How to Cite: Burkeyeva, G.K., Tazhbayev, Ye.M., Muslimova, D.M., Nurseiit, G.D., & Zhaparova, L.Zh. (2022). "Cold Curing" of Polyethylene Glycol Maleate with Acrylic Acid and some Physicochemical Properties of Their Solutions. *Bulletin of the University of Karaganda – Chemistry, 106(2), 23-32.* https://doi.org/10.31489/2022Ch2/2-22-22

Article Received: 28 February 2022 | Revised: 21 March 2022 | Accepted: 14 April 2022 | Published online: 27 April 2022

UDC 541.64 https://doi.org/10.31489/2022Ch2/2-22-22

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"Cold Curing" of Polyethylene Glycol Maleate with Acrylic Acid and Some Physicochemical Properties of Their Solutions

The possibility of using the copolymers based on unsaturated polyesters with acrylic acid (AA) as the main component (polymeric basis) for the creation of novel highly effective sealants and glues of domestic production was demonstrated. Polyethylene glycol maleate (p-EGM) was synthesized by step-growth polymerization of maleic anhydride with ethylene glycol using the catalyst, which shortened the process duration. A number of solutions of p-EGM with AA were obtained. Physicochemical characteristics of initial solutions were determined. Some rheological properties of the solutions of p-EGM in unsaturated carboxylic acid were studied. Radical polymerization — the process of "cold curing" of the solutions of p-EGM with AA at room temperature was carried out. The combination of initiating a system of cold curing consisting of initiator (benzoyl peroxide) and promoter (dimethylaniline) was selected and their optimal content in the initial monomer mixture was established. The main parameters of curing, namely gelation time and curing time, were determined. Identification of the copolymers was performed using IR-spectroscopy. The morphology of the surfaces of cured samples of p-EGM with AA was studied using SEM. The optimal composition requiring further studies as highly filled compositional polymeric materials for using as sealants and glue basis was established.

Keywords: sealant, glue, unsaturated polyester, polyethylene glycol maleate, unsaturated carboxylic acid, acrylic acid, radical copolymerization, cold curing.

Introduction

At present, the volume of house-building and reconstruction of buildings is consistently being increased in Kazakhstan. Modern building technologies require the use of high-quality products of construction chemicals. These are sealants, glues, mastics, which allow the construction to bond firmly and reliably. Polymeric materials are more commonly used nowadays as sealants and glues [1–3]. Glues and sealants based on polymers have a wide field of application and universal properties starting with the use at home, as well as in professional, repairing and mechanical installation, aircraft-, and automobile as well as shipbuilding industries. As it is known [4–8], among the wide assortment of glues and sealants, silicon-, polyurethane, acrylic, polysulfide, and others are the most widely spread ones. Advantage of such sealing and gluing materials is an opportunity for reliable surfaces pressurization of any kind of shapes directly on the objects being built almost without the evolution of solvents. Sealants and glues based on polymers possess high exploitation characteristics under any climatic conditions. High elastic properties allow using them for sealing various interfaces including the spaces between panels in house buildings, glass units, etc. [4–8]. The sealants and glues of curing types including those hardened with air oxygen are the most widely used. In this regard, it is more desired rather fast curing the sealing composition at rather low or room temperatures. It is necessary to note that along with general advantages one can accentuate the shortcomings, which are peculiar for curing sealants and glues depending on polymer basis.

So, the main drawback of Thiokol sealants is a high volume of production wastes, drain water, and salts. In turn, polyurethane sealants are known for their highest deformation-strength properties. However, the necessity of curing on ending isocyanate groups requires considerable preparation of the components (drying) before the introduction to the product composition, which limits the storage period before use, worsens the monolithicity of the hardened product and finally its quality [4–8].

The diversity of sealants and glues is confirmed by their variety in the market of building materials and the patents on their recipes. This, in turn, emphasizes a high interest of researchers in the search and development of new recipes for the above-said materials. Formulation of sealing and gluing systems includes a base, a filler, an accelerating system and an initiator. In a number of cases a stabilizing system, a plasticizer, a dye and a photoinitiating system, which provides the curing of the sealing agent by the exposure to UV radiation, are also included in the recipe. Examples can be acrylic sealants of the trade “ACH”, “Anatherm-50U”, “Anatherm-50UV”. The shortcomings of the above-mentioned trademarks are the followings: In the first case, it is a low-reliability index, which is less than 85 %, whereas in the case of using the trade “Anatherm” in spite of 100 % encapsulation there is a necessity of using additional equipment as UV-radiator, carrying out additional acts of controller and huge manufacturing areas. Also, there are other main drawbacks, including low water-proof ability, high sensitivity to UV-light and decrease of the firmness at high temperatures, application limitations (restoration inside the buildings) and the high price [4]. These shortcomings reduce essentially the quality indexes and rentability of production in general [1]. In this regard, modern technologies of obtaining the sealants are directed to the search for new raw materials, fillers and additives with the aim of improving the adhesion properties, time of curing, working life, optimal meanings of firmness and elasticity, and so on.

Promising compounds for the creation of this kind of materials are the solutions of unsaturated polyesters in vinyl monomers, which save necessary consistency in a wide range of concentrations [9–11]. Unsaturated polyesters are the main representatives of oligomers, which are capable of polymerization. They belong to thermoreactive materials with rather a useful complex of properties such as rather low viscosity, capability to harden not only at high but also at room temperature. Owing to the reactive double bond, the unsaturated polyesters can enter the copolymerization reaction with a lot of monomers obtaining the hardened products. Obtained hardened unsaturated polyester resins are materials with high durability, attrition hardness, very good dielectric properties, high chemical stability to various mediums, environmental safety during exploitation period and so on. In this case, there is a possibility of varying properties of the final product due to the variety of unsaturated polyester compositions.

Most part of the investigations in the field of unsaturated polyesters is devoted to the synthesis and study of their properties hardened with styrene [9–11]. The main drawback of these polymers is the limitations in application because of toxicity and flammability of styrene. At the same time, questions about modifying unsaturated polyesters by functional monomers aimed at improving their exploiting characteristics and technological properties of compositional materials in the processing stage have not been studied enough.

Considering the above-listed advantages of unsaturated polyesters, their use as an agent when obtaining adhesive materials of hardened type seems to be perspective. Therefore, the goal of this work is a study of the main physicochemical characteristics of glues and sealants based on polyethylene glycol maleate with acrylic acid, the establishment of kinetics parameters of cold curing (the lifetime and the curing) by selection and varying the initial composition of comonomers and the initiating system.

Experimental

The following reagents, namely ethylene glycol, acrylic acid, benzoyl peroxide, dimethylaniline (“Sigma-Aldrich”), maleic anhydride (“Vekon”), aluminum chloride (“Reachem”), were used in the work. All chemicals were used without additional purification.

Polyethylene glycol maleate (p-EGM) was obtained by the polycondensation reaction of ethylene glycol with maleic anhydride at a temperature of 423–433 K in a four-neck flask, which was equipped with a reflux condenser, a stirrer (was set from a top of a flask), a thermometer, a Dean-Stark apparatus, and a feeding tube (nitrogen). Step-growth polymerization was carried out according to the procedure given in [12] at a constant stirring in the presence of a catalyst (zinc chloride) in a nitrogen atmosphere to avoid the gelatinization process.

Molecular weight of p-EGM was determined using gel permeation chromatography (Agilent 1100 Ser) where polystyrene was chosen as a standard substance and dioxane was chosen as a solvent. The value of molecular weight was approximately M_w ~2358 Da.

Radical copolymerization of p-EGM with acrylic acid (AA) was carried out in bulk at various initial mass ratios of comonomers at a temperature of 293 K, where benzoyl peroxide (BP) was used as an initiator and dimethylaniline (DMA) served as an accelerating agent.

The dynamic viscosity of the initial solutions of p-EGM-AA was measured at 293 K on a vibrational viscosimeter SV-10 provided with a liquid thermostat BT3 for sustaining a given temperature [13].

The density of the initial solutions and the p-EGM-AA copolymers was measured using a pycnometer and hydrostatic methods correspondingly [14].

The gelation time was determined automatically on a Gel Timer Gelnorm GT-S. The curing time of p-EGM-AA was determined according to the procedure described in [15].

The samples IR-spectra were recorded in KBr tablets on an FSM 1201 spectrometer [16].

Electron microscopic pictures were made on a scanning electron microscope MIRA 3 (TESCAN) at an accelerating voltage of 20 kW.

Results and Discussion

Glue bonds are becoming an alternative to mechanical compounds in engineering applications and they provide a number of advantages in comparison to usual mechanical fixing parts. This kind of bond provides a more uniform distribution of tension on the binding area. As it is known from [17], the sealing materials have to meet the following requirements: they must totally prevent the juncture from moisture; do not allow filtering the air (exceeding the amount which is prescribed in the documents); to be capable of saving the sealing properties not depending on atmospheric influences; do not undergo aging for a long period of time; to have rather low price and to be produced from acceptable raw materials [18]. For the formation of glue sews, the following conditions are demanded. In the beginning, the sealant/glue should be in a liquid form; it should easily flow on the surface and wet properly the elements, which are to be glued; then a liquidlike sealant/glue should harden (either by drying, or by polymerization; either by curing with the help of a curing agent, or by cooling for the glue-alloy).

Thus, our studies should be divided into several stages for the goal accomplishment and obtaining polymers with adhesive properties of the hardened type, namely:

- obtaining the solutions of p-EGM in acrylic acid of various compositions and investigation of their rheological properties;
- selection of the initiating system, i.e. the curing additives;
- curing the initial solutions of p-EGM-AA at room temperature by radical copolymerization — “cold curing”.

Table 1 presents the data on the composition of initial solutions of p-EGM in acrylic acid and their properties. According to this data the content of unsaturated polyester (p-EGM) in initial compositions of the solutions varies within the interval 30-45 mass.%.

Table 1

Rheological properties of the initial solution of p-EGM-AA, T = 293K

Composition of the initial solution, mass.%		Dynamic Viscosity (η), mPa·s	Density of Solution (ρ), g/cm^3
p-EGM	AA		
31.21	68.79	25.6 ± 0.2	1.1428 ± 0.063
35.43	64.57	36.9 ± 0.2	1.1489 ± 0.084
40.59	59.41	83.4 ± 0.2	1.1687 ± 0.094
46.04	53.96	181.0 ± 0.2	1.1934 ± 0.058

Physical and rheological properties of polymers at different states not only predetermine the possibilities of their rational application in a certain field but also, determine the selection of investigation methods. In this regard, there was a necessity to study the dynamic viscosity and density of initial (liquid) solutions of p-EGM in AA at various mass ratios of co-reagents. As it is seen from the obtained results, the dynamic viscosity and the solution’s density increase with increasing the content of p-EGM. The results of dynamic viscosity and the solution’s density have a good correlation with each other. So, the solution with the composition of 31.21:68.79 mass.% is characterized by rather low viscosity values, namely 25.6 mPa·s and the density value is equal to 1.1428 g/cm^3, whereas these indicators are equal to 181.0 mPa·s and 1.1934 g/cm^3, respectively, for the solution of p-EGM-AA of the 46.04:53.96 mass.% composition. The increase in the viscosity (Fig. 1) and the solutions density is due to the increase in the content of p-EGM indices in the studied samples, which is characterized by the high viscosity of the latter.

As it has been noted before, the sealants/glues of curing type are the highly-demanded adhesives in the market. In this regard, fast curing of the sealing composition at rather low temperatures is preferred. It is necessary to note that the time and temperature of curing must be optimal depending on the exploitation field of the product. Controlling the parameters of curing process (time and temperature) in case of unsaturated polyesters and obtaining the copolymers with optimal properties is possible by introduction of special additives, namely inhibitors, initiators, and promoters.

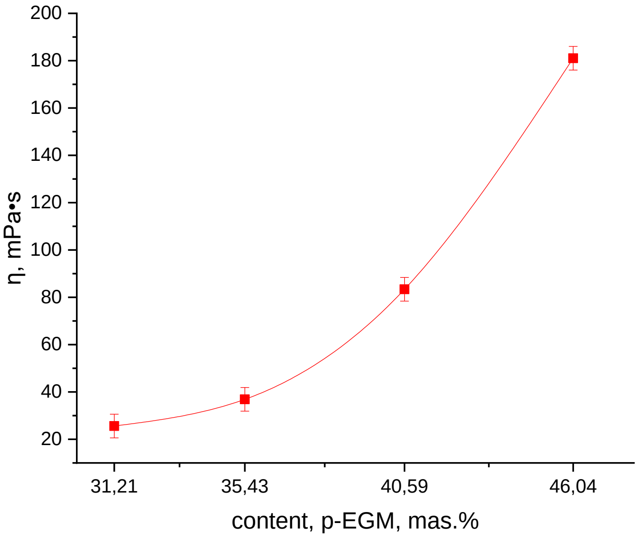


Figure 1. Dependence of a dynamic viscosity on a content of p-EGM in the initial solutions

In connection with this, the main task of controlling the curing process is the right choice of combination of the initiating system. Therefore, in the next stage of work, the selection of curing additives, which are introduced in different quantities, has been done. According to [10], the curing of unsaturated polyesters is carried out in the presence of the radical polymerization initiators, mainly, peroxides are used. As a rule, the use of such initiators requires high curing temperatures and long-term curing, which is not cost efficient, as well as uncomfortable during exploitation. Therefore, promoters play a significant role in initiating systems of cold curing of unsaturated polyesters, as they decompose the peroxides by forming free radicals at room temperature.

The double-component initial system of cold curing was used for curing the p-EGM at a temperature of the environment and lower. It comprised a BP as an initiator and DMA as a promoter (Table 2).

Table 2

Dependence of the promoter influence on a time of gelation and curing the solution of p-EGM-AA (BP+DMA, T=273 K)

Amount, %		Gelation time ($\tau_{gel.}$), min.	Curing time ($\tau_{curing.}$), min.
BP	DMA		
1	0.06	90.10 ± 1.66	150.18 ± 5.58
1	0.1	59.63 ± 1.30	101.06 ± 4.43
1	0.15	43.30 ± 1.08	72.49 ± 3.52
1	0.2	7.11 ± 0.47	13.51 ± 1.14

Figure 2 illustrates the mechanism of interaction between BP and DMA. According to this scheme, in the beginning, a formation of complex takes place, and as a result of electron transfer from DMA to BP, an ionic pair and benzoic radical appear [10]. In this case, DMA activates a high-temperature peroxide BP initiator and promotes generating free radicals during the cold curing process.

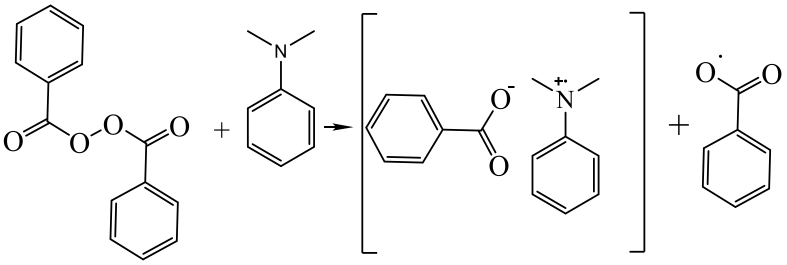


Figure 2. The reaction scheme of BP with DMA

According to Table 2, curing of the system is possible at a temperature range from 18 to 30 °C, when using a pair of initiating system BP+DMA. The correct selection of the quantity of the initiator and promoter allows for reaching the optimal time of curing (τ_{curing}) and gelation ($\tau_{gelation}$). Figure 3 demonstrates the dependence of curing time on the composition of initiating system, in particular, the content of the promoter DMA. It is necessary to note that the quantity of radical-forming peroxide initiator is constant and equal to 1 %. The practicability of the chosen BP concentration is based on the analysis of the works carried out before [11] and literature data [9–11]. It is known [10] that the curing systems/additives have a considerable influence on the properties of unsaturated polyesters. In particular, the quantity of BP affects extensible-structural characteristics and elasticity. Also, it should be pointed out that in case of the systems based on unsaturated polyesters, the gelation process is characterized by the term “adhesive working life” [10, 11]. Thus, one of the main technological properties of adhesives is adhesive working life, — the time within which a sealant or a glue is capable of used in a viscous-flow state after introduction of compounds that cause the curing (Table 2). The studies were carried out and the curing parameters were determined when the content of DMA was 0.01–0.2 %. However, when using DMA in a quantity within the interval of 0.01–0.05 % (from initial mass of the solution) the process of “cold curing” was lengthy and characterized by high values of curing time (t_{curing}) ~ 750.00–250.00 min. As it is seen from the table and graphical data, the time of gelation/working life and curing was decreased with increasing the DMA content. So, the introduction of 0.06 % of DMA to the initial solution of p-EGM-AA was characterized by rather high values of curing time, namely τ_{curing} =150.18 min and at 0.2 % the value was minimum and equal to τ_{curing} =13.51 min, which was not acceptable in exploitation.

In this regard, according to the purpose of the work the most optimal result was observed when using DMA as a promoter in a quantity of 0.15 %, at which the gelation time ($\tau_{gel.}$) and curing time (τ_{curing}) were equal to 43.30 and 72.49 min, respectively.

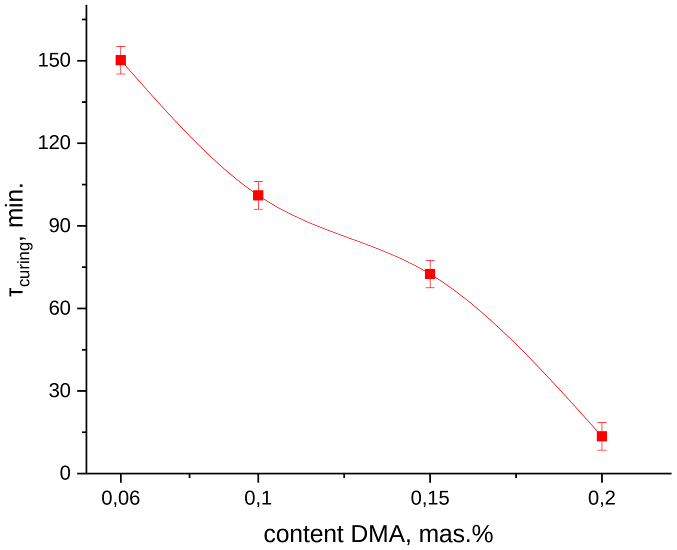
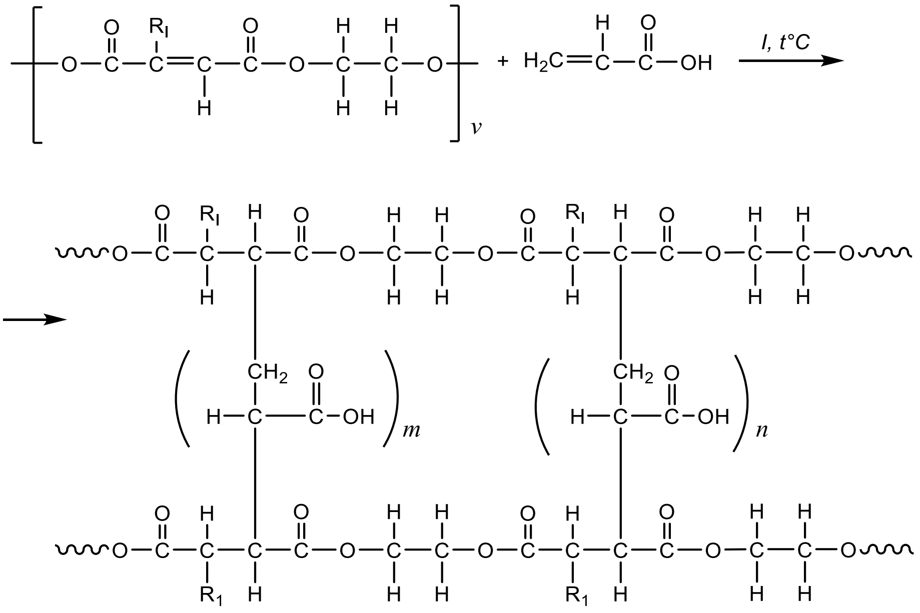


Figure 3. The influence of DMA promoter content on curing time of p-EGM-AA in the presence of BP at 20°C

In continuation of the studies the radical copolymerization, i.e., the process of “cold curing” of the solution of p-EGM-AA, was carried out at 293 K. PB was used as an initiator and DMA was a promoter in the quantities of 1.0 % and 0.15 %, respectively (calculated from the initial mass of the solution). The curing was carried out in the following way: 0.15 % of DMA was introduced to the initial solution of unsaturated polyester resin (p-EGM-AA), then after thorough stirring, the BP was added and the mixture was extensively stirred within 1 min. After that, the gelation time (adhesive working life) and the curing time were determined according to standard procedures [15]. Identification of the cured products of p-EGM-AA was performed by analyzing IR-spectroscopy data [16]. Thus, all IR spectra of p-EGM-AA contain stretching vibrations of C–O–C ether groups (1090 cm^{-1}), C–H groups (2940 cm^{-1}), and carboxyl groups–COOH (range 650–1000 cm^{-1}).

Figure 4 demonstrates the copolymerization process schematically. During radical copolymerization of p-EGM with unsaturated carboxylic acids the three-dimensional cross-linked polymers of non-solving nature are formed [11, 18].



where R_I — is the initiator radical

Figure 4. The p-EGM-AA synthesis scheme

Table 3

Parameters of the curing kinetics and copolymers properties depending on the composition of the initial mixture p-EGM-AA, BP+DMA (1.0 %+0.15 %), T = 293 K

Monomers initial ratio, mol.%		Density (ρ), g/cm^3	Gelation time ($\tau_{gel.}$), min.	Curing time (τ_{curing}), min.
31.21	68.79	1.2635± 0.023	43.30± 1.18	72.49± 2.10
35.43	64.57	1.2695±0.046	50.27± 1.92	83.45± 2.66
40.59	59.41	1.2961± 0.041	57.04± 2.42	94.15± 3.46
46.04	53.96	1.3347± 0.088	64.24± 2.94	107.19± 4.69

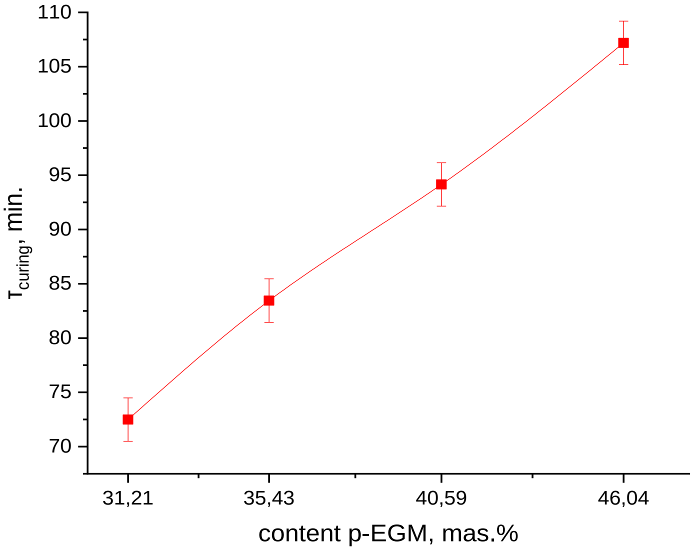


Figure 5. Dependence of the curing time on the content of p-EGM-AA

Thus, the investigation of the p-EGM-AA gelation time points to an increase in adhesive working life ($\tau_{gelation}$ = 43–64 min.) with the increasing the p-EGM content. The same dependence is observed when determining the curing time. This phenomenon can be explained by comparing the activity indexes of p-EGM and AA, where this parameter for the last one (r_2 1,22) is higher than the corresponding value for p-EGM (r_1 0,89). It is seen from the previously carried out investigations on studying the kinetic parameters of p-EGM-AA radical copolymerization that the reaction rate increases with the increasing AA content in the monomer mixture [19]. It is also necessary to note that the difference between the values of curing time is insignificant and it varies within the interval of 10–20 min. According to Table 1, with increasing the content of unsaturated polyester, the densities of the initial solutions of p-EGM and AA are increased, which has a good correlation with the data of dynamic viscosity. So, the solution of p-EGM-AA of 46.04:53.96 mass.% is characterized by the high value of dynamic viscosity (181 mPa·s) because of higher content of p-EGM and minimum rate of curing.

Surface morphology of the cured samples was studied using scanning electron microscopy (Fig. 6).

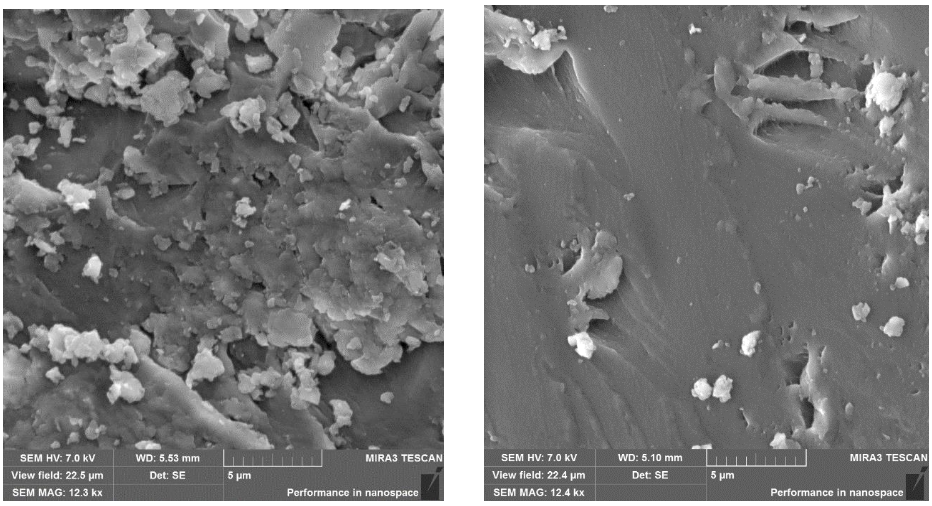


Figure 6. SEM pictures of the surfaces of p-EGM-AA cured samples
with the content of monomers 31.21:68.79 mass.% (in the left) and 46.04:53.96 mass.% (in the right)

According to the obtained pictures, there are some differences in morphological surfaces of the samples (Fig. 6). From the presented pictures, it is seen that the copolymers with higher content of p-EGM 46.04:53.96 mass.% (in the right) is characterized by a dense structure, which is also in good accordance with the results of dynamic viscosity and density of cured samples.

Conclusions

Thus, the investigation of physicochemical properties of the initial solutions of p-EGM-AA in different ratios points to promising prospective of using them as the basis for the sealing and glue composition. The solutions of polyethylene glycol maleate in acrylic acid are characterized by optimal values of viscosity, density, and water absorption. So, in all cases, the change of dynamic viscosity is correlated with the change of density of initial solutions samples. It is also established that the rheological properties of the solutions depend on the content of initial reagents, in particular, the increase of the p-EGM content within the interval of 31.21–46.04 mass.% increases the viscosity from 25.6 to 181.0 mPa·s. The results obtained by SEM point to non-uniformity of the surface with decreasing the unsaturated polyester content. So, monolithicity of the surface is observed in the cured samples with the exceeding p-EGM content. During the work presented the optimal combination of initial system of cold curing has been found. So, the curing system consisting of BP and DMA (1.0 % and 0.15 %, respectively) can be used in the composition of polymeric basis of p-EGM-AA and it is characterized by energy-effective temperature-time regimen of curing without using additional devices, such as UV-lamps. The introduction of the “cold curing” method excludes the stage of exposure to UV light from the production loop. It is also should be noted that varying the composition of the initial polymer-monomer mixture and initiating system allows operating not only physicochemical properties (viscosity, density and water-absorbance) of obtained products, but also to control the conditions of curing (time, working life in viscous-flow state, volume contraction), which is an important characteristic of sealing and glue systems depending on the application field. In this regard, it can be concluded from the results obtained that the composition of p-EGM-AA 46.04:53.96 mass.% is optimal for further investigations as highly-filled compositional polymer materials for use as sealing and glue basis.

Acknowledgments

The work was fulfilled within the framework of program-targeted funding of the Ministry of Education and Science of the Republic of Kazakhstan No. BR10965249 “Development of new sealants and adhesives based on unsaturated polyester resins for the construction and defense industries”.

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Полиэтиленгликоль малеатын акрил қышқылымен «суық» қатайту және олардың ерітінділерінің кейбір физика-химиялық қасиеттері

Отандық өндірістің жаңа тығыздағыштар мен желімдер үшін негіздік компонент (полимер негізі) ретінде акрил қышқылымен (АҚ) қанықпаған полиэфирлер негізіндегі сополимерлерді пайдалану мүмкіндігі көрсетілген. Процесс ұзақтығын азайтатын катализаторды қолдану арқылы малеин ангидриді мен этиленгликольді поликонденсациялау әдісімен полиэтиленгликоль малеинаты (п-ЭГМ) синтезделді. АҚ-дағы п-ЭГМ бірқатар ерітінділер алынды. Бастапқы ерітінділердің физика-химиялық сипаттамалары анықталды. Осылайша, қанықпаған карбон қышқылындағы п-ЭГМ ерітінділерінің кейбір реологиялық қасиеттері зерттелді. Радикалды сополимерлеу — бөлме температурасында п-ЭГМ-АК ерітінділері «суық» қатайту процесінде жүргізілді. Зерттеу барысында суық қатайтудың бастамашы жүйесінің (бастамашы мен промотордың) үйлесімі таңдалды, олардың бастапқы мономерлі қоспасындағы оңтайлы құрамы анықталған. Қатайтудың негізгі параметрлері табылған: желатиндеу уақыты (өміршеңдігі), қатайту уақыты. Сополимерлерді анықтау ИҚ-спектроскопиялық талдау арқылы жүзеге асырылды. п-ЭГМ-АҚ өңделген үлгілерінің беткі морфологиясы сканерлеуші электронды микроскоп арқылы зерттелді. Оңтайлы құрамы (бастапқы реагенттердің қатынасы) анықталды, ол тығыздауыш және жабысқақ негіз ретінде пайдалану үшін жоғары толтырылған композиттік полимерлі материалдар ретінде әрі қарай зерттеуді қажет етеді.

Кілт сөздер: герметик, желім, қанықпаған полиэфир, полиэтиленгликоль малеинаты, қанықпаған карбон қышқылы, акрил қышқылы, радикалды сополимерлеу, суық қатайту.

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«Холодное» отверждение полиэтиленгликольмалеината с акриловой кислотой и некоторые физико-химические свойства их растворов

Показана возможность применения сополимеров на основе ненасыщенных полиэфиров с акриловой кислотой (АК) в качестве базового компонента (полимерной основы) для новых герметиков и клеев отечественного производства. Методом поликонденсации малеинового ангидрида и этиленгликоля с применением катализатора, сокращающего длительность процесса, синтезирован полиэтиленгликольмалеинат (п-ЭГМ). Получен ряд растворов п-ЭГМ в АК. Определены физико-химические характеристики исходных растворов. Так, изучены некоторые реологические свойства растворов п-ЭГМ в ненасыщенной карбоновой кислоте. Проведена радикальная сополимеризация — процесс «холодного отверждения» растворов п-ЭГМ-АК при комнатной температуре. В ходе исследований подобрано сочетание инициирующей системы холодного отверждения (инициатора и промотора), выявлено их оптимальное содержание в исходной мономерной смеси. Определены основные параметры отверждения: время желатинизации (жизнеспособность), время отверждения. Идентификацию сополимеров осуществляли методом ИК-спектроскопии. Методом сканирующей электронной микроскопии исследована морфология поверхности отвержденных образцов п-ЭГМ-АК. Выявлен оптимальный состав (соотношение исходных реагентов), требующий дальнейших исследований в качестве высоконаполненных композиционных полимерных материалов для применения в качестве герметизирующей и клеевой основы.

Ключевые слова: герметик, клей, ненасыщенный полиэфир, полиэтиленгликольмалеинат, ненасыщенная карбоновая кислота, акриловая кислота, радикальная сополимеризация, холодное отверждение.

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