetic curves of MMA compositions polymerization depending at different nature and conditions of PM synthesis: 1, 2, 4 – PVP-gr-PMMA; 3 – PVP-gr-PS; 5 – PMMA. The ratio MMA:PVP in the synthesis of PM (mol/mol monomer concentration): 3:1 (1–3) and 1:1 (4). T_d PM (K): 313 (1, 3, 5) and 343 (2, 4)

The activity of the polymer matrix also depends on the conditions of its synthesis. A polymer matrix synthesized with a smaller amount of PVP exhibits significantly more activity during block polymerization of MMA. This, along with other factors, is a consequence of a greater affinity of the monomeric and polymeric phases. It should be noted that the drying temperature of the polymer matrix also affects its activity. The copolymers dried under

milder conditions (313 K) show higher activity.

Since the ratio between the monomeric and polymeric phases will also have an effect on the kinetic patterns of MMA polymerization, the study of polymerization of MMA at different ratios between phases has been carried out.

It should be noted that the highest polymerization rate and the highest conversion limit are observed with a polymer matrix-MMA ratio of 2:1. With this ratio, the optimal kinetic conditions for chain growth are achieved due to the uniform distribution of the monomer in the polymer matrix and the strong intermolecular interactions between the PVP copolymer and the monomer. Intermolecular interactions are accompanied by the formation of a complex with charge transfer involving the double bond of MMA and the carbamate group of PVP.

It is established that the kinetic characteristics of the polymerization process are affected by the comonomer and mineral filler (Al_2O_3 , SiO_2). The addition of comonomers such as 2-hydroxyethylenemethacrylate (HEMA), glycidyl methacrylate (GMA) and vinylpyrrolidone (VP) to MMA leads to a decrease in the polymerization rate, regardless of the nature of the polymer matrix (PVP-gr-PMMA or PVP-gr-PS).

It should be noted that the polymerization of MMA in the presence of PVP copolymers is an exothermic reaction with a significant thermal effect. Therefore, thermometric study was conducted aimed to establish the temperature change of polymer-monomer compositions during polymerization (Fig. 4).

During the mixing of a finely dispersed polymer with a monomeric phase, a homogeneous composition is formed, the polymerization of which is characterized by the presence of an induction period. During the induction period, the composition has plasticity and the temperature does not increase. The duration of the induction period and the maximum of the heating temperature of the composition essentially depend on the nature of the monomeric and polymeric phases. The duration of the induction period increases with the addition of a comonomer. This is most likely due to the effect of the HEMA and GMA comonomers on the MMA activity towards the formation of a charge-transfer complex between the double bond of the monomer and the carbamate group of the copolymer. As a result of this increase in temperature during polymerization, the monomer can be evaporated. The comonomer and water content in the monomeric phase affect the evaporation process.

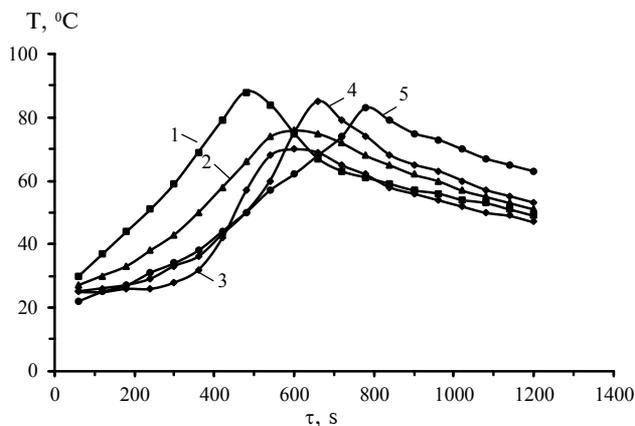


Fig. 4. Thermometric polymerization curves for polymer-monomer compositions. Polymer matrix (PM): PVP-gr-PMMA (1, 4, 5); PVP-gr-PS (2); PMMA (3). Monomer phase (MPh): MMA (1–3); MMA:HEMA=8:2 (4); MMA:GMA=8:2 (5). PM:MPh=2:1

The obtained modified materials on the basis of the developed MMA-copolymer compositions have an enhanced operational properties, such as surface hardness, Vicat softening temperature and adhesive bond strength to supports of different nature.

The surface hardness and Vicat softening temperature depend on the nature and conditions of the synthesis of the polymer matrix, and also on the nature of the comonomer. The addition of bifunctional GMA to the composition results in a significant increase in surface hardness and heat resistance. It may be caused by the formation of more structured materials. Vinylpyrrolidone increases these values, apparently as a result of the formation of a more uniform structure due to the better swelling of the copolymer that contains the PVP units in the monomeric phase. The introduction of comonomers with polar groups into the composition leads to an increase in the strength of the adhesive compound of polymethylmethacrylate materials.

The content of the filler has a significant influence on the surface hardness and Vicat softening temperature (Fig. 5, 6).

It can be seen that the introduction of SiO_2 and the heat treatment at 333 K lead to an increase in the surface hardness and Vicat softening temperature.

It should be noted that the developed materials have a high strength of the adhesive bond, regardless of the nature of the substrate. The highest adhesive bond strength is observed when gluing PMMA materials (35–37 MPa). Probably, it is caused by their partial swelling due to the diffusion of MMA from the monomer-polymer composition.

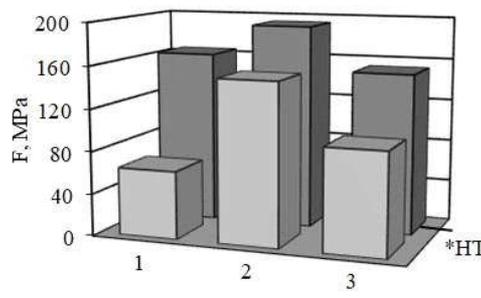


Fig. 5. Surface hardness of materials based on MMA and PVP-gr-PMMA as a function of the nature of the filler: 1 – without filler; 2 – SiO_2 ; 3 – Al_2O_3 . The content of the filler is 10 wt.%. *HT – heat-treated samples

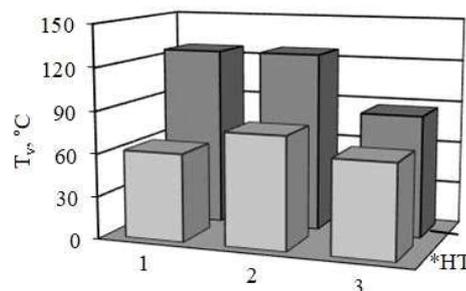


Fig. 6. Vicat softening temperature of materials based on MMA and PVP-gr-PMMA as a function of the nature of the filler: 1 – without filler; 2 – SiO_2 ; 3 – Al_2O_3 . The content of the filler is 10 wt.%. *HT – heat-treated samples

Conclusions

Monomer-polymer compositions based on MMA and graft copolymers PVP-gr-PMMA or PVP-gr-PS have a high reactivity at room temperature. It can be adjusted by the nature of the polymer matrix, the introduction of comonomers and fillers due to the influence of physicochemical factors on the polymerization process.

Materials based on the developed compositions have low content of the residual monomer and enhanced operational properties, such as surface hardness, heat resistance and adhesion to supports of different nature.

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СИНТЕЗ І ВЛАСТИВОСТІ КОМПЗИТИВ НА ОСНОВІ КОПОЛІМЕРІВ ПОЛІВІНІЛПІРОЛІДОНУ ТА МЕТИЛМЕТАКРИЛАТУ

У.В. Хром'як, В.Є. Левицький, К.В. Степова, В.Й. Скорохода

Досліджено вплив природи мономера (вінілацетат, метилметакрилат, стирол), концентраційних чинників, температури і швидкості перемішування на кінетичні закономірності процесу емульсійної полімеризації вінілових мономерів у присутності полівінілпіролідону та встановлено раціональні технологічні параметри синтезу кополімерів. Встановлено, що властивості одержаних емульсійною полімеризацією латексів: поверхневий натяг, рН, радіус частинок залежить від умов здійснення процесу: співвідношення мономерної і водної фаз, температури, концентрації мономера та ініціатора, а також від вмісту полівінілпіролідону. Синтезовані емульсійною полімеризацією прищеплені кополімери полівінілпіролідону були використані як полімерна матриця для одержання метилметакрилат – кополімерних композицій. Блокова полімеризація метилметакрилату в присутності кополімерів полівінілпіролідону відбувається з високою швидкістю і залежно від природи полімерної матриці за 10–15 хв досягається ступінь конверсії мономера 70–90%. Найвища швидкість полімеризації і граничний ступінь конверсії досягається під час використання прищепленого кополімеру полівінілпіролідону з метилметакрилатом. Одержані модифіковані матеріали на основі розроблених композицій відзначаються достатньо високими експлуатаційними властивостями, такими як поверхнева твердість, теплостійкість за віка, міцність клейових з'єднань до підкладок різної природи.

Ключові слова: метилметакрилат; полівінілпіролідон; кополімери; емульсійна полімеризація; блокова полімеризація.

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**SYNTHESIS AND PROPERTIES OF COMPOSITES
BASED ON COPOLYMERS OF
POLYVINYLPIRROLIDONE AND METHYL
METHACRYLATE**

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