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# SYNTHESIS AND APPLICATION OF ACRYLIC FILMS IN PAINT AND VARNISH MATERIALS

**Abstract.** Copolymerizations of unsaturated compounds with different ratios of acrylic monomers were synthesized. The synthesized copolymers exhibit good adhesion, flexibility and waterproofing performance may be used in the paint industry. The behavior of the copolymers of MMA and BuMA and proven by IR spectroscopy. This paper describes the synthesis, structure and properties of certain block copolymers. The practical application of scanning electron microscopy used for investigation of materials.
**Keywords**: methyl methacrylate, butyl methacrylate, copolymers, paint, films, tensile strength, elongation at break, shore hardness.

**Introduction.** Polymers based on methacrylic monomers have optical, mechanical properties, they are biocompatible, easy to functionalize, that causes a wide application in various fields ranging from coatings and ending medicine. This explains the need for controlled synthesis of polymers based on [1] of the class of monomers.

Methyl methacrylate and butyl methacrylate copolymers are widely used adhesive compositions, paint, varnish, materials for restoration work, due to its transparency, good film-forming properties, high adhesion to various substrates, increased bio and weather. Block copolymers of the structure is used to improve the compatibility of the polymer components in the solutions and the mixtures.

In this paper, the synthesis of new hydrophobic copolymers based on butyl methacrylate (BuMA) and methyl methacrylate (MMA) investigated their physicochemical and surface properties. Methyl methacrylate as a monomer contains a highly polar ester group, which confirms the hydrophilic nature while the methylene and methane groups in the main chain and side chain support the hydrophobic nature, respectively.

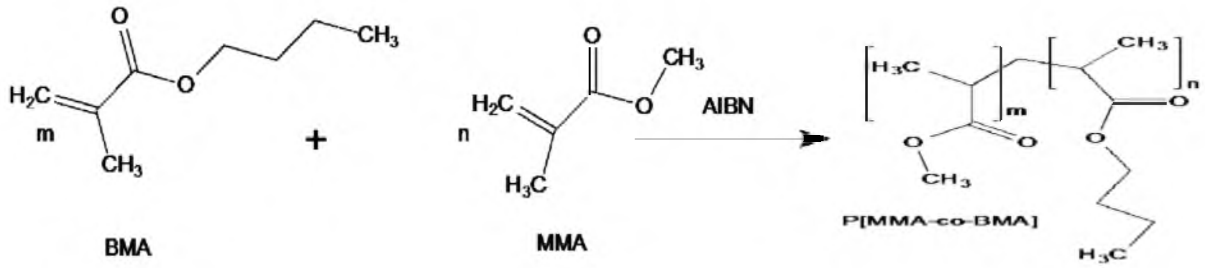
This work relates to paints and can be used to protect various surfaces in the home and in industry. Methacrylic paint composition according to the first embodiment comprises a film-forming methacrylate - acrylic organic soluble copolymer of butyl methacrylate with methyl methacrylate. This relates to the production of coatings and can be used to generate protection against various external surfaces aggressive action and giving the appearance of the corresponding products. Paints and coatings based on methacrylic copolymers such as a copolymer of butyl methacrylate and methyl methacrylate are highly weather- and light resistance [2]. This elastic coating resistant to shock, have good adhesion to the surface.

The structure of the copolymers block of is used to improve the compatibility of the polymer components in the solutions and the mixtures. The thermal behavior of the copolymers is important to predict the lifetime of materials. The aim of this work is to study of methyl methacrylate (MMA) with butyl methacrylate (BuMA) by IR spectroscopy, SEM and physical-mechanical properties.

**Experimental (Materials and apparatus).** Methyl methacrylate, butyl methacrylate, Azobisisobutyronitrile acid production company «Aldrich Chemical Co.» USA was used without further purification and other chemicals as ethanol and acetone used in this experiment. Benzoyl peroxide (BPO) (supplied by Melbourne), N,N-dimethyl-p-toluidine (DMPT) (supplied by Fluka) and hydroquinone (HQ) (supplied by Merck) were used as purchased.

**Synthesis of copolymers.** In the ground-glass prepared monomer mixture of 450g methyl methacrylate (MMA) mixed with 50g butyl methacrylate (BuMA) and a molar ratio of 90:10 after assembly of the device in a three-necked reaction flask was charged with a stirred mixture of 100 g and the reaction mixture was stirred for 10 minutes at stirring heated air bath to 800S. When the temperature reached 500C, the supply of nitrogen or argon that extends almost to the surface of the reaction mass. Gas flow rate was controlled clamp so that the bottle was held through an intermediate air bubbles. To the residue was added a mixture of the dinitrile 0,5gr azobisisobutyronitrile acid (AIBN) and the stirrer and dissolve with vigorous stirring. After dissolving the mixture and stirring the cooling slowly drop wise over 1 hr through the addition funnel administered initiator (Scheme 1).

Methyl methacrylate Poly methyl radical obtained by reacting a copolymer of methyl methacrylate with methyl methacrylate according to the following scheme:




Scheme 1 - General reaction for the synthesis of MMA/BMA copolymer

Copolymerization is carried out to syrup state. The mixture was then cooled in cold water, carefully opened, and dissolved in acetone. Copolymers transferred to a beaker dissolved in acetone, the contents of the solution was purified by precipitation in ethanol. This occurs because the copolymer is not soluble in ethanol. Then they were dried in a pre-weighed Petri dish, first in air and then vacuum circuit drier.

**Tests.** This paper was carried out by IR spectroscopy on 65 Spectrum FT-IR spectral range between 4000 – 4500 $cm^{-1}$ and a scanning electron microscope "EVO 50 XVP" (Carl Zeiss) (Wolverhampton Instruments) synthesized copolymers were filmed in different proportions. Experimental part [The tensile properties of the copolymers and terpolymers cast films were measured by using MTS 10/M tensile testing machine at a crosshead speed of 50 mm/min. An average of at least four measurements was taken, and the 1-kN load cell was used. Shore A, D hardness was measured using an indentation hardness tester according to ASTM D2240-75.]

**Results and discussion FT-IR spectra.** Infrared spectroscopy method was used to solve the problem in our research. It is one of the most informative methods for optical investigation of solids as well as allows you to record the vibrations of the structure of molecules and surface groups of atoms, as well as to observe the change in the chemical bonds in the process of adsorption of the reactants. With the help of IR - spectroscopy we can determine the structure of molecules, as in the infrared region contains the majority of the vibrational and rotational spectra of molecules.

For the determination of [3] components in the copolymers there should have a spectrum characteristic, easily identifiable intense absorption bands by IR spectroscopy (see table 1).

Table 1 - The compositions of the copolymers obtained by IR - spectroscopy

| IR - spectra, the oscillation frequency | MMA: BuMA 90:10, $cm^{-1}$ | MMA: BuMA 50:50, $cm^{-1}$ | MMA: BuMA 10:90, $cm^{-1}$ |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| $CH_2$ tension | 2930 | 2955 | 2957 |
| CH, $CH_2$ и $CH_3$ tension | – | 2874 | 2873 |
| C=O tension | 1722 | 1722 | 1722 |
| C=C bending | 1434 | 1447 | 1464 |
| $CH_3$ bending | 1386 | 1385 | 1384 |
| C-O-C tension | – | 1267 | 1267 |

*Continuation of table 1*

| 1 | 2 | 3 | 4 |
|---|---|---|---|
| C-O-C tension | 1237 | 1238 | 1239 |
| O=C–O– tension | 1142 | 1142 | 1143 |
| –C–O–C– tension | 1061 | 1063 | 1063 |
| –C–O–C– tension | – | – | 1019 |
| –C–C– tension | 985 | 964 | 945 |
| –C–C– tension | 840 | 844 | 844 |
| C–H bending | 749 | 748 | 748 |
| O–C–O shears | – | – | 517 |
| O–C–O shears | 478 | 482 | 438 |

If any, by comparing the value of this peak with the gauge dependence of the peak intensity - concentration of the component, it is possible to determine the content of the copolymer. The copolymers synthesized based on MMA: BuMA were recorded IR spectra (figure 1).

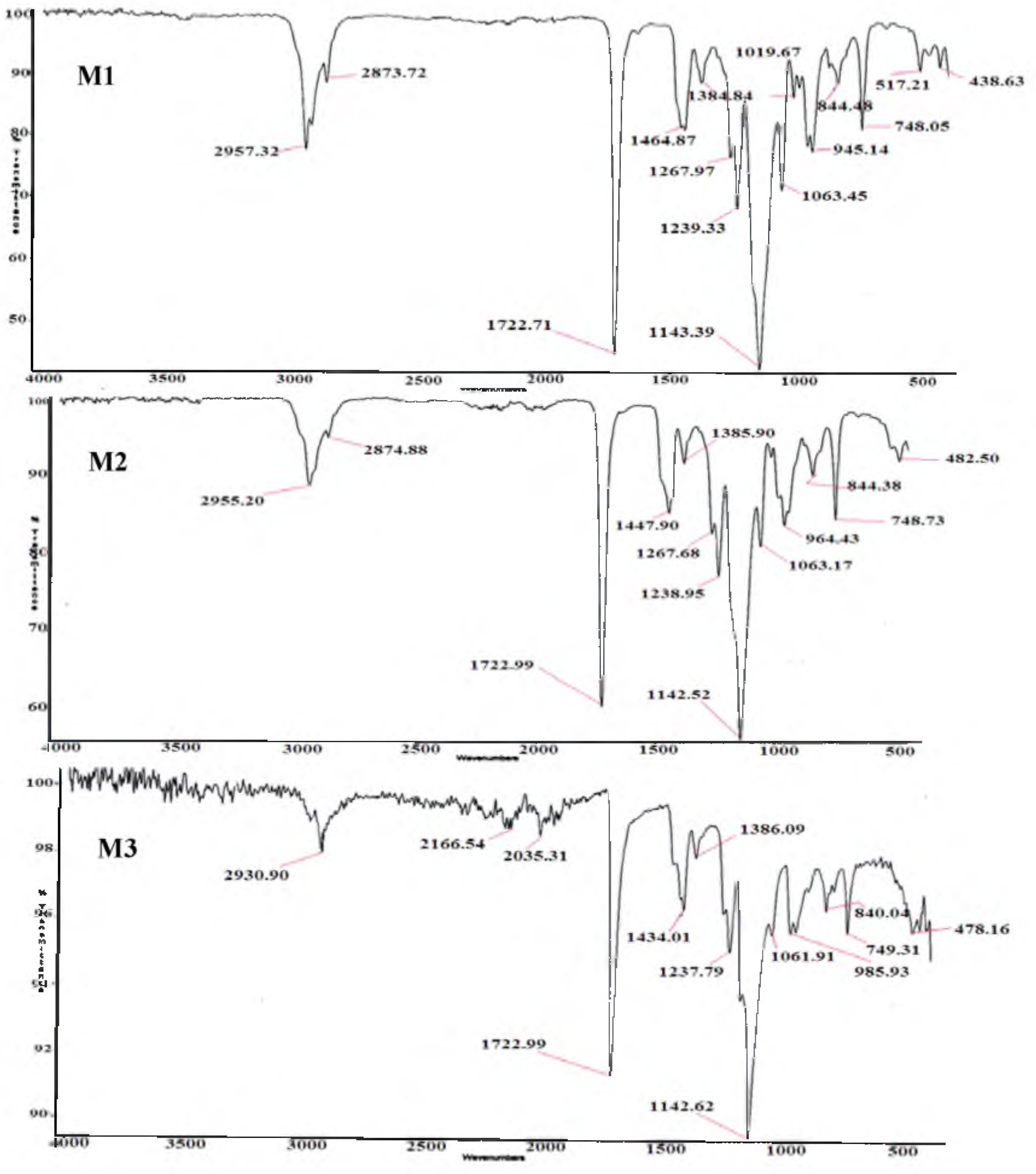



Figure 1 - IR spectra of copolymers based on MMA: BuMA

Composition [MMA]: [BuMA] mol.%: 90:10 (M1), 50:50 (M2), 10:90 (M3)

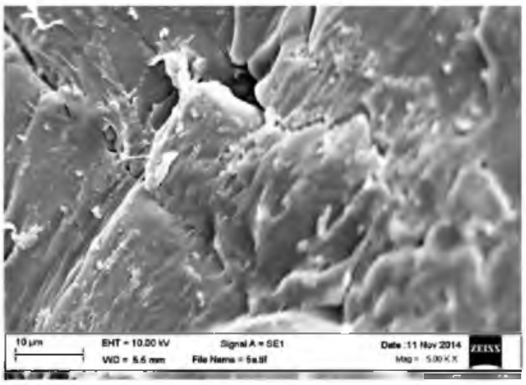
The spectra of copolymers based on MMA: BuMA are characterized by an absorption band in the band range 2874cm$^{-1}$ – 2873cm$^{-1}$ can be attributed to the stretching vibrations of aliphatic and by the presence of methyl groups CH, $CH_2$ and $CH_3$ bonds.

Meanwhile, the signal can be seen in 2957cm$^{-1}$ – 2930cm$^{-1}$ is the result sp$^3$ carbonyl monomer butyl methacrylate and most intensive absorption bands esters [4] are in 1723cm$^{-1}$ – 1722cm$^{-1}$ stretching vibrations of unsaturated carbonyl groups C=O.

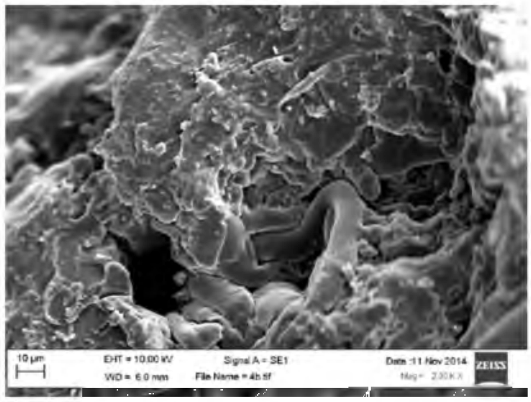
Absorption band at 1434 cm$^{-1}$ – 1464 cm$^{-1}$ monomer spectrum [5] due to the presence of a double bond C = C stretching vibrations and vibrations = CH - groups, with absorption bands in the region 1267cm$^{-1}$ - 1237cm$^{-1}$, 1142cm$^{-1}$ -1143cm$^{-1}$ и 1061cm$^{-1}$ - 1063cm$^{-1}$ -C-O-C- ester group, indicating the formation of a copolymer of MMA: BuMA. In the 1019 cm$^{-1}$ there is a series of four absorption bands, which together with the strip in 790 см$^{-1}$ are characteristic of methacrylate structure. Intensive pass band frequency range 1019 cm$^{-1}$ - 790 cm$^{-1}$ and 2957cm$^{-1}$ – 2930cm$^{-1}$ traced in the spectra of all the samples. The IR spectra of different ratios of copolymers were observed changes in the intensity of transmission bands of carbonyl functional groups in all the samples, which allowed us to estimate the degree of polymerization of MMA and BuMA [6]. The composition of the copolymers MMA: BuMA identified by IR - spectra, which are stretching vibrations of the respective functional groups. The intensity of the bands corresponding to the characteristic depends on the composition of the starting monomeric mixture. It is clearly seen that the copolymer consists of units of different amounts of methyl methacrylate and butyl methacrylate [7].

**Scanning electron microscope (SEM).** Scanning electron microscopy (SEM) to analyze the materials have been widely used to solve specific scientific and technological problems due to their high information content and reliability of the results of the study. The physical and mechanical properties of the materials are determined by their microstructure which depends on the electronic structure, chemical composition, and their fabrication technology [8].

**1. MMA:BuMA 10:90**



**2. MMA:BuMA 50:50**



**3. MMA:BuMA 90:10**

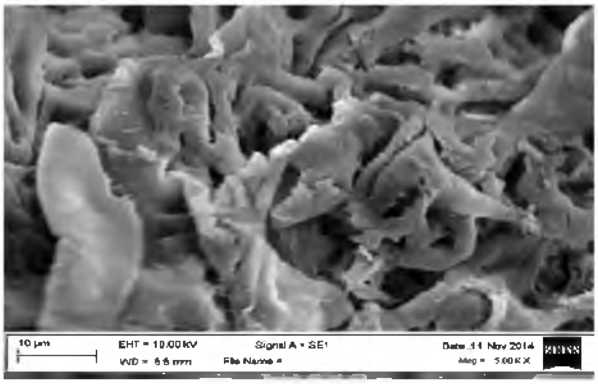


Figure 2 - Images of copolymers based on MMA: BuMA obtained by the SEM method

Different ratios of copolymers were evaluated by scanning electron microscopy. From figure 2 the copolymers of MMA: BuMA are porous, and swelling due to a large capacity of the copolymers.

SEM images showed copolymers, species such as a structure that provides a large surface area for improved adsorption. Structure existed small pores and is indicated for the better solubility. For the copolymerization reaction of MMA: BuMA in different proportions structure was porous and irregular look strong and changed the structure is not uniform.

**Filler and fine aggregate.** In this work, fine - dispersed calcium carbonate was used as a filler in paint products, and fine quartz sand was used as a fine filler. Before using these fillers, they were dried at 105 ° C for 48 hours to remove moisture at least 0.1%. Table 2 presents the characteristics of the filler and the fine aggregate [9].

Table 2 - Properties of filler and fine aggregate

| Filler or fine aggregate | Size (μm) | Density (20 °C, g/cm$^3$) | Water content (%) | Organic impurities |
|---|---|---|---|---|
| Calcium carbonate | <2.5 | 2.7 | <0.1 | Nil |
| Silica sand | 106-121 | 2.61 | <0.1 | Nil |

**Preparation of copolymer syrups.** Copolymer syrup was produced by dissolving copolymer (MMA/BuMA) and BPO into MMA monomer at normal temperature (25$^0$C). Then, a liquid component was produced using MMA monomer, DMPT and HQ. BPO and DMPT were added at 1.5 and 0.75 parts per hundred (pph) to syrup to act as initiator and accelerator, respectively. HQ was added in the syrup as an inhibitor. Paraffin wax was as added 1% wt. of syrups. This copolymer syrup was then placed into the liquid component mixed with ratio 10/90 % wt/wt to maintain the mixing ratio at 100% as shown in table 3.

Table 3 - Formulation of copolymer syrup for acrylic paint

| Group | Syrups | Copolymer (Powder, gm) | MMA (Liquid, gm) |
|---|---|---|---|
| Group 1 | Syp10/M1 | 10 | 90 |
| | Syp10/M2 | 10 | 90 |
| | Syp10/M3 | 10 | 90 |

Film preparation. Films were prepared by casting the acryl syrups on leveled surfaces and allowing them to dry at room temperature for 3 hours. The films were stored in a desiccator at room temperature for further characterization and measurements [10-11].

**Mechanical Properties of polymer films.** The mechanical properties of the copolymer films with respect to the amount of MMA and BuMA are shown in figures 3-5.

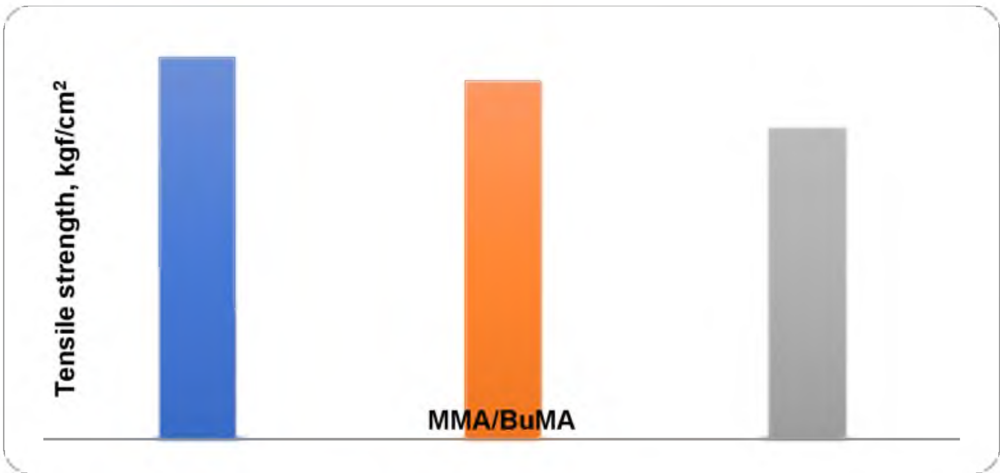



Figure 3 - Tensile strength of copolymer films as a function of MMA/BuMA content

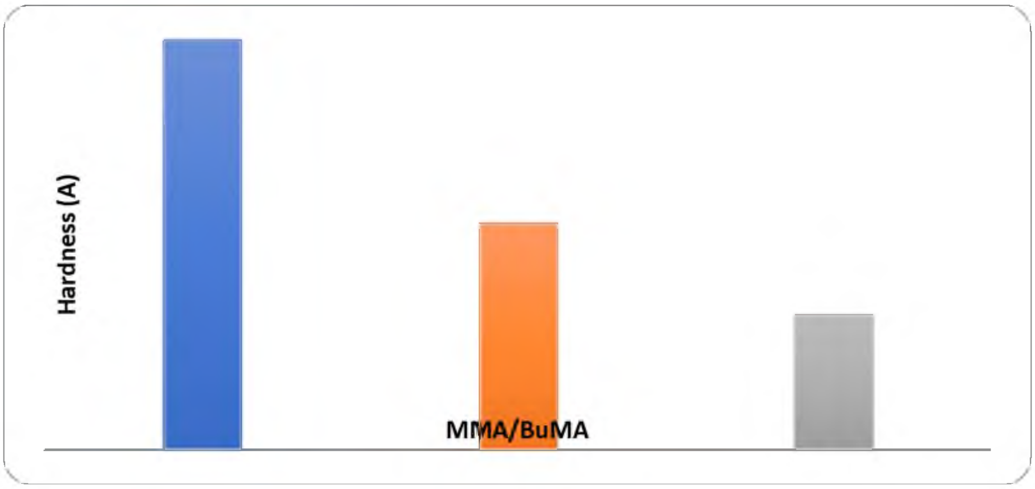



Figure 4 - Hardness of copolymer films as a function of MMA/BuMA content

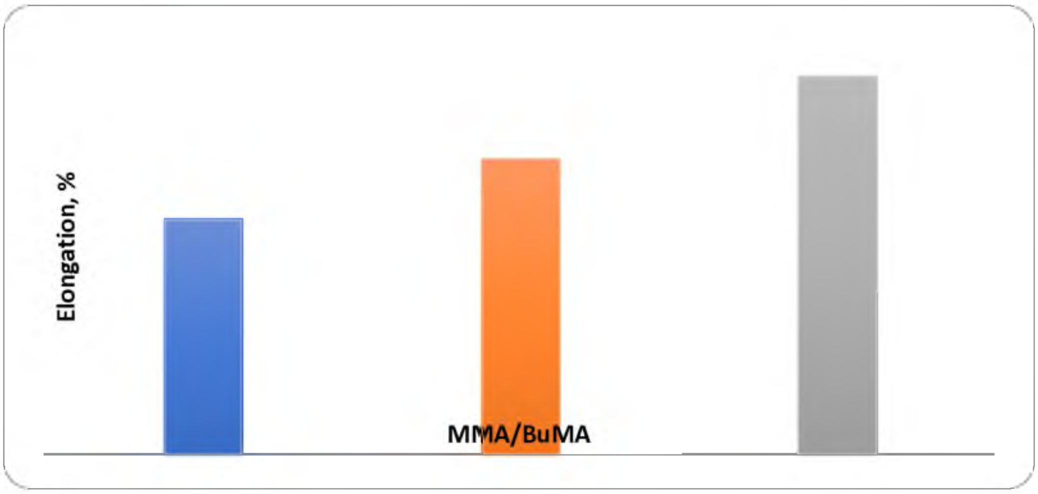



Figure 5 - Elongation at break of copolymer films as a function of MMA/BuMA content

It can be seen that tensile strength increased with increasing amounts of MMA in the copolymer (figure 1). MMA/BuMA (90/10) showed the largest tensile compared with MMA/BuMA (50/50). This is presumably due to the increased hard segment contents (MMA) in the copolymer film. The elongation at break was increased with increasing amount of BuMA as shown in figure 2. It may be due to the increased in chain flexibility (BuMA). Similarly, hardness shore (A) was found to increase with increasing of MMA content in the copolymer films as shown in figure 3 [12].

**Conclusion.** We have obtained a new synthetic copolymers based on methyl methacrylate (MMA) and butyl methacrylate (BuMA), with use of the dinitrile as an initiator of Azobisisobutyronitrile acid (AIBN).

The result of research, the molecular interaction with the MMA: BuMA liquid phase methacrylic copolymer dispersions, which had a significant impact on the protective properties of the coatings. Polyampholytic properties of cross linked copolymers of MMA: BuMA, partly due to the presence of unsaturated groups and carboxyl methacrylate structure characteristic for which presence confirmed also that by decreasing the content of the hydrophobic monomer MMA copolymers are obtained which are insoluble in water. Ionization of the carboxyl groups is a major contributor to the process of swelling and aspirations to the distribution of solvent throughout the volume of the polymer network.

Studies have confirmed the effectiveness of dispersion paints using MMA: BuMA staff 50:50 mole. %, can improve water repellency, resilient flooring, as well as to reduce the drying time of coatings to touch on various mineral substrates [13].

Study waterproofing properties of the films showed that the higher content of the copolymer composed of MMA contributes to obtaining films with lower adsorption capacity and hence higher waterproofing properties.

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**АКРИЛ ҮЛДІРЛЕРІН СИНТЕЗДЕУ ЖӘНЕ ЛАК-БОЯУ МАТЕРИАЛДАРЫНА ҚОЛДАНУ**

**Аннотация.** Берілген мақалада метилметакрилат (ММА) пен бутилметакрилат (БМА) және тігуші агент АИБН инициаторын қосу арқылы жаңа полимерлерді синтездеп алу және олардың негізгі заңдылықтары қарастырылды. Осыған байланысты сыр-бояу материалдары саласындағы өзекті мәселенің бірі – өнеркәсіпте қолдану үшін қасиеттері жақсартылған, жылдам кебетін, экологиялық таза, сольвентсіз бояулар алу. Әлемде сольвентсіз бояулар ретінде эпоксидті және полиуретанды бояулар ұсынылған. Акрил бояуларының құрамында судың және органикалық еріткіштердің болмауы сольвентсіз бояулар деп аталатын, құрамында ұшпа органикалық қосылыстар өте төмен болатын бояуларды синтездеп алуға және физика-механикалық қасиеттері мен экологиялық сипаты жағынан таза, жақсы өнім алуға мүмкіндік береді.

Зерттеу тақырыбының өзектілігі. Қазақстанның құрлықтық климат түрінің тез өзгергіштігіне және күрделі гидрогеологиялық жағдайына байланысты, гимараттар мен құрылыстарды гидроизоляциялық қорғау маңызды болып саналады. Осыған байланысты, Қазақстанда бояу жабындыларын дайындау, олармен қамту және осындай өндірісті дамыту – өзекті мәселелердің бірі.

Өнеркәсіп әрқашан өте жоғары эксплуатациялық қасиеттерге ие жаңа сыр-бояу материалдарын өндіруге талпынады. Акрильді сыр-бояу материалдары (СБМ) бірқатар баға жетпес қасиеттерге ие, оның ішінде атмосфераға және жарыққа тұрақтылығы және су мен сілтілерге төзімділігі бар.

**Жұмыс мақсаты** – әртүрлі мономерлермен қанықпаған метакрильді шайырлар – метил метакрилаты негізінде жаңа сополимерлер алу. Жаңа сополимерлер негізінде метилметакрилат пен бутилметакрилат синтездеу және оның физика-химиялық қасиеттерін зерттеу. Гидроизоляциялық қасиеттері бар акрилат бояуларын қолданудағы полимерлі акрилаттар негізін алудың технологиясын құру.

Әртүрлі қатынастағы жаңа сополимерлер – ММА және БМА синтезделді, сондай-ақ физика-химиялық қасиеттері зерттелді. Үлдірлер, сірнелер дайындау үшін сополимер қолданылды, олардың физика-механикалық қасиеттері зерттелді және бояудың құрамына әсері қарастырылды.

Негізгі нәтижелері:

– алғаш рет ММА-БМА негізінде сополимерлер бастапқы қоспадағы мономердің әртүрлі қатынастағы массада бос радикалды сополимерлену әдісі арқылы синтезделді;

– алынған сополимер ИҚ спектроскопия әдісімен сипатталды. Осы алынған мәліметтер негізінде, сополимерлер құрылымы ұсынылды;

– алынған сополимердің беткі қабатының морфологиясын зерттеу үшін сканерлеуші электрондық микроскоп әдісі қолданылды;

– алынған сополимерлердің үлгілері СЭМ әдісімен талдау арқылы мономердің әртүрлі қатынастарына байланысты, беткі қабатының морфологиясында айтарлықтай айырмашылықтар бар екенін көрсетеді. Бутил метакрилатымен метил метакрилат негізінде жаңа сополимерлердің физика-химиялық қасиеттерін синтездеу және зерттеу. Бутил метакрилатымен метил метакрилат негізінде жаңа сополимерлердің физика-химиялық қасиеттерін синтездеу және зерттеу. Мономердің әртүрлі қатынастары полимер бөлшектерінің морфологиясына әсер ететіні зерттелді;

– синтезделген сополимерлер үлдірлер, акрилат сірнелері, бояу жабындыларын алуда қоданылды;

– акрилат бояуларын алу үшін катализаторлар, толтырғыштар қолданылды. Катализаторлар айтарлықтай жабындарлардың кептіру уақытын қысқартатыны, ал толтырғыштар, бояу кепкен кезде, ондағы полимердің көп отырмауына себепші болатыны, әртүрлі ортаның әсеріне тұрақтылығын арттыратыны, полимерлік композиттік материалдардың механикалық қасиеттерін жақсартатыны және полимерлік материалдардың өзіндік құнын төмендететіні анықталды;

– заманауи физика-механикалық зерттеу әдістері көмегімен полимер үлдірлерінің және акрильді сірнелерінің физика-механикалық қасиеттері анықталды, оның ішінде созылу беріктілігі, ажырау кезіндегі салыстырмалы ұзаруы, Шор тәсілі бойынша қаттылығы зерттелді.

**Түйін сөздер:** метилметакрилат, бутилметакрилат, сополимерлер, бояу, үлдірлер, созылу беріктілігі, ажырау кезіндегі салыстырмалы ұзаруы, Шор тәсілі бойынша қаттылығы.

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## СИНТЕЗ И ПРИМЕНЕНИЕ АКРИЛОВЫХ ПЛЕНОК В ЛАКОКРАСОЧНЫХ МАТЕРИАЛАХ

**Аннотация.** Данная статья посвящена синтезу новых полимеров, установлению основных закономерностей получения сополимеров на основе метилметакрилата (ММА) с бутилметакрилатом (БМА) с 2,2-азо-бис-изобутиронитрил (АИБН). В связи с этим, решение задачи получения экологически безопасных быстросохнущих красок (не содержащие органические растворители) с улучшенными эксплуатационными характеристиками промышленного назначения является актуальной в области создания лакокрасочных материалов. В мире безсольвентные краски в основном представлены эпоксидными и полиуретановыми лакокрасочными покрытями. Предлагается создание акрилатных лакокрасочных материалов, не содержащих органические и водные растворители, так называемые безсольвентные краски с очень низким содержанием летучих органических соединений, что позволяет сочетать отличные физико-механические и эксплуатационные характеристики и экологичность.

В Казахстане в связи с резко континентальным типом климата и сложной гидрогеологической обстановкой, гидроизоляционная защита зданий и сооружений является необходимой мерой. В связи с этим разработка гидроизоляционных лакокрасочных покрытий является актуальным.

Промышленность непрерывно стремится производить новые лакокрасочные материалы с лучшими эксплуатационными свойствами. Акриловые лакокрасочные материалы обладают рядом ценных свойств, в том числе атмосфер- и светостойкостью, устойчивостью к воздействию воды и щелочей.

**Целью работы** является создание новых сополимеров на основе ненасыщенных метакриловых смол – метилметакрилата с различными мономерами. Синтезирование и исследование физико-химических свойств новых сополимеров на основе метилметакрилата с бутилметакрилатом. Получение полимерной акрилатной основы для применения в акрилатных красках с гидроизоляционными свойствами.

Синтезирование новых полимерных связующих и реагентов при различных соотношениях мономеров ММА-БМА и исследование их физико-химических свойств. Сополимеры были использованы для приготовления пленок, сиропов, затем были изучены их физико-механические свойства и влияние их на свойства красок.

Основные результаты:

- Впервые получены сополимеры на основе ММА и БМА методом радикальной полимеризации в массе с различным содержанием мономеров в исходной смеси.
- Полученные сополимеры охарактеризованы методами ИК-спектроскопии. На основании полученных данных предложена структура полимеров.
- Для исследования морфологии поверхности полученных сополимеров был использован метод сканирующей электронной микроскопии (СЭМ).
- СЭМ-анализ образцов сополимеров четко показывают, что существуют заметные различия в количестве мономеров в зависимости от стадии эксперимента. Разные составы мономеров влияет на морфологию частиц полимера.
- Синтезированные новые сополимерные пленки, акрилатные сиропы можно использовать в лакокрасочных покрытиях.
- Для получения акрилатных красок были использованы катализаторы и наполнители. Выявлено, что катализаторы значительно сокращают время высыхания лакокрасочного покрытия, когда краска высыхает, то наполнитель не дает полимеру осаждаться, повышают устойчивость к воздействию различной среды, улучшают механические свойства полимерных композиционных материалов и снижают стоимость полимерных материалов.
- С помощью современных физико-механических методов были определены физико-механические свойства акриловых сиропов и полимерных пленок, в том числе прочность на растяжение, относительное удлинение при разрыве, твердость по Шору.

**Ключевые слова:** метилметакрилат, бутилметакрилат, сополимеры, краска, пленка, прочность на растяжение, относительное удлинение при разрыве, твердость по Шору.

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