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SYNTHESIS AND RESEARCH OF COPOLYMERS ON THE BASIS OF METHYL METHACRYLATE AND THEIR APPLICATION IN PAINT AND VARNISH COVERINGS

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ABSTRACT

Copolymerizations of unsaturated compounds with different ratios of methacrylic 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 BMA 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. By using the applications as differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) shows that the copolymer is resistant to heat and aging temperature ranges set methacrylic copolymers. As a result of research analysis TGA curve revealed that the mass of solid residue is higher in samples with a high content of methacrylate monomers. It was found that the thermal degradation of butyl methacrylate copolymers studied by the mechanism of copolymerization and decomposition side butyl substituent.

Key words: Methyl methacrylate, Butyl methacrylate, Copolymers, Paint, Thermal degradation.

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.

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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.

The synthesis and study of new water-repellent polymer, name as a combination of monomer units of different nature, different hydrophobic balance of considerable interest, due to the continuous expansion of their practical application areas.

In this paper, the synthesis of new hydrophobic copolymers based on butyl methacrylate (BMA) 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[2].

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[3]. 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 (BMA) by IR spectroscopy, SEM, thermo gravimetric analysis (TGA) and differential scanning (DSC) and discuss the results.

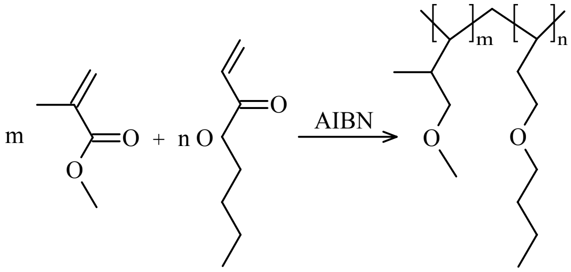
EXPERIMENTAL

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.

Synthesis of copolymers

Methyl methacrylate Poly methyl radical obtained by reacting a copolymer of methyl methacrylate with methyl methacrylate according to the following Scheme 1:



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

In the ground-glass prepared monomer mixture of 450 g methyl methacrylate (MMA) mixed with 50 g butyl methacrylate (BMA) 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 mins at stirring heated air bath to 800S. When the temperature reached 500°C, 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 0.5 g 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)**.

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 range between 4000-450 cm^{-1} and a scanning electron microscope "EVO 50 XVP" (Carl Zeiss) (Wolverhampton Instruments) synthesized copolymers were filmed in different proportions. DSC was carried out using a Perkin-Elmer Differential Scanning Calorimeter (DSC). The samples were tested under N_2 atmosphere at a scanning rate ± 20°C min^{-1}. The thermal gravimetric analysis (TGA) was conducted on a TGA/SDTA 851e under nitrogen flow. The heating rate was 20°C/min. For SEM, the samples were gold sputtered and observed at an accelerating voltage of 10 kV, in order to avoid membrane degradation.

RESULTS AND DISCUSSION

Characterization of copolymers

Copolymers of MMA: BMA having different compositions were prepared by using AIBN as a free-radical initiator in 1-4 dioxane solutions, under nitrogen atmosphere and degree of temperature 80^{o}C.

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 to 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 components[4] in the copolymers must have a spectrum characteristic, easily identifiable intense absorption bands by IR spectroscopy. 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 (Table 1). The copolymers synthesized based on MMA: BMA were recorded IR spectra (Fig. 1).

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

IR-Spectra, the oscillation frequency	MMA: BMA 90:10 (cm^{-1})	MMA: BMA 70:30 (cm^{-1})	MMA: BMA 50:50 (cm^{-1})	MMA: BMA 30:70 (cm^{-1})	MMA: BMA 10:90 (cm^{-1})
CH_2 tension	2930	2949	2955	2956	2957
CH, CH_2 and CH_3 tens.	–	–	2874	2873	2873
C=O tension	1722	1723	1722	1722	1722
C=C bending	1434	1447	1447	1448	1464
CH_3 bending	1386	1386	1385	1385	1384
C-O-C tension	–	1268	1267	1268	1267
C-O-C tension	1237	1238	1238	1239	1239

Cont…

IR-Spectra, the oscillation frequency	MMA: BMA 90:10 (cm^{-1})	MMA: BMA 70:30 (cm^{-1})	MMA: BMA 50:50 (cm^{-1})	MMA: BMA 30:70 (cm^{-1})	MMA: BMA 10:90 (cm^{-1})
O=C–O–tension	1142	1142	1142	1143	1143
–C–O–C–tension	1061	1062	1063	1063	1063
–C–O–C–tension	–	–	–	1019	1019
–C–C–tension	985	965	964	964	945
–C–C– tension	840	842	844	845	844
C–H bending	749	749	748	748	748
O–C–O shears	–	–	–	517	517
O–C–O shears	478	480	482	439	438

The spectra of copolymers based on MMA: BMA are characterized by an absorption band in the band range 2874 cm^{-1} – 2873 cm^{-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 2957 cm^{-1} – 2930 cm^{-1} is the result sp^3 carbonyl monomer butyl methacrylate and most intensive absorption bands esters[5] are in 1723 cm^{-1} – 1722 cm^{-1} stretching vibrations of unsaturated carbonyl groups C=O.

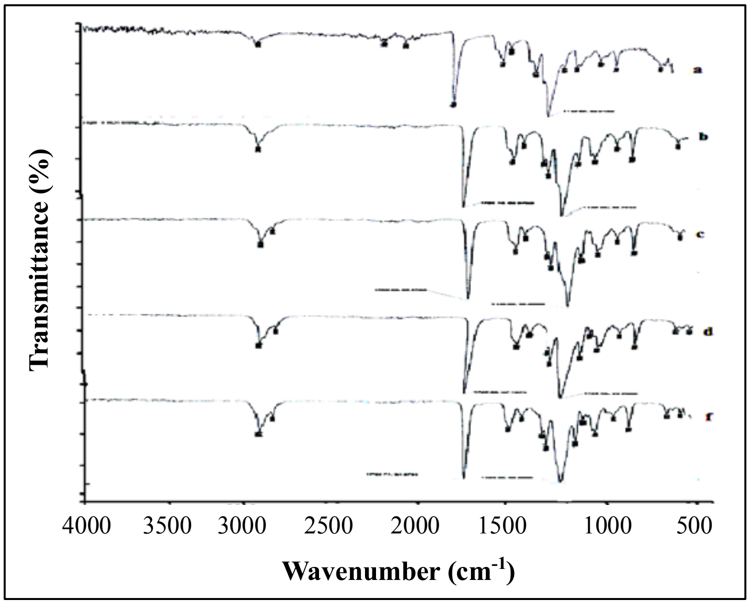


Fig. 1: IR spectra of copolymers based on MMA: BMA Composition [MMA]: [BMA] mol.%: 90:10 (a), 70:30 (b), 50:50 (c), 30:70 (d), 10:90 (f)

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 1267 cm^{-1} – 1237 cm^{-1}, 1142 cm^{-1} – 1143 cm^{-1} и 1061 cm^{-1} – 1063 cm^{-1} –C–O–C– ester group, indicating the formation of a copolymer of MMA: BMA. In the 1019 cm^{-1} there is a series of four absorption bands, which together with the strip in 790 cm^{-1} are characteristic of methacrylate structure. Intensive pass band frequency range 1019 cm^{-1} – 790 cm^{-1} and 2957 cm^{-1} – 2930 cm^{-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 BMA[7]. The composition of the copolymers MMA: BMA 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[8].

Thermo gravimetric analysis (TGA)

To study the thermo physical properties of the synthesized copolymers and the starting reagents, studying these thermal properties by thermo gravimetric analysis (TGA)[9,10]. TGA results are presented in Table 2.

Table 2: Thermal analysis data MMA: BMA

Copolymer MMA: BMA	Temperature (°C) for expansion		
	T_H	T_{max}	T_K
90:10 70:30 50:50 30:70 10:90	325	425	450

T_H – Initial decomposition temperature.
T_{max} – Maximum rate of temperature for weight loss.
T_K – The final temperature of the decomposition.

In a first step (20...280°C) going destruction of oxygen-containing groups: the carbonyl and ether, which is accompanied by mass loss of the sample 12, 5...13, 6% (Table 2). Intensive thermal destruction corresponds to the interval 280-400°C, the loss of mass is 67, 5...68, 4%.

Fig. 2 shows the TGA-curves copolymer MMA: BMA, weight loss of the copolymer observed at 250°C, this is due to the loss and removal of volatile impurities. A loss of mass 10% observed at 225ºC. The rate of thermal-oxidative decomposition of the copolymer increases markedly with temperature 425° C. The endothermic effect at 325°C, in which 450ºC becomes exothermic peak showing the thermal oxidative degradation of the polymer[11,12]. Over 450ºC mass is removed and the remaining 20% of solid residue (Fig. 2). The total drop weight is 80%.

The glass transition temperature of copolymers obtained by radical copolymerization in the presence of a dinitrile, Azobisisobutyronitrile acid, is higher than for the homopolymers, which indicates the formation of block copolymers. To analyze the properties of the copolymers are selected in the two monomers, which were used in the copolymerization reactions of methyl methacrylate (MMA), butyl methacrylate (BMA).

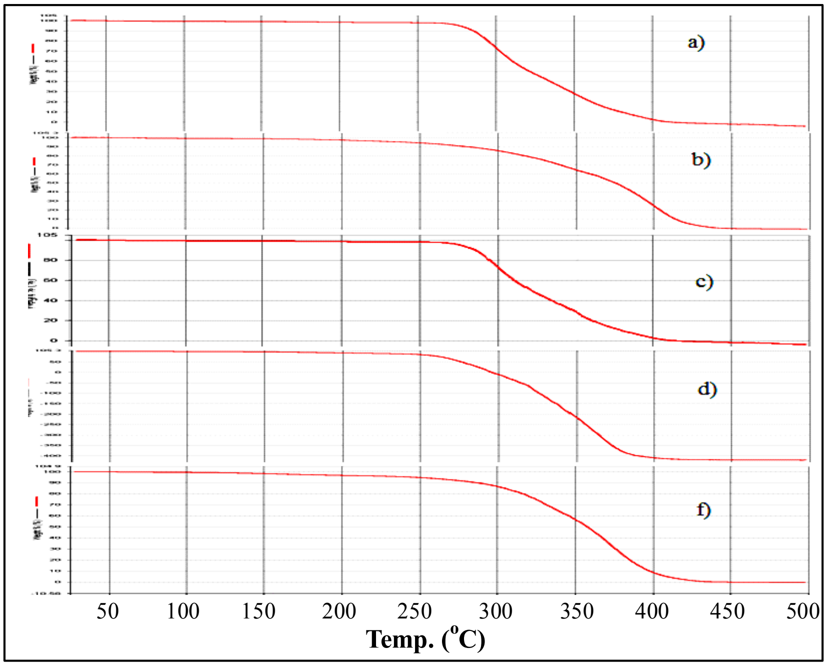


Fig. 2: The mass loss versus the temperature of copolymer. Composition MMA: BMA 90:10 (a), 70:30 (b), 50:50 (c), 30:70 (d), 10:90 (f)

Copolymers based on these compounds are completely amorphous high molecular weight substances, which are easily formed in the block and suitable for thermal characteristics of study[13].

The glass transition temperature of copolymers T_C calculated by the following equations.

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

Where T_C – The glass transition temperature of the copolymer, T_{g1} and T_{g2} – two glass transition temperatures of homopolymers and W_1, и W_2 – weight of the two repeat units in the copolymer (Table 3).

Table 3: To calculate the temperature copolymer T_C, MMA: BMA depend on the Fox equation

Copolymer MMA: BMA	T_C
90:10	94.34
70:30	74.74
50:50	57.12
30:70	42.10
10:90	34.15

In general, there is good agreement between the calculated and experimental values of T_C. When using the experimental values of T_C for homo polymers and substituting them into the equation in most cases corresponds to the calculation experiment is somewhat improved. The calculated values of the characteristics defined for the ideal polymer system.

Differential scanning calorimetry (DSC)

This assumption confirmed by the results of differential scanning calorimetry. DSC curves obtained are shown in Fig. 3 and in Table 4.

Table 4: Differential scanning calorimetry copolymer of MMA: BMA

Copolymer MMA: BMA	T_C
90:10	98.40
70:30	71.30
50:50	63.10
30:70	58.09
	43.30

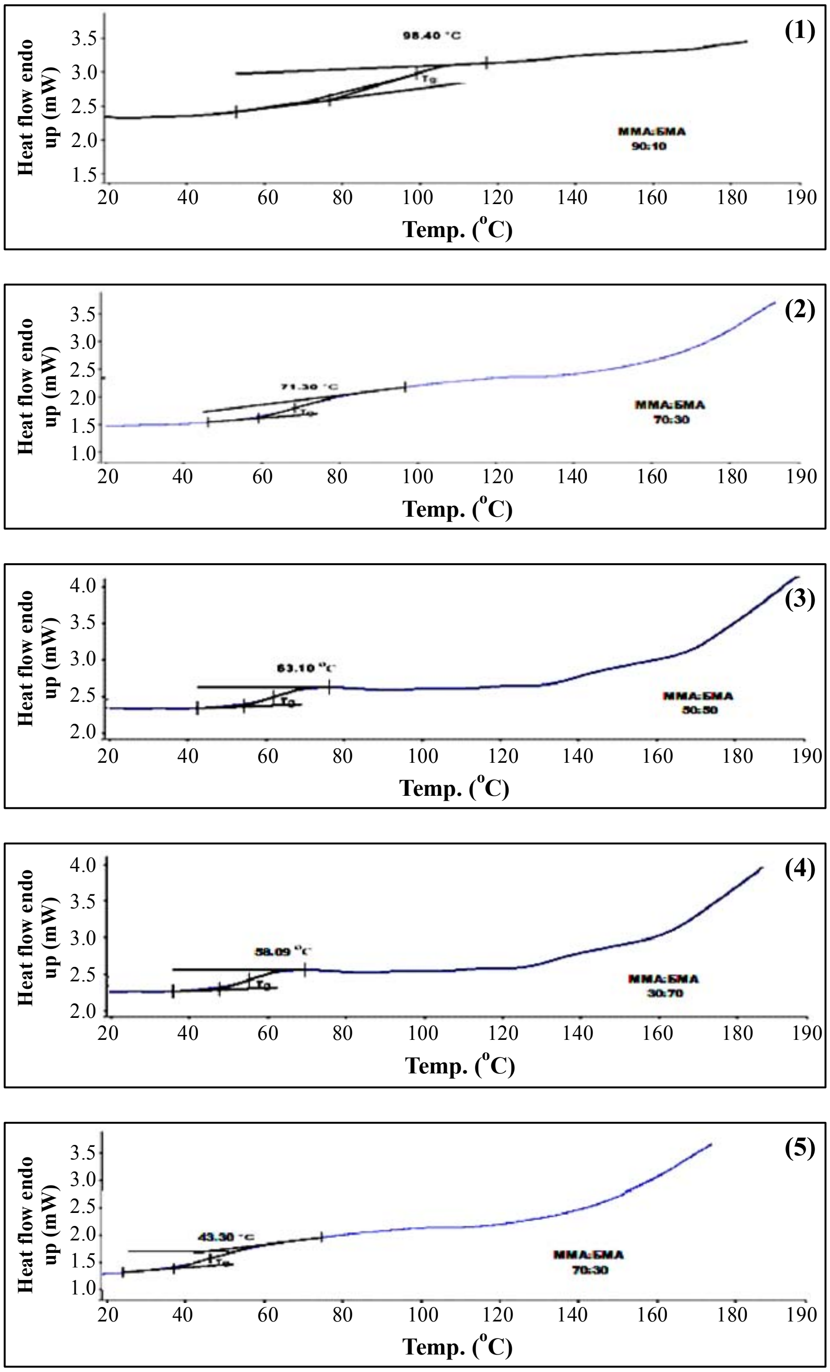


Fig. 3: DSC curves for polymers MMA: BMA; (1) 90:10, (2) 70:30, (3) 50:50, (4) 30:70, (5) 10:90

Fig. 3 shows a differential scanning calorimetry (DSC) of the studied samples. Seen from the curves that the samples undergo transformations, there is no monotony and regularity of change DSK - signal with increasing temperature. Therefore, we can assume that the melting copolymers requires energy, which is reflected by a sharp decrease in the DSC signal. From the DSC data, it follows that the curve of the copolymer of MMA: BMA has an endothermic peak at 98^0C, which corresponds to the glass transition temperature. Then, from 100 to 200^0C in all systems, probably no chemical reaction occurs, and DSC - signal changes due to the removal of volatile impurities. The results obtained are in good agreement with the known views on the mechanism of thermal transformations of methacrylates[14], DSC and TGA data are in good agreement. Based on TGA and DSC data expansion process systems investigated under the temperature can be divided into three areas:

I - 10 to 250^0C - an area resistant to aging;

II - from 325 to 425^0C - region of rapid aging of the destruction of the copolymer;

III - above 450^0C - the area of destruction.

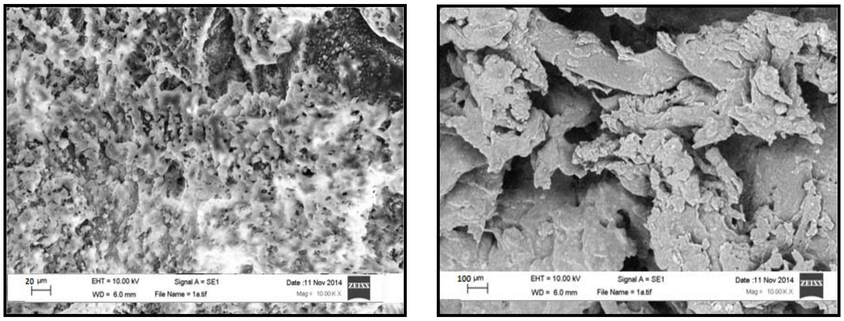
Decomposition MMA: BMA is mainly on the mechanism of copolymerization, and accompanied by the destruction of lateral substituents of the methacrylate units in the copolymer can be expanded through the destruction of the lateral ester groups.

Destructive flow starts at 250^0C. In which the endothermic peak at 325^0C indicates the gap of methacrylate linkages and an exothermic peak area at 450^0C – resulted by oxidation. Thus, copolymers based on MMA: BMA possess high thermal stability and are more resistant to thermal degradation.

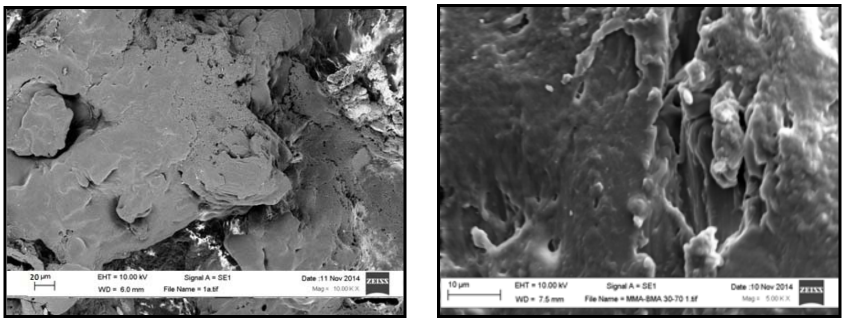
Scanning electron microscope (SEM)

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[15].

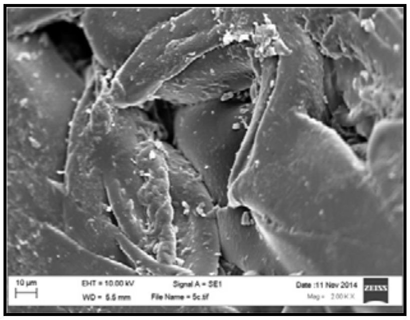
Different ratios of copolymers were evaluated by scanning electron microscopy. From Fig. 4, the copolymers of MMA: BMA are porous, and swelling due to a large capacity of the copolymers. SEM images showed copolymers, species such as a structure that provides a large surface area for improved adsorption. Structure existed small pores and is indicated for the better solubility. For the copolymerization reaction of MMA: BMA in different proportions structure was porous and irregular look strong and changed the structure is not uniform.



(1). MMA:BMA 90:10 **(2). MMA:BMA 70:30**



(3). MMA:BMA 50:50 **(4). MMA:BMA 30:70**



(5). MMA:BMA 10:90

Fig. 4: Images of copolymers based on MMA: BMA obtained by the SEM method Composition [MMA]: [BMA] mol.%: (1) 90:10, (2) 70:30, (3) 50:50, (4) 30:70, (5) 10:90

Thus the possibilities for scanning electron microscopy, is the method of study the microstructure of materials.

CONCLUSION

We have obtained a new synthetic copolymers based on methyl methacrylate (MMA) and butyl methacrylate (BMA), with use of the dinitrile as an initiator of Azobisisobutyronitrile acid (AIBN). All electron-microscopic studies presented in this work, carried out in the laboratory of electron microscopy in the training centers for communities "Wolverhampton University (UK)".

The result of research, the molecular interaction with the BMA: MMA 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: BMA, 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.

Hence, the obtained results show the important role of the structure of the polymer melt at a specific temperature or heat resistance intensive degradation of polymeric materials and other characteristics of the TGA. Heat resistance, as well as a certain temperature loss of the samples depends on the chemical structure of polymers, expressed in terms of the glass transition temperature, the compactness of the macromolecular coil in the copolymer, which is also determined by the structure of the coil. The role of the latter in determining the thermal resistance decreases as the glass transition temperature of the copolymer. It was found that the thermal degradation of butyl methacrylate copolymers studied by the mechanism of copolymerization and decomposition side butyl substituent.

Studies have confirmed the effectiveness of dispersion paints using MMA: BMA 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.

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