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Development of Energy-Efficient “Cold” Curing Method for Polypropylene Glycol Fumarate Using an Optimized Initiating System

The possibility of using the polymeric matrix obtained as a result of “cold” polymerization of polypropylene glycol fumarate (p-PGF) with methacrylic acid (MAA) as a polymeric base for obtaining new adhesives of domestic production was demonstrated. The starting reagent (p-PGF) was synthesized by condensation polymerization of fumaric acid with propylene glycol in the presence of a catalyst, which reduced the temperature and shortened the process time. A number of solutions of p-PGF in MAA of different mass compositions were obtained and their rheological properties were determined. Curing of the studied solutions was carried out by radical polymerization at room temperature in the presence of the “cold curing” initiating system. The optimum composition and amount of components of the “cold” curing initiating system consisting of an initiator (benzoyl peroxide) and a promoter (dimethylaniline) were established. Technological parameters of curing (temperature, lifetime and curing time, the value of volume shrinkage) were determined. The obtained compounds were identified by infrared spectroscopy. The surface morphology of the cured samples was studied by scanning electron microscopy. It was found that varying the composition of the initial polymer-monomer mixture allows controlling the physicochemical properties.

Keywords: sealant, unsaturated polyester, polypropylene glycol fumarate, unsaturated carboxylic acid, methacrylic acid, radical copolymerization, “cold” curing, initiating system.

Introduction

With the widespread increase in the rate of construction, sealants and adhesives derived from polymer matrices by incorporating various fillers, plasticizers and others have gained great importance [1, 2]. At the same time, the polymer matrix-base has meet a number of requirements, namely optimal size of polymer network cells, structure stability under the influence of negative external factors, including the effect of UV radiation, resistance to organic solvents and alkalis, heat and cold resistance, resistance to mechanical loading and other deformation changes, low shrinkage and a sufficiently long lifetime and curing time [3, 4]. It is more preferable that the system is capable of curing with air oxygen [5] at room temperature or under low-temperature conditions without using additional curing conditions (increased pressure, photo or UV initiation, etc.).

Thus, promising co-reagents for obtaining a polymeric matrix are unsaturated polyesters of various compositions, which cure with vinyl monomers to form a polymer network with good elastic properties [6]. The undoubted advantages of the solutions of unsaturated polyesters in vinyl monomers before curing include the ability to control the consistency of solutions in a wide concentration range by varying the composition of the initial polymer-monomer mixture [7]. With their sufficiently low viscosity and ability to enter into reaction of radical copolymerization with reactive vinyl monomers of hydrophilic and hydrophobic nature both when heated and at room temperature, the unsaturated polyesters become suitable co-reagents for obtaining polymer bases for sealants and adhesives. Thus, the resulting cured products have abrasion resistance and high resistance to mechanical stress, high resistance to aggressive environments, UV- and frost-resistance and heat resistance, and as a result of the absence of by-products in the curing process their operation is environmentally friendly and safe. Given the wide range of co-reagents used for the synthesis of initial unsaturated polyesters and their good compatibility with vinyl monomers due to the presence of a highly reactive double bond, it is possible to obtain final products with the required physicochemical and mechanical properties and performance characteristics [6].

Previously, the physicochemical characteristics of polymer bases obtained from polyethylene glycol maleate and acrylic acid solutions were studied, and the parameters of “cold” curing kinetics depending on the initial composition of co-reagent solutions were established [7].

The aim of this work is to study a number of rheological properties of the solutions of polypropylene glycol fumarate with methacrylic acid, to select the optimal composition of the initiating system and to establish technological parameters (temperature, lifetime and curing time, volume shrinkage) of the “cold” curing of the solutions of above said co-reagents.

Experimental

The reagents used in the study were propylene glycol, methacrylic acid, benzoyl peroxide, dimethylaniline (“Sigma-Aldrich”), fumaric acid (“Vekon”), aluminium chloride (“Reachem”). All reagents were used without additional purification.

Synthesis of the initial unsaturated polyester, namely polypropylene glycol fumarate (p-PGF) was carried out by polycondensation reaction of propylene glycol with fumaric acid at 423-433 K in a four-neck flask equipped with a stirring shaft, two reflux condensers, thermometer to control reaction temperature, Dean-Stark trap to collect water removed during the process and a tube to supply nitrogen. Polycondensation was carried out according to the procedure given in [8] under constant stirring in the presence of aluminum chloride catalyst in an inert nitrogen environment, which was fed into the system to avoid undesirable gelatinization processes.

Determination of the molecular weight of the obtained p-PGF in dioxane solution was performed by gel permeation chromatography on a VISCOTEK 270 DUAL DETECTOR MALVERN chromatograph, where polystyrene was used as a standard. Molecular mass was M_w ~1488 Da.

Radical copolymerization of p-PGF with methacrylic acid (MAA) was carried out in bulk at various initial mass ratio of co-monomers at 293 K in the presence of “cold” curing initiation system consisting of benzoyl peroxide (BPO) initiator and dimethylaniline (DMA) promoter.

The dynamic viscosity of the initial p-PGF-MAA solutions was determined at 293K using a vibrating viscometer SV-10 equipped with a liquid thermostat VT3, which allows to maintain the set temperature during the entire process [9].

Density values of the initial solutions and p-PGF-MAA copolymers were studied by pycnometric and hydrostatic methods according to all-Union State Standard 18329-2014 [10].

The total volumetric shrinkage was determined by calculation, according to State Standard 18616-80 [11] based on the difference in density of the initial solution and the mixture in the cured state:

$$X = \left(1 - \frac{\rho_0}{\rho}\right) \cdot 100\,\% , \tag{1}$$

where ρ_0 is the density of initial solution; ρ is the density of cured solution.

The gelatinization time (lifetime) of p-PGF-MAA solutions was recorded automatically on a GelTimer Gelnorm GT-S instrument according to ISO 57884-2017 [12]. Curing time was measured according to ISO 2535-2017 [13].

The presence of functional groups in the cured p-PGF-MAA samples was determined by analyzing infrared spectra performed in KBr tablets on a FSM 1201 spectrometer [14].

The surface morphology of p-PGF-MAA samples was studied using a MIRA 3 TESCAN scanning electron microscope at an accelerating voltage of 20 kV [15].

Results and Discussion

The field of application of sealants is determined by their physicochemical and mechanical properties and is not limited to the construction industry only. Thus, sealing materials are also used for sealing aquariums, in engines and gearboxes. However, the main consumers are organizations engaged in repair and finishing and repair-decorative works.

Not depending on the composition of sealing materials and direct field of application there are general operational requirements, among which are good adhesion to different surfaces and other physico-mechanical properties (according to regulatory standards): gas and vapor permeability [16], water resistance, the ability to retain sealing properties under the influence of negative external factors for a long period of time [17]. From an economic point of view, important indicators are also quite low price and availability of initial reagents for their production [18].

Given the ability of unsaturated polyesters to interact with vinyl monomers to form a three-dimensional polymer network, the resulting products are called thermosetting composites [19]. This implies the need for a number of conditions for their curing. Thus, the curing process of thermosetting plastics to form a three-dimensional network of copolymer occurs as a result of exposure to elevated temperature, radioactive or UV radiation, or in the presence of curing agents and catalysts — when the curing occurs in air [20].

Therefore, the development of techniques and research of new polymer sealants curing at room temperature (so-called “cold” curing) should take place in stages, including the following tasks:

1. Synthesis of one of the reagents used as a p-PGF filler;
2. Preparation of the solutions of p-PGF in vinyl monomer of different composition and study of their rheological properties;
3. Optimization of technological parameters (temperature, solution lifetime, and curing time) of curing process for the unsaturated polyester-vinyl monomer (p-PGF-MAA) binary system by selecting the composition and concentration of the “cold” curing initiating system;
4. Curing of the studied solutions at room temperature by radical copolymerization in the presence of an optimized “cold” curing initiating system;
5. Identification of reaction products and study of a number of their physicochemical properties.

According to earlier studies [7], it was found that the most optimal compositions for obtaining adhesion materials were solutions of unsaturated polyesters in vinyl monomer with the amount of the first co-reagent 30-45 mass. %. In this study, p-PGF-MAA ratios where the unsaturated polyester content was in the above range were chosen as test samples.

Rheological properties are the main physicochemical characteristics of polymer compounds the knowledge of which is of great importance for improving the technologies of preparation and operation processes of the final polymer product. Knowledge of rheological characteristics is necessary in the chemical engineering industry to control the kinetics of chemical reactions, phase transitions, etc. [21]. In this regard, the dynamic viscosity and density of initial solutions of unsaturated polyester (p-PGF) in MAA of different compositions were studied. The results obtained are presented in Table 1.

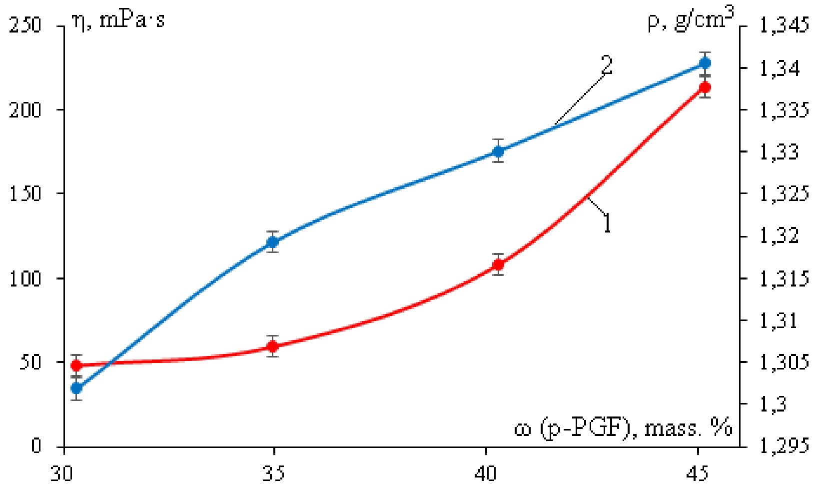
Table 1

Rheological properties of initial solutions of p-PGF-MAA, T = 293 K

Composition of initial solution, mass.%		Dynamic viscosity (η), mPa·s	Density of solution (ρ), g/cm^3
p-PGF	MAA		
30.32	69.68	48.2±0.2	1.3019±0.075
34.96	65.04	59.3±0.2	1.3193±0.066
41.27	58.73	107.9±0.2	1.3301±0.073
45.14	54.86	213.7±0.3	1.3405±0.077

Analyzing the data presented in Table 1, it should be noted that the obtained values of dynamic viscosity and density correlate well with each other, as well as with what p-PGF contains in the solution. Thus, the results obtained indicate rather low values of dynamic viscosity and density, which are 48.2 mPa·s and 1.3019 g/cm^3, respectively for the ratio with the minimum amount of p-PGF (~30:70 mass. %), whereas increasing its content in the initial polymer-monomer mixture to ~45 mass.% leads to increasing the values of the studied parameters to 213.7 mPa·s and 1.3405 g/cm^3, respectively. This can be explained by the high viscosity values of p-PGF, the increase in the content of which in the studied solutions provokes a jump in their viscosity and density values. Dependence of the dynamic viscosity and density of the studied solutions on the p-PGF content is shown in Fig. 1.

Currently, in automobile and construction structures, as well as in technological processes for repairing equipment in oil-gas-, mining and mountain fields there are used synthetic sealants based on phenol formaldehyde, epoxy and polyester resins, which can be divided into two classes, namely containing solvent and solvent-free. Despite the good adhesion properties to metals and other surfaces, sealants containing solvent (phenol formaldehyde), have a number of drawbacks, the most important of which is the presence of traces of solvents (water or organic solvents) in the adhesive composition. In this regard in many cases there are empty spaces, micro pores and micro cracks in the sealing seam. They are formed during evaporation of solvent and water eliminated as a result of polycondensation of phenol formaldehyde resin. Therefore, this type of packing seams cannot always provide a high degree of sealing the compounds. Another disadvantage of similar sealants containing a solvent is often the high curing temperature and the high degree of shrinkage of a polymer layer, which is also due to the evaporation process.



1 — dependence of the dynamic viscosity of the solution on the content of p-PGF in it;
2 — dependence of solution density on the content of p-PGF in it

Figure 1. Dependence of rheological properties of initial solutions of p-PGF-MAA on the content of p-PGF in them

The above disadvantages are absent in sealants that do not contain solvent, have high adhesive properties and can cure without heating or at rather low temperatures. Sealants based on epoxy oligomers, polyurethanes and unsaturated polyesters are widely used.

The curing of sealants of this group (without solvents) occurs during the polymerization reaction of the oligomers or monomers contained in its composition. It is not accompanied by elimination of by-products such as low molecular compounds unlike in polycondensation.

At the end of the curing process, the reaction product is a monolithic polymer with high cohesive hardness. The curing process of a solvent-free sealant is accompanied by negligible shrinkage. Sealants of this type by their characteristics meet the operating conditions in the construction industry, as well as in the car and tool building, so their use for the repair of technological devices is more promising [5]. Another characteristic indicator of sealant quality is its lifetime (the gelation time and gelatinization time), i.e. the time interval during which the thermosetting polymer retains the ability to be applied and processed in viscous-flow state after the introduction of compounds that facilitate its transition to a cured state.

In this regard, the main technological parameters for obtaining high-quality adhesive polymer bases are temperature, gelation time and curing time, the control of which is possible by using an optimally selected initiator system. Considering the possibility of interaction of unsaturated polyesters with vinyl monomers at low temperatures in the presence of an initiator and a promoter, a number of studies were carried out to select the optimal ratio of the components of the initiating system consisting of benzoyl peroxide (BPO) and dimethylaniline (DMA).

The results are presented in Table 2.

Table 2

Dependence of the influence of a promoter on gelatinization time and curing time of the solution of p-PGF-MAA (30.32:69.68 mass. %) (BP + DMA, T = 293 K)

Content, %		Gelatinization time ($\tau_{gelat.}$), min.	Curing time ($\tau_{curing.}$), min.
BPO	DMA		
1	0.05	141.24±5.37	207.18±8.70
1	0.1	98.31±3.74	169.06±7.10
1	0.15	82.36±3.13	145.13±6.09
1	0.2	49.15±1.87	78.17±3.28
1	0.25	14.25±0.54	26.03±1.09

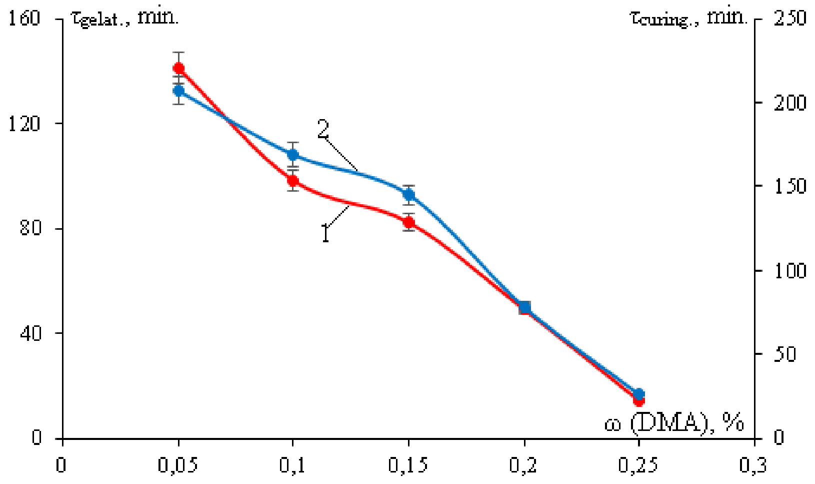
Thus, the activity of the “cold” curing initiating system consisting of BPO as an initiator and DMA as a promoter is preserved over a wide temperature range, which allows varying the gelatinization and curing times of the binary p-PGF-MAA system in order to identify the most optimal values. It should be noted that when choosing the quantitative content of the components of the initiating system, only the amount of the DMA promoter was varied (from 0.05 to 0.2 % by mass of the initial solution of the p-PGF-MAA mixture), while the amount of the initiator was constant and equal to 1 %.

The choice of this amount of BPO was based on the analysis of a number of works [6, 22] and literature sources [23–25]. At the same time, as noted above [7], the BPO concentration affects a number of mechanical properties of the final product, in particular, at its high content the cured polymer is capable of a partial or a complete loss of elasticity and reduction of the numerical values of stress-strain indicators.

Analyzing the data in Table 2, we can say that with the minimum amount of DMA in the initiating system, which is 0.05 %, the gelatinization time ($\tau_{gelat.}$) and curing time (τ_{curing}) of the initial solution of p-PGF-MAA of 30.32:69.68 mass.% are 141 min and 207 min, respectively, whereas increasing the amount of the promoter to 0.25 % reduces the parameters under study to 14 min ($\tau_{gelat.}$) and 26 min (τ_{curing}): in the first case the curing time is rather long, while in the second case it is very short, which may cause significant difficulties during operation.

According to the data given in Table 2, the most suitable values of gelatinization and curing times of the p-PGF-MAA binary systems under consideration are 49 min and 78 min, respectively, which determines an optimal composition of initiating system in the amount of 1 % of initiator and 0.2 % of promoter (out of mass of initial solution of p-PGF in MAA).

The dependence of the effect of the amount of the DMA promoter on gelatinization time and curing time for the p-PGF-MAA binary system of the composition of 30.32:69.68 mass.% in the presence of the BPO initiator at 293 K is clearly presented in Fig. 2.



1 — the effect of the amount of the DMA promoter on gelatinization time of the solution of p-PGF in MAA;
2 — the effect of the amount of the DMA promoter on curing time of the solution of p-PGF in MAA

Figure 2. The effect of the amount of the DMA promoter on curing time of p-PGF-MAA in the presence of BPO at 293 K

To continue the research, a radical copolymerization reaction of initial solutions of p-PGF in MAA was performed at 293 K in the presence of a “cold” curing initiating system with a BPO content of 1 % and DMA of 0.2 % (of the mass of the initial curing solutions). Thus, a promoter DMA (0.2 %) was added to the studied p-PGF-MAA solutions of various mass ratios (Table 1) and the mixture was stirred until homogeneous mass was obtained. After that, the initiator was added with constant vigorous stirring for 1 min and then the gelatinization and curing times were determined according to ISO 57884-2017 [11] and ISO 2535-2017 [12].

Schematically the copolymerization process of p-PGF in MAA with the formation of three-dimensional cross-linked products is shown in Fig. 3.

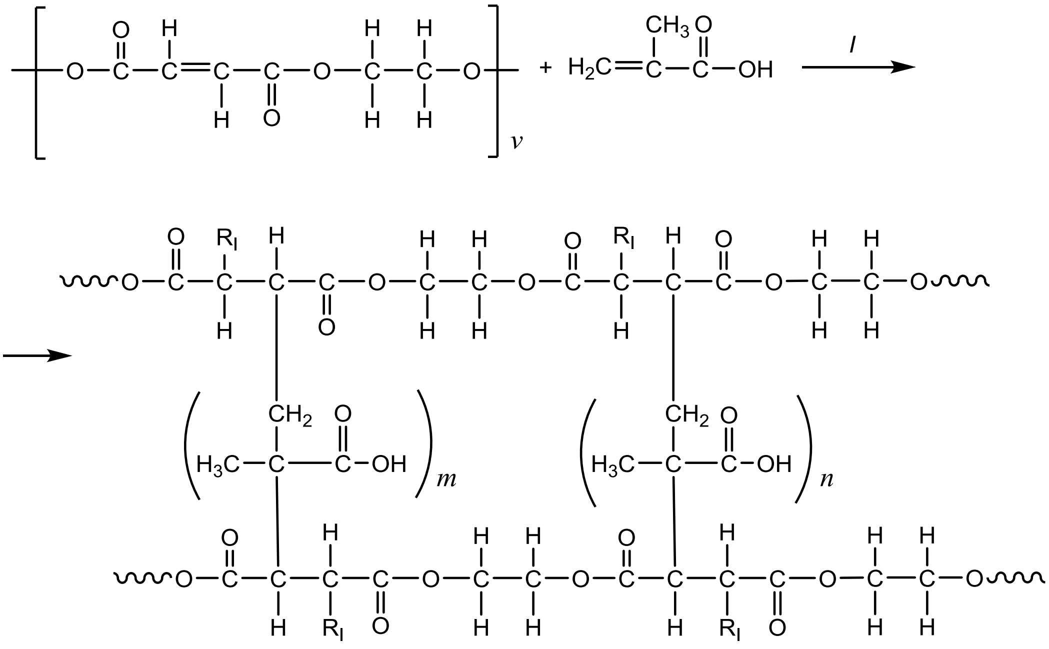


Figure 3. Scheme of p-PGF-MAA synthesis

Identification of the cured p-PGF-MAA binary systems with different mass ratios was carried out by analyzing the corresponding IR spectra. Figure 4 shows the IR spectrum of the solidified reaction product of p-PGF with MAA at the initial ratio of the co-reagents in the solution of 45.14:54.86 mass.%, respectively.

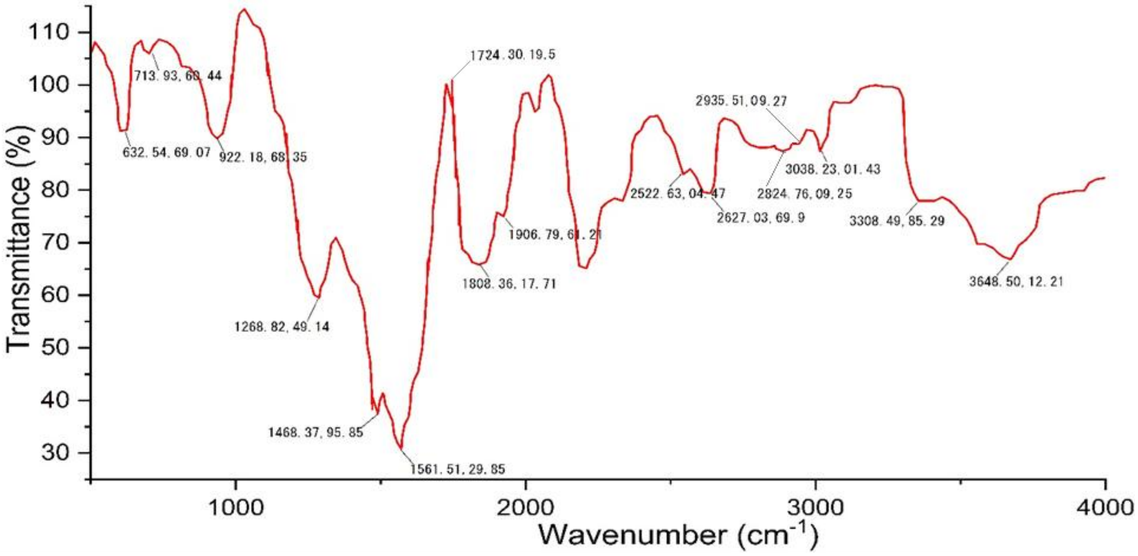


Figure 4. IR-spectra of the cured p-PGF-MAA system with an initial ratio of co-reagents in solution 45.14:54.86 mass. %

Hence, there are absorption bands in the 1720–1740 cm^{-1} (1724 cm^{-1}) and 3300-3600 cm^{-1} (3308 cm^{-1}) ranges in the IR spectra, which is a confirmation of the presence of –COOH groups. The presence of absorption bands at 2935 cm^{-1} is characteristic of MAA methylene groups. Also in the IR spectra there are characteristic stretching vibrations of ether groups C–O–C and –C=C– characteristic of fumarate (1268 and 1468 cm^{-1}) as well as C-H groups at 2824 cm^{-1}.

Further, Table 3 shows the data for determining the gelatinization time ($\tau_{gelat.}$) and curing time (τ_{curing}), as well as the densities of the obtained cured p-PGF-MAA products of different mass composition in the presence of the initial "cold" curing system (BPO 1 % and DMA 0.2 %).

Table 3

Dependence of kinetic curing parameters and properties of cured reaction products on the mass composition of p-PGF-MAA, BPO+DMA (1 % +0.2 %), T = 293 K

Composition of initial solutions, mass. %		Density (ρ), g/cm^3	Gelatinization time ($\tau_{gelat.}$), min.	Curing time (τ_{curing}), min.	Volume shrinkage, %
30.32	69.68	1.4485±0.074	49.15±1.87	78.17±3.28	10.1
34.96	65.04	1.4594±0.074	58.36±2.22	90.43±3.71	9.6
41.27	58.73	1.4802±0.075	68.04±2.59	102.08±4.19	10.1
45.14	54.86	1.4889±0.076	77.13±2.93	118.14±4.84	10.0

Therefore, analyzing the data obtained, it can be noted that with the increase of p-PGF content in the initial mixture the density value of the cured reaction product increases, hence, the gelatinization time (working life) and curing time increase. This dependence can be explained by comparing the activities of the initial co-reagents p-PGF and MAA. Thus, according to earlier studies [20], the copolymerization constant r_1 (p-PGF) in the p-PGF-MAA system is 0.72, and the constant r_2 (MAA) is 1.33. The obtained data correlate well with the studies of the copolymerization kinetics of the considered binary system at T = 333 K, which allowed to establish an inverse dependence of the reaction rate on the unsaturated polyester content in the initial polymer-monomer mixture.

Analyzing the data in Table 3, it should be noted that, despite the difference in gelatinization and curing time of solutions, this difference is not significant and varies in the range of 25-30 minutes.

According to the data in Table 3, we can conclude that the density of the cured product increases depending on the amount of p-PGF in it, which also correlates well with the indicators of the dynamic viscosity of the initial solutions. In particular, the highest value of dynamic viscosity was determined in the solution of p-PGF in MAA of 45.14:54.86 mass.% (with the maximum content of the first co-reagent — p-PGF) and was 213.7 mPa·s, which was characterized by the minimum curing rate.

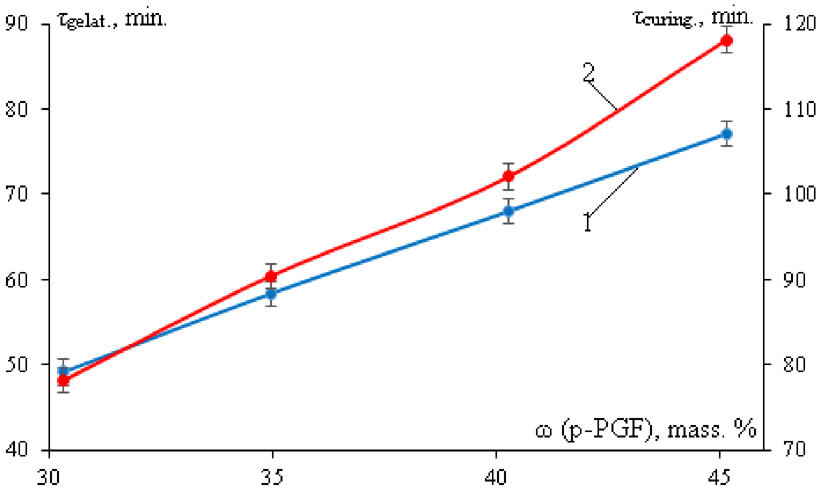
Based on the obtained values of final product densities, the total volumetric shrinkage of the solutions of p-PGF in MAA during curing was calculated. So, a significant disadvantage of most polymeric materials is their high shrinkage during curing [23], which is characterized by a change in linear dimensions as a result of system curing and which causes a decrease in their adhesion strength. During the operation of sealants, this indicator becomes particularly important because of not only a decrease in the level of tightness of the seam during curing, but also the appearance of additional adhesions directly in places of contact of the sealing material with the product surface. In this regard, the permissible range of the value of the volume shrinkage indicator for sealants is 4–10 %.

Thus, the data presented in Table 3 indicate that the volume shrinkage values of the solutions of p-PGF in MAA during transition to the cured state are within the acceptable limits used for sealants. It should be taken into account that the cured products were obtained for the purpose of their use as a polymer base for the creation of filled sealant materials. Inclusion of fillers, plasticizers and other additives in polymer matrix contributes to significant reduction of volume shrinkage value of the final product, i.e. highly filled sealant, which will give an opportunity to obtain sealing material with low volume shrinkage, not exceeding 3 %.

Then, the dependence of gelatinization time ($\tau_{gelat.}$) and curing time (τ_{curing}) on the p-PGF content in the stock solution in the presence of the initiating system (BPO+DMA) at 293K was plotted based on the data in Table 3 (Fig. 5).

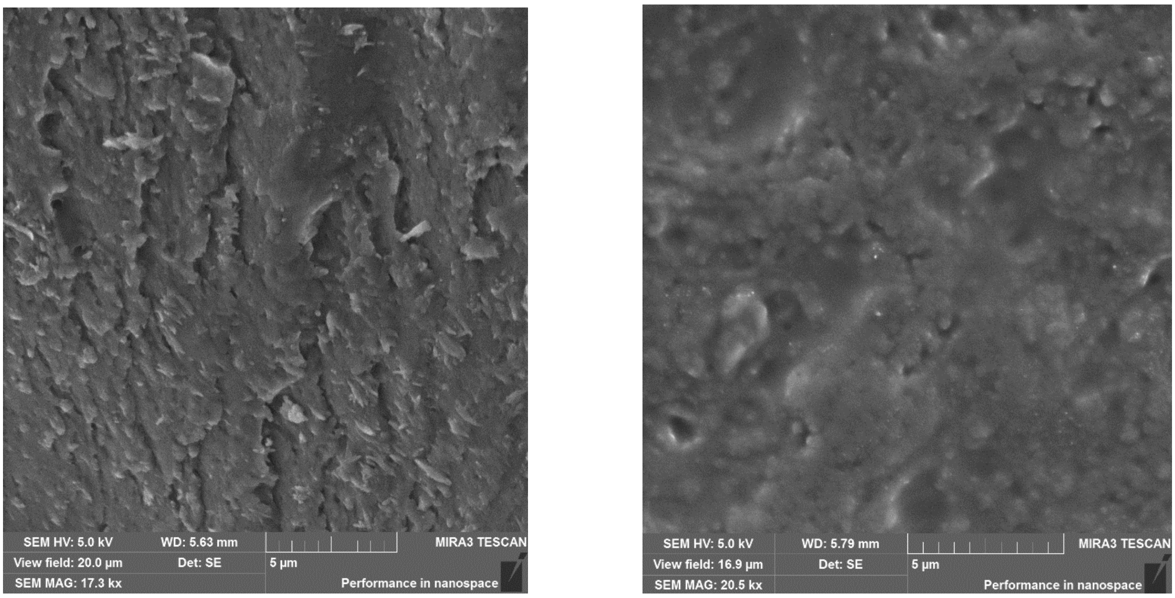
The surface morphology of the cured p-PGF-MAA binary systems of different mass composition was studied by scanning electron microscopy (Fig. 6). SEM image analysis (Fig. 6, b) shows some differences in surface morphology, i.e., a denser structure of the cured sample with the maximum p-PGF content was obtained, while the SEM image of the sample with the lowest amount of unsaturated polyester has a more cellular structure (Fig. 6, a).

The figures show that the copolymers with a higher p-PGF content of 46.04:53.96 mass. % (in the right) are characterized by a denser structure, which correlates well with the results of dynamic viscosity and density of cured samples.



1 — the effect of p-PGF content on gelatinization time of the solution of p-PGF in MAA;
2 — the effect of p-PGF content on curing time of the solution of p-PGF in MAA.

Figure 5. Dependence of gelatinization and curing time on the content of p-PGF in the stock solution in the presence of BPO+DMA initiating system at 293 K



a *b*

Figure 6. SEM images of surfaces of cured samples of p-PGF-MAA of the following compositions: *a* — 30.32:69.68 mass. %; *b* — 45.14:55.86 mass. %

The established rheological and some other physico-chemical properties of the initial solutions of polypropylene glycol fumarate in methacrylic acid at different mass ratios of co-reagents and cured reaction products justify the prospects of using the considered p-PGF-MAA binary system as an adhesive polymer base. The study found that by varying the content of co-reagents in the initial solutions of polypropylene glycol fumarate in methacrylic acid, it is possible to control the rheological properties of the cured mixture and the kinetic parameters of the curing reaction. In particular, increasing the amount of p-PGF in the stock solution from 30.32 mass.% to 45.14 mass. % leads to a more than 4-fold increase in the dynamic viscosity index from 48.2 mPa·s to 213.7 mPa·s. It should be noted that all the results obtained during the study correlate well with each other. Therefore, the values of the dynamic viscosity of the solutions of p-PGF in MAA of different mass composition are in good agreement with the values of the densities of both these initial solutions and the cured reaction products. The gelatinization time (lifetime) as well as curing time of the p-PGF-MAA binary system increased from 49 to 77 min. ($\tau_{gelat.}$) and from 78 to 118 min (τ_{curing}), respectively, when the amount of p-PGF in the stock solution was increased from 30.32 mass.% to 45.14 mass. %.

Analysis of IR-spectra and SEM images showed qualitative and quantitative "cold" curing of the solutions of p-PGF in MAA in the presence of BPO+DMA initiating system (1 % and 0.2 % by mass of the cured solution, respectively).

Conclusions

The optimized composition and concentrations of the components of the "cold" curing initiating system BPO+DMA (1 % and 0.2 % by mass of the curing solution, respectively) is the most energy-efficient for curing p-PGF-MAA solutions, not requiring additional reaction conditions (UV-emitter, high temperature, expensive catalysts, etc.). The resulting polymerization products can later be used as a polymer base for the production of filled sealing composites.

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