СӘТБАЕВ
УНИВЕРСИТЕТІ

KAZAKH NATIONAL RESEARCH TECHNICAL UNIVERSITY named after K.I. SATBAYEV

INSTITUTE OF CHEMICAL AND BIOLOGICAL TECHNOLOGIES

DEPARTMENT OF CHEMICAL AND BIOCHEMICAL ENGINEERING

KAZHYMURATOV AIBOL ABIMURATULY

“SYNTHESIS AND CHARACTERIZATION OF ETHYLENE GLYCOL-BASED POLYMERS»

DIPLOMA WORK

5B072100 – "CHEMICAL TECHNOLOGY OF ORGANIC SUBSTANCES".

Almaty 2020

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«Eligible for defense»
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DIPLOMA WORK

On the theme: “SYNTHESIS AND CHARACTERIZATION OF ETHYLENE GLYCOL-BASED POLYMERS”

5B072100 – "Chemical Technology of Organic Substances".

Prepared by Kazhymuratov Aibol

Scientific supervisor,
PhD doctor, senior lecturer Nakan Ulantay

Almaty 2020

РЕФЕРАТ

Жұмыс 30 беттен, 9 суртен, 3 кестеден, 56 әдеби деректен тұрады.

Мәселенің өзектілігі: Елімізде құрлыс саласы қарқынды дамып келе жатқан негізгі экономикалық салалардың бірі. Бұл саланың дамуы көптеген маңызды мәселелердің шешім табуына қажеттіліктің артуына, сұраныстың жоғарлауына байланысты. Сол маңызды міселелердің бірі бетонның беріктігі. Көптеген зерттеушілер жақсы ғылыми зерттеу жұмыстарды жасап жақсы нітижеге қол жеткізгенімен, олардың жасаған пластификаторларды бетонның беріктігін жақсарту үшін өндіріске енгізгенімен Қазақстанның климаттық жағдайына байланысты көптеген талаптарға сәйкес келмейді. Сондықтан бұл зерттеу бағытында әлі де экологиялық, экономикалық т.б жағынан тиімді сапалы бетонның беріктігін арттыратын материал жасау өзекті мәселе болып табылады.

Жұмыстың мақсаты: жалғанған сополимерлеу арқылы полиэтиленгликоль және акрил қышқылы негізіндегі полимерді синтездеу және бетонның беріктігін арттыру үшін осы полимерді қолдану.

Түйінді сөздер: Полиэтиленгликоль, акрил қышқылы, модификацияланған полимерлер.

Зерттеу нысаны: бетонның беріктігін арттырға арналған полиэтиленгликоль мен акрил қышқылы негізіндегі модификацияланған сополимерлер.

Зерттеу әдістері: вика аспабының көмегімен үлгінің қату уақытын анықтау, конус нысанын пайдалана отырып қоспаның жайылу диаметрін анықтау, пресс-машинаның көмегімен үлгінің беріктігін анықтау.

Алынған нәтижелер мен олардың практикалық маңыздылығы: Эмульсиялық полимерлеу әдісімен полиэтиленгликоль мен акрил қышқылы негізіндегі модификацияланған сополимерлер синтезделіп алынды. Синтезделген полимердің құрылымы мен құрамын анықтау мақсатында ИҚ спектоскропия әдісі қолданылады. Бетонның беріктігін арттыратын пластификатор ретінде қолдану мақсатында модификацияланған сополимерлерді әр түрлі зерттеу әдістері қолданылды. Цементпен араластырылып құйылған құрамында полимерлі бар және полимерсіз үлгіні салыстырғанда беріктігі, су сіңіргіштігі және жылдам жайілуі жағынан полимерлік қоспасы бар үлгінің жоғары нәтиже көрсететіні анықталды.

РЕФЕРАТ

Работа состоит из 30 страниц, 9 рисунков, 3 таблиц, 56 литературных данных.

Актуальность вопроса: Сегодня строительная отрасль является одной из самых быстрорастущих в Казахстане. В связи с развитием науки и техники и растущим спросом, желание увеличить прочность бетона растет с каждым днем. Несмотря на то, что многие ученые провели обширные исследования и внедрили много пластификаторов для повышения прочности бетона, они не смогли удовлетворить многие требования из-за климатических условий в стране. Поэтому разработка экологически чистых, экономичных и т.д. высококачественных полимерных пластификаторов в этой области до сих пор является актуальным вопросом.

Цель работы: Синтез полимера на основе полиэтиленгликоля и акриловой кислоты путем полимеризации в эмульсии и использование этого полимера для повышения прочности бетона.

Ключевые слова: Полиэтиленгликоль, акриловая кислота, модифицированные полимеры.

Объект исследования: Модифицированный сополимер на основе полиэтиленгликоля и акриловой кислоты, предназначенный для повышения прочности бетона.

Методы исследования: Определение времени застывания образца при помощи инструмента ВИКА, определение диаметра разбрасывания смеси по форме конуса, определение прочности образца при помощи пресса.

Полученные результаты и их практическая значимость: Модифицированные сополимеры на основе полиэтиленгликоля и акриловой кислоты синтезированы методом эмульсионной полимеризации. Метод инфракрасной спектроскопии используется для определения структуры и состава синтезируемого полимера. Использованы различные методы изучения модифицированных сополимеров для их использования в качестве пластификаторов, повышающих прочность бетона. Установлено, что образец со смесью полимеров показал хорошие результаты по прочности, водопоглощению и быстрой диффузии по сравнению с образцом, не содержащим полимеров.

ABSTRACT

The work consists of 30 pages, 9 figures, 3 tables, 56 literature data.

Relevance of the issue: Today, the construction industry is one of the fastest growing sectors in Kazakhstan. Due to the development of science and technology and increasing demand, the desire to increase the strength of concrete is growing every day. Although many scientists have conducted extensive research and introduced many plasticizers to increase the strength of concrete, they have not been able to meet many requirements due to the climatic conditions in the country. Therefore, the development of environmentally friendly, economical, etc. high quality polymer plasticizers in this field is still a relevant issue.

Purpose of work: Synthesis of a polymer based on polyethylene glycol and acrylic acid by emulsion polymerization and use of this polymer to increase the strength of concrete.

Keywords: Polyethylene glycol, acrylic acid, modified polymers.

Object of study: Modified copolymer based on polyethylene glycol and acrylic acid, designed to increase the strength of concrete.

Methods of research: Determination of sample solidification time with vika tool, determination of mixture spreading diameter using cone shape, determination of sample strength using press.

The results obtained and their practical significance: Modified copolymers based on polyethylene glycol and acrylic acid were synthesized by emulsion polymerization. The infrared spectroscopy method is used to determine the structure and composition of the polymer to be synthesized. Different methods of studying modified copolymers have been used for their use as plasticizers to increase concrete strength. It was found that a sample with a polymer mixture showed good results in terms of strength, water absorption and rapid diffusion compared to a non-polymer sample.

CONTENTS

INTRODUCTION

Relevance of the issue: Today, the construction industry is one of the fastest growing sectors in Kazakhstan. Due to the development of science and technology and increasing demand, the desire to increase the strength of concrete is growing every day. Although many scientists have conducted extensive research and introduced many plasticizers to increase the strength of concrete, they have not been able to meet many requirements due to the climatic conditions in the country. Therefore, the development of environmentally friendly, economical, etc. high quality polymer plasticizers in this field is still a relevant issue.

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1 Literary review

1.1 Methods of producing oligo(ethylene glycol)methacrylates

The main application in practice among polyoxyethylated methacryl esters is methoxyoligoethylene glycolmetacrylates, so the absolute majority of works is devoted to the synthesis of these very representatives of this group of compounds. In order to obtain them on an industrial scale, methacrylic acid (MAC) etherification or methoxyoligoethylene glycols (MOEG) with varying degrees of oxyethylation and, consequently, molecular weight are used.

The esterification reaction is as follows:

$$CH_2{=}C(CH_3)COOH + HO(CH_2CH_2O)R \leftrightarrow CH_2 = C(CH_3)COO(CH_2CH_2O)R + H_2O \quad (R.1)$$

Etherification reaction takes place at an elevated temperature, the interval 110 - 120 °C is considered optimal. At temperatures above 130 °C, side processes, mainly the formation of esters, begin to take place [1]. In the absence of catalysts, the reaction is very slow. Acid-type catalysts are used to intensify the process. Strong inorganic and organic acids such as sulfuric acid, methane sulfonic acid, alkylbenzene sulfonic acids, phosphoric acid, hydrochloric acid, chloric acid, acidic ionites and Lewis acids (boron chloride, aluminum sulfate, trichloride iron, etc.) can be used as catalysts [2]. An acid catalyst should have a high boiling point (at least 150 °C, preferably 200 °C). In many papers preference is given to sulphuric acid (T_{boil} = 317 °C) and p-toluene sulphonic acid (T_{boil} = 185-187 °C). The optimal concentration of sulfuric acid is considered to be 0.5 - 0.7% of the total mass of reagents [3]. If the concentration is less than 0.1%, the reaction takes place at a low rate, at the same time the use of high concentrations of the catalyst leads to the formation of a large number of by-products, in particular resins. In addition, a strong acid catalyst can cause destruction of the polyethylene glycol chain, which impairs product quality.

Along with the etherification reaction, the reverse reaction of complex ether hydrolysis takes place. At etherification of MAC, taken in 4-fold excess in relation to MOEG with molecular weight 1000 (i.e. with degree of oxyethylation n=23), at 120 °C 85% equilibrium conversion of alcohol is achieved [2]. To achieve high conversion rates of initial substances it is necessary to remove reaction water from reaction zone. Water forms hydrogen bonds with polyalkylene glycols, and water activity coefficient decreases approximately to 0,3, therefore, water volatility is insufficient to conduct its distillation at atmospheric pressure [2]. The literature suggests several ways to solve this problem. In the first variant it is suggested to use inert azeotrophic solvents, they can be n-paraffins, iso-paraffins, cyclo-paraffins, aromatic hydrocarbons and their mixtures with boiling point of azeotrope 70-130 °C. Use of solvent with boiling point 110-130 ° C not only facilitates water removal, but also prevents excessive temperature increase during synthesis. It is suggested to introduce a different amount of solvent. Thus, in the work [3] the authors use as a solvent a mixture containing 30 parts of heptane for 70 parts of toluene, the share of solvent is from 40 to 60% of the total mass of the mixture. In work

[4] it is suggested to use benzene and its content is 30-40 %. In works [5] and [6] preference is given to toluene; its concentration makes 4-15 % and 16-20 % accordingly. In [7] cyclohexane is used, mass fraction in initial mixture is 14 %.

The course of side polymerization and the formation of "microgels" is sharply increased if the initial methoxyoligoethylene glycols contain impurities of oligoethylene glycols, for which the etherification reaction can take place with the participation of two hydroxyl groups:

$$2CH_2=C(CH_3)COOH + HO(CH_2CH_2O)H \leftrightarrow$$
$$\leftrightarrow CH_2=C(CH_3)COO(CH_2CH_2O)OOCC(CH_3)=CH_2 + 2H_2O \qquad (R.2)$$

The monomers formed have two active vinyl groups, which results in the formation of cross-linked polymers (which is the basis of "microgels") when the polymerization cannot be completely suppressed. The formation of "microgels", in turn, further accelerates the polymerization of monomers and reduces their yield.

1.2 Emulsion polymerization of polymers based on acrylic acid and ethylene glycol and their application

Acrylates and methacrylates are universal building blocks that can be easily cured or copolymerized with many other monomers. Many homopolymers and copolymers are considered membrane materials. One of the main requirements for a polymer to form a film is good adhesion to various hard surfaces such as metals, wood, cement, glass and so on. Acrylic acid is used in emulsion polymerization to improve colloidal stability in latex products [8].

Copolymers of acrylic and methacrylic acids are one of high-molecular weight compounds and are used in engineering, agriculture, medicine and various fields. They have availability, transparency of raw materials, stability of fuel and oil and good physical and chemical properties.

Soft acrylic polymers obtained by emulsion polymerization without plasticizers have high weather resistance. They can be used to produce waterproof membranes. They are part of a cellulose lacquer to improve adhesion, water resistance and weathering resistance. Acrylic dispersion is used to improve the water resistance of concrete and as a primer for porous building materials and interior walls.

The problem of emulsion polymerization as one of the main methods of obtaining polymers is constantly attracting attention of researchers. This is primarily due to the need to improve the quality of polymer and latex synthesis processes and create materials based on this set of properties. These problems are especially important for polymerization of acrylic monomers, which are characterized by high reactivity, high dispersion of primary emulsions and insufficient stability of the reaction system during the polymerization process.

One of the most effective ways to improve cement quality is to use various modified additives and plasticizers.

Plasticization is one of the methods to modify the polymer. Here, low molecular weight compounds are introduced into the polymer, as a result of which their glazing temperature and fluidity are reduced and their plasticity and plasticity are improved. The plasticizer can be added to a mixture of monomers or to finished polymers in the solution and melted before synthesis [9].

Plasticizers are water-soluble powder materials to form viscous solutions or weakly alkaline, neutral solutions. They can be pure inorganic substances, their mixtures, organic compounds, organic-mineral complexes. The polymers differ in composition, production methods and physical and chemical properties. This allows them to be widely used in various technical fields, including construction.

In today's world cement concrete is used in many construction industries and in various structures. Due to a wide range of characteristics of cement, concrete, its physical-mechanical and other characteristics require constant improvement. The key task is to find various ways to improve the properties of cement, reduce possible defects and give them special properties. One of the ways to improve the properties of cement is the introduction of special modifying additives-plasticizers, which are classified by origin and chemical and mineralogical composition [10,11].

Acrylates mainly act as internal plasticizers, which are part of an acrylic copolymer macromolecule. Conventional plasticizers move over the plastic surface over time, accelerating its aging. Each time it remains on the polymer surface it becomes sticky, unpleasant, and if it leaks, the material becomes brittle. Internal plasticizers, on the other hand, give polymers flexibility, which is stable. The plasticizer for building solutions based on lignosulfonates, inorganic salts and acrylic polymers is strong.

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1.3 Usage of ethylene glycol based polymers

Oligo (ethylene glycol) methacrylates are a promising class of monomers, polymers based on which are increasingly being used. First of all it concerns the MOEGM. The presence of methacryloilic fragment allows to obtain polymers by cationic, anionic, free-radical, controlled radical and other polymerization variants [17]. The most applicable is free-radical polymerization, in which OEGMs show high reactivity.

Homopolymers and copolymers of MOEGM, depending on the length of the oxyethylated chain in polyoxyethylated links and other parameters, can be soluble or not soluble in water and, due to the amphiphilicity of MOEGM links, can exhibit heat-sensitive properties, ie at certain temperatures and other conditions are able to perform reversible conformation and phase transitions. By changing the structure of methoxyoligoethylene glycolmetacrylates, the hydrophilic-hydrophobic properties of polymers based on them can be varied within a wide range. For example, homopolymer MOEGM, which contains one oxyethylene link, shows only weak hygroscopic properties. Polymer MOEGM containing two oxyethyl links becomes water-soluble, but it has the lowest critical solubility temperature (LCST) of 26 °C only. Polymer based on MOEGM with values n=8 - 9 has the value of LCST about 90 °C, and poly(MOEGM) with values n=10 and more do not have temperature-sensitive properties in aqueous solutions, because they are water soluble up to boiling point of solutions [18, 19].

In [20] the authors have shown by the example of two MOEGMs with the number of okyethylated links 2 and 6 - 7 that by changing the ratio of monomers it is possible to obtain polymers with a given value of LCST with an accuracy of 0.5 - 1 °C. Therefore, in recent years, heat-sensitive ("smart") polymers based on homopolymers of MOEGM are actively researched in many world scientific centers. These copolymers combine the advantages of polyethylene glycols (biocompatibility, low toxicity, good biodestruction) and thermosensitive polymers. In addition, they have a number of advantages over traditional polymers based on N-isopropylacrylamide: excellent biohydrophobicity at temperatures below LCST values, absence of hysteresis in reverse phase transitions, bioinert properties (no specific interaction with biological materials) [21].

Thermosensitive polymers based on MOEGM can be used as hydrogels. The authors of the work [22] obtained cross-linked MOEGM thermopolymer (with 2 and 9 links in the oxyethylated chain) and ethylene glycol dimetacrylate by means of controlled polymerization by ATRP mechanism. Value of LCST of cross-linked copolymers is comparable with values of their uncross-linked analogues. The resulting hydrogels are capable of swelling at room temperature, but at temperatures above LCST the swelling quickly disappears. In [23] the method of obtaining monodisperse microgels based on MOEGM with adjustable diameter in the range of 100-1000 nm is described. Later the same authors developed a method for obtaining temperature-sensitive microgels of the "core-shell" type [24]. Microgels based on MOEGM are self-organized in aqueous medium with formation of linear-crystalline structures, giving iridescent colors to solutions [23, 24]. Besides, these colloidal crystals can be stabilized by inter-particle cross-linking, which allows obtaining stable photonic hydrogels [25]. Researches have shown, that microgels of type "kernel- The "envelope" can also be used for controlled drug release [26]. Medicinal substances, poorly soluble in water, are retained in the hydrophobic nucleus of the microgel and released during the transition of macromolecules from micellar to open form in conditions of elevated temperatures and changes in pH.

Due to the low adsorption of proteins and cell adhesion of polyethylene glycol fragments, there is growing interest in using MOEGM to create bioactive surfaces. Surfaces modified with MOEGM polymers prevent biofouling (27, 28). These surface coatings are hydrophilic even at high temperatures and are capable of inhibiting protein and cellular adsorption (29). Anti-fouling coatings can find wide application in biosensors and implants [30-32]. In [33] it was suggested to modify hydrophobic acrylic interocular lenses by covalent grafting of OEGM to their surface. The obtained results showed that on the hydrophilic-modified surface the adhesion of platelets, macrophages as well as their spreading and growth decreased significantly. In work [34] the study of physicochemical and biological properties of polydimethylsiloxane surface (widely used in prosthetic devices) modified by OEGM grafting was carried out.

OEGM thermosensitive polymers have significantly expanded the use of modified surfaces. By measuring the equilibrium wetting angles [35] by means of neutron refractometry [36] and atomic force microscopy [37] the thermo-sensitive properties of the modified surface have been proved. These measurements have shown that the adhesion properties of modified MOEGM polymer surfaces differ significantly at temperatures below and above LCST of polymers. In addition, thermally induced transition for such polymer coatings is fast and reversible. Thus, surfaces based on thermosensitive OEGM polymers are very promising for creating modern materials. In particular, they can be used for controlled bioadhesion (38). For example, work [39] shows that on a surface modified by an MOEGM copolymer, fibroblasts are almost quantitatively detached. OEGM-modified silica can be used for steroid and protein chromatography [40]. Heat-sensitive stationary phases allow fast and effective separation at isocratic elution in high performance liquid chromatography. It was demonstrated in [41, 42] that surface "brushes" based on MOEGM can be used to create intelligent antibacterial surfaces.

The above described temperature-sensitive properties of homo- and copolymers of MOEGM and new promising applications of such polymers are directly related to the amphiphilic nature of these monomers. Amphiphilic properties of MOEGM have not been studied before, therefore the studies in this direction, important for practical application of oligoethylene glycolmetacrylates of different structure, became a part of the presented thesis.

In addition to MOEGM thermosensitive copolymers with limited water solubility, MOEGM-based polymers with a high degree of oxyethylation that are well soluble in water have found wide application. In industry MOEGM copolymers with (meth)acrylic acid, maleic anhydride and other hydrophilic monomers in large scale are used as highly effective plasticizing additives in concrete [43, 44]. The main purpose of such additives is to increase the mobility of concrete mixture or reduce its water content, which provides a reduction in energy and labor costs when laying concrete in monolithic building structures, precast concrete products and contributes to the intensification of the technological cycle, improving the quality of concrete materials. Used as plasticizers, OEGM copolymers have a comb structure and consist of a chain containing carboxylic groups and side alkylenoxide branches of different molecular weight. Carboxylic acid links in the main chain of the copolymer ensure anionic charge and are "responsible" for the adsorption capacity of the plasticizer. Long side polyoxyethylene chains in macromolecules are responsible for stabilization and dispersion of cement particles in the moving mixture (by a mechanism called "spatial effect"). The authors [45] show that the length of side chains of oxyethylene methacrylate affects the hydration rate of cement and, consequently, the growth of mechanical strength of the finished concrete. When added to the concrete polymer plasticizer obtained on the basis of OEGM with a high molecular weight of 4468 (number of oxyethylene links n = 100), cement curing occurs very quickly, even in adverse climatic conditions. To preserve the mobility of the concrete mixture for a long time (1 hour and more), plasticizers based on OEGM with an average molecular weight of 1000 - 2000 (n = 23 - 45) are used [46, 47].

In order to improve the dispersion ability of plasticizers, sulphonic-containing links, such as sodium metal sulfonate, are introduced into their composition [48]. In work [16] the copolymer OEGM with AMPSA is offered as a plasticizer. One of the new directions in plasticizers efficiency increase is creation of cross-linked macromolecules. Cross-linked polycarboxylates due to regulation of speed of their hydrolytic splitting allow to maintain mobility of concrete mixture for a long time as quantity of active product is constantly fed at transition of the main product to normal polycarboxylate plasticizers [45, 49]. Another method to increase plasticizer duration is replacement of part of carboxylic links with non-ionic ones, which are capable of hydrolysis in alkaline medium with carboxylic group release. Most often acrylamide [50] or methylacrylate is used for this purpose [51]. Choosing the types of monomers and their ratio, it is possible in wide limits regulate the ionic charge in the macromolecule, number of stitches, molecular weight, number and length of side oxyethyl chains. This allows the creation of copolymers with predefined properties depending on the intended application of plasticizers.

One of the potentially promising uses of OEGM is the production of materials with variable phase state, which are used for thermal energy conservation. Thus in [52] homopolymers of MOEGM with average molecular weight of 1100 and 2080 were obtained by polymerization in mass. These samples have good thermal stability and high value of phase transition enthalpy.

There is a growing interest in using MOEGM to obtain super-sorbents. Thus, in [14] a cross-linked copolymer of partially neutralized acrylic acid and MOEGM with molecular weight 475 was obtained. The introduction of MOEGM reduces the glass transition temperature of the polymer and allows reducing the content of residual monomers in the process of their extraction, which is a key parameter when using superabsorbents for hygienic purposes. However, the increase in MOEGM content leads to a reduction in the amount and speed of water adsorption. In [15] a salt tolerant super-sorbent obtained by reverse-suspension polymerization of partially neutralized acrylic acid, acrylamide and MOEGM with molecular weight 2080 was proposed. The dependence of the absorptive capacity of the super-sorbent on the mass fraction of MOEGM passes through the maximum (39.4 % wt.). It is also shown that MOEGM acts as a co-dispergent during polymerization, improving the quality of products.

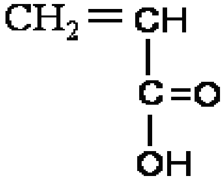
One of the promising directions is the production of organosoluble copolymers OEGM with hydrophobic monomers, which polar oxyethyl fragments can give dispersing, adhesive and other properties. In particular, organosoluble copolymers of OEGM and higher alkyl(meth)acrylates are proposed as viscosity-dispersion additives to motor oils [53-56]. However, they are wide no research has yet been carried out on the production, properties and application of organ-soluble copolymers of OEGM.

Thus, oligo(ethylene glycol)(meth)acrylates are widely used monomers, and the development of new effective materials based on them is developing rapidly all over the world. In the given work the task of development of the complex technology providing synthesis of MOEGM and MOEGA and reception of final products on their basis - effective plasticizers for cement compositions and additives for oil products is set.

2 Experimental part

2.1 Characterization of initial substances and solvents

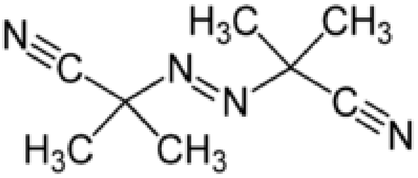
Acrylic acid «Sigma-Aldrich» firm’s product, 98%. Used without addition purification. ($T_{boil.}$=300.3K/4kPa, n_D^{20}=1.4222; $T_{boil.}$=414K/101kPa, n_D^{20}=1.4224).



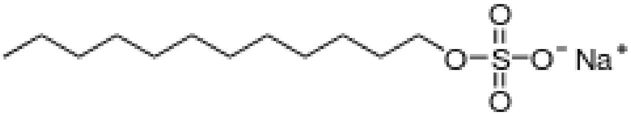
Polyethylene glycol (PEG) «Sigma-Aldrich» firm’s product, molecular weight is equal to 2000, density 1.21g/cm^3(20°C).

$$H-(O-CH_2-CH_2)_n-OH$$

2,2-azo-bis-isobutyronitrile (AIBN) used as initiator, (produced by Aldrich firm) twice crystallized from ethyl alcohol solution, $T_{melt.}$=101^{0}C.



Sodium dodecyl sulfate (SDS) consisting of 99% of anionic surfactants. «Sigma-Aldrich» firm’s product.

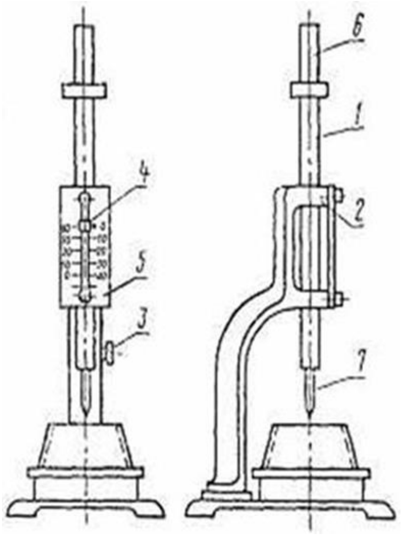


or ($NaC_{12}H_{25}SO_4$)

Ethyl alcohol ($T_{boil.}$=78°C/101.325kPa, n_D^{20}=1.3612-1.3618).

2.2 Physico-chemical methods of research and description of devices used

The Vika tool is used to determine the normal density of viscous materials as well as the initial and final solidification time of cement. Measurement of these characteristics is specified in ГОСТ 310.3-76. This tool is mainly used in construction industry. The small tool consists of a needle, pestle, ring and plate. The standard length of a needle with a diameter of 1 mm is 50 millimeters. The size of the gun (diameter x length) is 10 x 50 millimeters (the image of the tool is shown in Figure 1).



1 - cylindrical metal rod; 2 - frame; 3 - locking tool; 4 - index; 5 - scale; 6 - pistil; 7 – needle

Figure 1 – Vika tool for determining the solidification time

The consistency of the cement dough is determined using a cone and shaking table (Fig. 2). The cone is located in the center of the shaking table disk. Cement paste with normal density is used to determine the consistency of the cement paste. The inner surface of the cone and the table surface are pre-wiped with a damp cloth. Fill the cone with cement paste. Place the cone in the center of the table disk for shaking and level the surface, tapping on the table 10 times. After smoothing the surface of the mixture remove the cone and shake the table 15 times, then measure the diameter of rolling cement paste (device for measuring the diameter of rolling cement paste shown in Figure 2).

Figure 2 – Apparatus for shaking and compacting the mixture in the cone

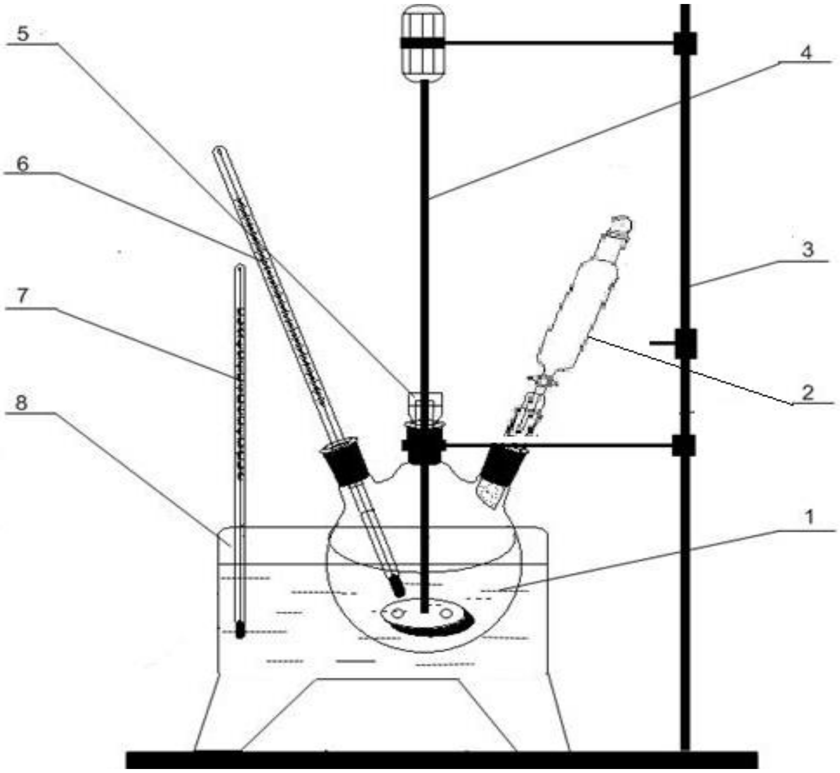
A hydraulic press (ИП-500) was used to determine the strength of a cement test (Figure 3). To determine the strength of a cement dough, pour the pre-cooked cement mixture into cubes. Three samples (one form) are made for each specified test period (a drawing of the hydraulic press and forms is shown in Figure 3).

Figure 3 – Hydraulic press and forms for strength determination

The cubes are stored in a form for 24 ± 1 hour. After a short time, the cubes are gently removed from the form and then marked. The ready-made cubes are placed horizontally in a water bath so that they do not touch each other. The water changes every 14 days. The cubes are removed from the water after 3, 7, 21 days. Before placing the cubes in the water and after a certain time, their weight is measured, i.e. water absorption is calculated. At the end of the storage period, the cubes are removed from the water and checked at the latest after 30 minutes.

2.3 Preparation of polyethylene glycol -grafted- acrylic acid

The polymer was synthesized in a special unit. A mechanical stirrer and a drip tray equipped with a thermometer, a 250 ml round bottom flask placed in a water heater, the internal temperature was controlled by a regulator (the synthesis unit is shown in Figure 4).



1 - three-neck flask; 2 - drip tray; 3 - tripod; 4 - mechanical stirrer; 5 - gas pipe; 6,7 - thermometer; 8 - water bath

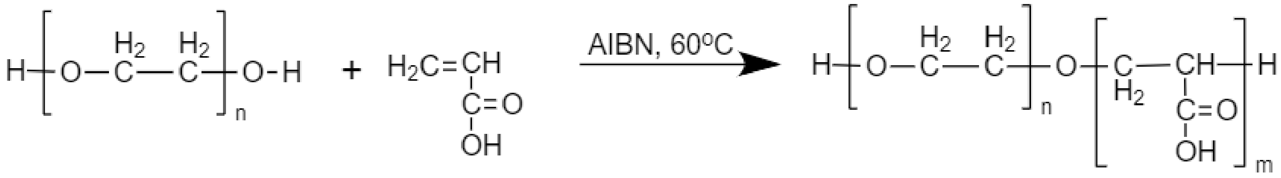
Figure 4 - Polymer synthesis unit

A mixture of polyethylene glycol (MW=2000) and sodium dodecyl sulphate (DDS) is added to the three-necked flask located in the synthesis unit and mixed until the polymer is completely dissolved in water. Add a certain amount of acrylic acid (AA) to the fully dissolved mixture and increase the temperature to 60 °C and accelerate the rotation of the mixer to a certain level. After a while, 2.2-azo-bisobutyronitrile (AIBN), dissolved in water, dropped through a drip tube. The synthetic mixture starts to turn into a viscous in more than 2 hours. The mixture is then cooled, poured into another container and sent for further study and use.

3 Results and their analysis

3.1 Copolymer based polyethylene glycol-and its use to increase concrete strength

A mixture of polyethylene glycol and sodium dodecyl sulphate (DDS) is added to the three-necked flask located in the synthesis unit and mixed until the polymer is completely dissolved in water. Add a certain amount of acrylic acid (AA) to the fully dissolved mixture and increase the temperature to 60 ° C and accelerate the rotation of the mixer to a certain level. After a while, 2.2-azo-bisobutyronitrile (AIBN), dissolved in water, dropped through a drip tube. The synthetic mixture starts to turn into a viscous in more than 2 hours. The mixture is then cooled, poured into another container and sent for further study and use.



The infrared spectroscopy method was used to determine the structure and composition of the polymers under study. Although infrared spectroscopy is one of the oldest methods of studying polymers, it has not lost its relevance in modern studies (infrared spectrum of polyethylene glycol and acrylic acid polymers is shown in Figure 5).

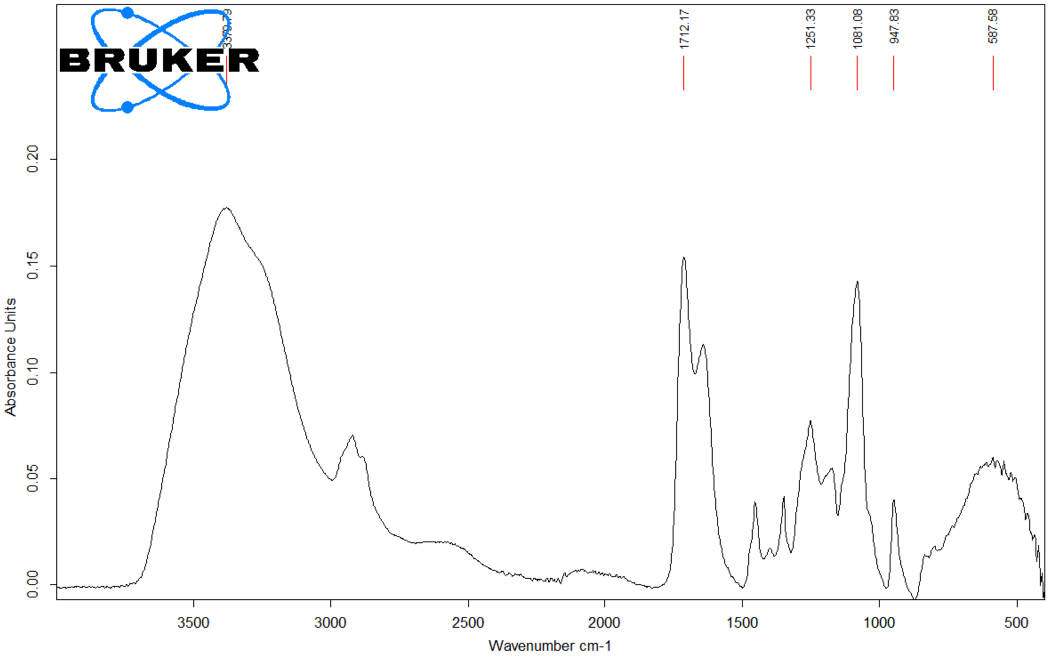


Figure 5 – Infrared spectrum of polyethylene glycol and acrylic acid polymer

Absorption bands in the infrared spectrum were recorded in the range of 400-4000 cm^{-1} . Here are the signals given by the functional groups of ethylene glycol and acrylic acid copolymer, i.e. groups O-H (3379 and 3400 cm^{-1}), C = H (1712 and 1726 cm^{-1}), C-O (1081 and 1270 cm^{-1}), and C-H (820 and 970 cm^{-1}).

Different research methods have been used to use synthesized ethylene glycol and acrylic acid-based polymer as plasticizers to increase concrete strength.

Initial chemical composition of used cement paste is showed in the table 1.

Table 1 – The chemical composition of the cement paste

Compounds	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Losses
Mass, %	21.48	6.03	4.22	64.29	0.68	0.39	0.21	0.11	2.59

Portland cement used as cement sample.

Determination of the normal density of the cement slurry (cement/water ratio). The comparative analysis of plasticizer-based cement paste and pure cement-water paste is performed.

Determining the normal density of cement paste is necessary for further testing of cement (determining the residence time, determining the spraying diameter of cement paste). The normal density value depends on water consumption, density and strength of the cement paste.

Normal density of cement paste is determined in accordance with ГОСТ 310.3-76 and by Vika tool with pestle.

According to the standard, 400 g of cement, 116 g of water and 2 g of plasticizer are added. The plasticizer is a synthetic polymer based on ethylene glycol and acrylic acid (pH = 7). Wait 30 seconds until water is absorbed, then vigorously stir the paste in perpendicular directions for 5 minutes. Fill the cement paste into the Vika tool ring. The ring is in the centre of the Vika tool and the paste is filled until the surface touches the pestle. Push the fixed screw so that the pestle can fall freely. 30 seconds after the release of the rod, the depth of penetration of the pestle is determined on the scale of the device. The density of the cement paste is normal if the pestle does not reach the 5-7 mm plate. The pestle was immersed in the cement paste and did not reach 6 mm on the plate. That is, for normal paste density, the ratio of 400 g of cement to 116 g of water was preferred.

Normal cement density is the ratio of the cement weight required to prepare the cement paste to the amount of water, expressed as a percentage. According to the results, the Cement Water Ratio is determined by the following formula. It is taken 22-30% of the cement weight.

$$d = \frac{G_{water}}{G_{cement}} * 100\ \%$$

where, G_{water}, is the amount of water in the paste, g;

G_{cement} - mass of cement, g.

$$d = \frac{116}{400} * 100\% = 29\%$$

$$d = \frac{107}{400} * 100\% = 25{,}75\%$$

The normal density of plasticizer-based paste is 29%, and the normal density of pure cement-water paste is 25.75% (a comparative analysis of normal densities of cement-water paste is shown in Figure 6).

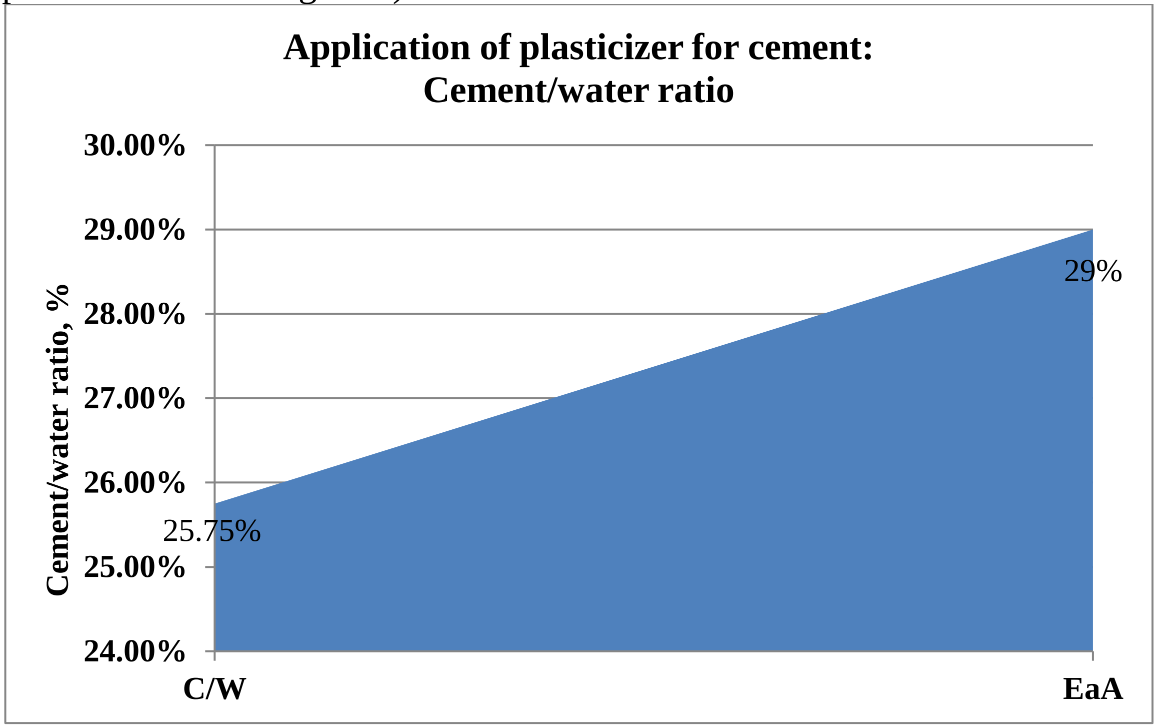


Figure 6 – Comparative analysis of normal cement paste densities

Vika needle tool was used to determine the initial and final hardening time of a cement test (ГОСТ 310.3-76). Normal density cement paste is used to determine the hardening time. Cement paste, which is poured into the Vika tool ring, is fed before it touches the tool needle. It allows the needle to drop freely when pressed on a fixed screw. The needle is dipped in the cement paste every 5 minutes before the hardening time and every 15 minutes from the beginning of the hardening time to the end of the hardening time. Hardening time starts at 1 hour and ends at 1 hour 50 minutes.

The start of hardening time of pure cement-water paste was 1 hour 40 minutes and the end of hardening time was 3 hours 58 minutes (comparative analysis of cement paste hardening time is shown in Fig.7).

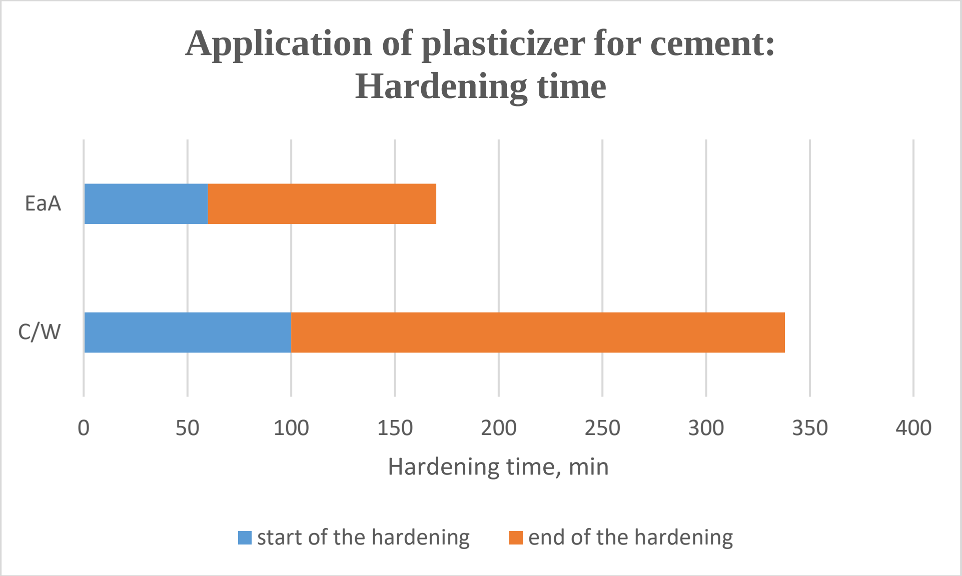


Figure 7 – Comparative analysis of cement test hardening time

The initial and final hardening time of cement paste was measured in a room with a temperature of 15 - 20 ° C. The initial hardening time of plasticizer-based cement paste was 1 hour and the end was 1 hour 50 minutes. That is, at normal temperatures, the hardening time was ± 30 minutes. For reference: in industrial production hardening time of concrete products does not exceed 10-20 minutes.

To obtain a high strength cement paste, it is necessary to apply it before the initial hardening time. Too fast or too slow hardening of a cement paste is one of the main disadvantages. If cement hardens quickly, it will harden before use. When working with such cements, they must be transported quickly after mixing with water, which is a problem. And if hardening time is slow, it slows down the construction pace. According to ГОСТ10178-85, the initial time of cement hardening should not exceed 45 minutes and the end should not exceed 10 hours.

The consistency of a cement paste is necessary to determine the diameter of its spread. If the spreading diameter of the paste is in the range of 142-149 mm, the consistency of the cement paste is normal.

The consistency of the cement paste was determined using a cone and a shaking table. Cement paste with normal density is used to determine the consistency of the cement paste. Fill the cement paste in the form of a cone. Place the cone in the centre of the shaking table disc and align the surface by pressing 10 times. After aligning the mixture surface, remove the cone shape, shake the table 15 times and then measure the diameter of the cement paste. The diameter of the paste has spread d = 14.7 cm = 147 mm. The distribution diameter of the pure cement-water paste is d = 14.2 cm = 142 mm (a comparative analysis of the consistency of the cement paste is shown in Figure 8).

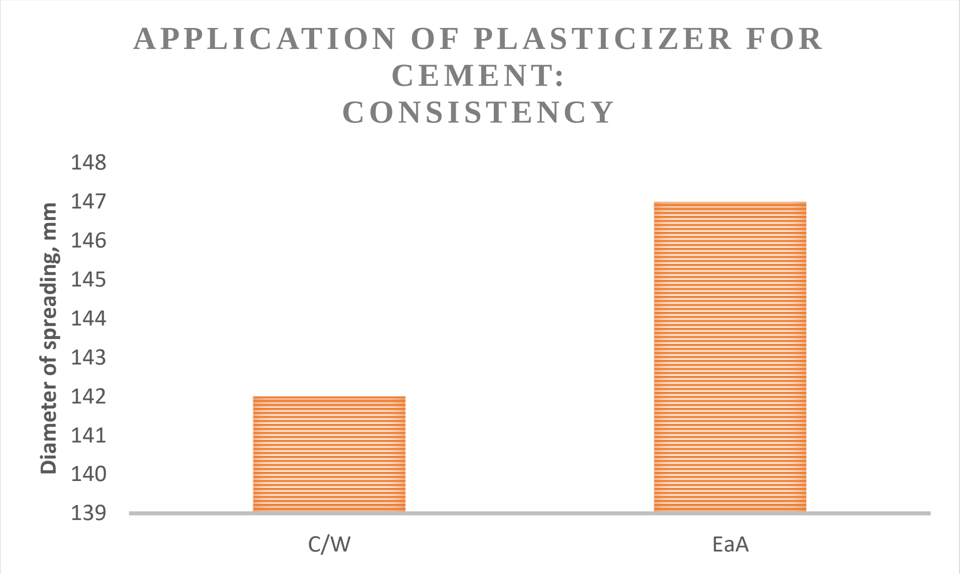


Figure 8 – Comparative analysis of the consistency of the cement paste

The diameter of the cement paste should be between 142-149 mm. The large spreading diameter increases its overall area coverage in production, resulting in material savings.

A hydraulic press is used to determine the strength of a cement paste. To determine the strength of a cement paste, pour the pre-cooked cement paste into cubes lubricated with machine oil. Three samples (one form) are prepared for each specified test period. The dice shall be stored in a mould for 24 ± 1 hours. After a certain time, the dice shall be carefully removed from the mould and then marked. The finished cubes shall be placed horizontally in a water bath so that they do not touch each other. The dice are removed from the water after 3, 7, 21 days. Before placing the cubes in the water and after a certain time, their weight is measured, i.e. water absorption is calculated. At the end of the storage period, the cubes are removed from the water and tested after 30 minutes at the latest.

Mass of cubes after 24 hours and after 3,7,21 days (water absorption of cement paste based on plasticizer is given in table 2).

Table 2 – Water absorption of cement paste based on plasticizer

Mass, g.				
№	1 day	3 day	7 day	21 day
1	720	746	-	-
2	664	678	-	-
3	720	-	740	-
4	702	-	721	-
5	730	-	-	765
6	738	-	-	750

Mass of cubes (pure cement-water paste) after 24 hours and after 3,7,21 days (water absorption of pure cement paste is shown in table 3).

Table 3 – Water absorption of pure cement paste

Mass, g.				
№	1 day	3 day	7 day	21 day
1	716	742	-	-
2	712	738	-	-
3	710	-	738	-
4	736	-	762	-
5	734	-	-	760
6	718	-	-	744

The strength of the cement test is one of the main factors. It is not used in industry without determining the strength. Pure cement-water paste has high water absorption, but low strength. That is, cement paste based on plasticizer has high strength (comparative analysis of the strength limits of cement paste is shown in Figure 9).

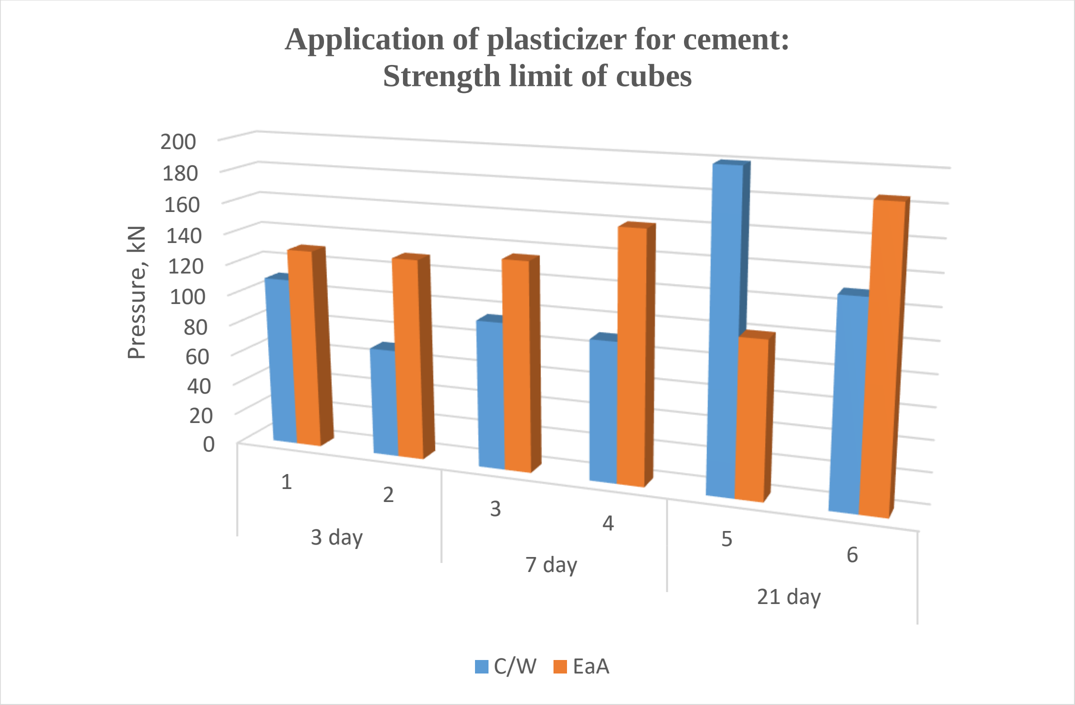


Figure 9 – Comparative strength limit analysis of a cement paste

We conducted a study using a polymer based on synthesized ethylene glycol and acrylic acid as a plasticizer. According to the analysis, the plasticizer has a large spreading diameter, good water absorption, high strength, as well as colorless, odorless, low cost.

CONCLUSION

1. Copolymer based on polyethylene glycol and acrylic acid was synthesized by emulsion polymerization.

2. The IR spectroscopy method is used to determine the structure and composition of the polymer to be synthesized.

3. Various research methods have been used to use cross-linked copolymer based on polyethylene glycol and acrylic acid as a plasticizer to increase concrete strength.

4. To increase the strength of concrete, the ratio of cement to water, as well as the hardness and pressure resistance of a standard sample (without polymer) and a sample with polymer were studied.

LIST OF ABBREVIATIONS

AA	acrylic acid
AIBN	2,2-azo-bis-isobutyronitrile
PEG	polyethylene glycol
DDS	dodecyl sulfate
IR	infrared spectroscopy
M	molecular weight
AMPSA	acrylamide propane sulfonic acid
MOEGA	methoxyoligoethylene glycol acrylate
LCST	lowest critical solubility temperature
OEGM	oligoethylene glycol methacrylate
MOEGM	methoxyoligoethylene glycol methacrylate
MAC	methacrylic acid
MOEG	methoxyoligoethylene glycols

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