THE EFFECT OF METHYL METHACRYLATE ON THE PROPERTIES OF SYNTHESIZED ACRYLATE EMULSIONS

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Abstract: The effect of methyl methacrylate (MMA) addition on the properties of synthesized acrylate emulsions based on butyl acrylate (BA) and 2-ethylhexyl acrylate (EHA) was investigated. The samples were synthesized by addition of MMA in copolymer structure, ranging from 10 to 50 wt% of the total mass of BA and EHA. Fourier transformation infrared (FTIR) spectroscopy was used to analyze the molecular structure of synthesized acrylate emulsions and the results confirmed that a quantitative polymerization reaction occurred. The analysis of thermal properties showed that the addition of methyl methacrylate increases the glass transition temperature of the acrylate films obtained by drying the synthesized emulsions. The tensile strength and elongation at break increased proportionally with the increase of the content of MMA in the synthesized samples. Since the obtained acrylate materials can be used to improve the water impermeability of paper and other materials, the obtained emulsion was applied in a thin layer on a sheet of paper and the resistance of the paper to water and oil was investigated. The results showed that all emulsions were impermeable both to water and oil.

Keywords: emulsion polymerization, acrylic coatings, polymer synthesis, methyl methacrylate.

1. INTRODUCTION

The materials we use in our everyday life are exposed to various harmful effects of the natural environment, the commonest of which are corrosion, electromagnetic radiation (particularly sunlight), cracks, fractures, blistering, etc. Material deterioration is prevented or retarded by surface treatment, having in mind that harmful effects and processes mainly begin to develop on the surface of the material. Polymer coatings prove to be an effective in protection against these harmful effects [1].

Coatings usually consist of one or more types of precursor, which either have a simple structure or they are complex pre-polymers, as is much more often the case. The synthesis of a polymer film by precursor cross-linking is a complex process. Understanding the kinetics and mechanism of the formation of a polymer network and its structure, is of essential importance because these factors ultimately determine the properties of the coating and, consequently, the range of its application [2].

There have been significant advances in the findings on coatings in the last couple of decades.

Today paints and lacquers are everywhere around us, covering buildings, automobiles, planes, solar cells, metals, plastics, etc. [3]. Lately, the focus has been on the development of coatings with minimum polluting effects, i.e. the coatings should contain the least possible amount of organic solvents, while at the same time retaining their excellent performance, durability and economic justification. Academic researchers and industry in the field of coatings therefore closely cooperate with each other in order to achieve these high standards, which allow design of coatings with desired structures and properties, suitable for a specific purpose [4].

Material protection using coatings is economically justifiable and, consequently, the most commonly utilized form of protection [5]. In some cases, coatings can affect the electrical conductivity of the material and improve its mechanical treatment [6].

The Law on Standardization contains regulations which define the proper techniques of coating application [7]. Protective coatings characterized by service (protective) life depending on the operating conditions, which may involve high levels of humidity and temperature, a high content of

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salts and other harmful compounds, as well as mechanical vibrations. If they are applied to dry surfaces and kept in heated rooms, coatings can last for 30 years, whereas surfaces exposed to weathering must be coated every 10 years.

The substances most commonly used as binders are plant oils and resins. Depending on their origin, resins can be natural and synthetic; they are organic compounds, usually with complex structures and large molar masses in most cases. Due to their advantageous properties, synthetic resins have almost completely substituted the natural ones in modern industry [8,9].

In order to satisfy all these requirements (or some of them, at least), it is necessary to pay attention to the technology of application of coatings. It should always be kept in mind that even the most adequately selected and most expensive coating material may easily be destroyed if not handle with caution before, during and after application [10,11].

As there is no synthetic binder that could meet all the requirements of a good binder, an additional binder is often needed to adjust the rheology and water retention to the required level. Acrylic binders have found significant use in the field of paper coatings for transparent grease-resistant coatings, excellent mixture quality, oil and solvent resistance, and lasting flexibility [12].

Acrylic coatings are capable of enduring high mechanical loads without cracking or collapsing. However, application on large surfaces is not always justifiable due to the high costs of the material. Acrylic coatings are widely used to create a glossy or matte finishing because they are capable of forming a durable opaque coating on almost every substrate. The main component in this class of coatings is acrylic resin [2].

Acrylic resins are one of the most widely used binders in the coatings industry, because of their photo-stability and resistance to hydrolysis.

Acrylic resins with hydroxyl groups are copolymers of non-functional monomers (methyl methacrylate, styrene and butyl acrylate) and hydroxy-functional monomers (2-hydroxyethyl methacrylate, or HEMA) which can be cross-linked by melamine-formaldehyde resins (MF) or polyisocyanates. Those are resins in the molar mass range between 10 000 and 20 000 g/mol [2,6].

The hydroxyl group can also be obtained in the reaction of methacrylic (MA) acid or acrylic (AA) acid, on the one hand, and glycidyl ester (low glass transition temperature T_g) on the other. The proper modulation of the ratio of non-functional monomers (important for "setting" the desired value of T_g) to hydroxy-functional monomers, the degree of crosslinking can be varied to satisfy different purposes. Depending on the crosslinking mechanism, it is also necessary to modulate the composition and properties of the acrylate binder (lower T_g values are usually obtained with polyisocynate cross-linkers, as is the case with MF resins due to the formation of intermolecular hydrogen bonds). The molecular weight of the binder is decreased through the use of transfer agents, which can have different effects on the stability of the binder [2,4,13].

Thermoplastic acrylic resins have excellent performance (environmental resistance), but their production has significantly decreased due to legal restrictions on the use of organic solvents (volatile organic compounds, VOC). They were mainly used in the automotive industry from the 1950s through the 1970s. Since they produce coatings with glossy, metallic effects, they are still used for special types of coatings only restrictively. Thermoplastic acrylic resins are formed by chain polymerization. They are usually copolymers with acrylic acid and methacrylate acid. In automotive coatings, the T_g of these resins must be above 70 °C. The non-volatile matter content of these coatings is only 11–13% [2,7].

Thermoset acrylic resins can increase the content of binder in the coatings. Prior to application, polymers have low molecular weight; during the process of crosslinking they form polymer networks which give desired properties of film. The obtained polymer network is also insoluble in any solvent. Although the term thermoset refers to the properties of the resins which can be cross-linked by heat, the majority of thermoset acrylic resins contain suitable functional groups which react with different polymers or are cross-linked through suitable functional elements of pendant groups even at room temperature [2].

The method most commonly used to obtain acrylic resins is free radicals polymerization.

The impossibility of controlling the heat of reaction in bulk polymerization, the products with low molecular weight, the low reaction rate and the presence of solvents in traces during solution polymerization are all problems that can be successfully resolved by emulsion polymerization of one or more monomers. The process of emulsion polymerization is, therefore, of great practical significance and a large number of industrial polymerizations of different monomers were developed. Very important component of all systems for emulsion polymerization are emulsifiers/surfactants. These are substances with

the ability to reduce surface tension, which is crucial for the formation of stable emulsions [2,7]. Recently, acrylic emulsions based on methyl methacrylate and butyl acrylate have been gaining increasing industry attention. In these processes, polymerization is achieved by means of catalysts and initiators soluble in water or oil, water with one or more water-immiscible monomers and oil-in-water emulsifiers. These emulsions are mostly opaque, milky and viscous solution, but can also be transparent depending of a particle size in the range of about 8–80 nm when a very high concentration of surfactant is used. When the aqueous acrylate-polymer emulsion obtained by emulsion polymerization is dried at room temperature or at elevated temperature, a transparent coating having a good durability is obtained [14].

This paper investigates the effects of adding methyl methacrylate on the properties of acrylate emulsions obtained in the copolymerization of butyl acrylate and 2-etylhexyl acrylate. The properties of acrylate coated films (both mechanical and thermal) were investigated with the aim to gain insight into the effect of the structure of synthesized emulsions on their performances.

2. EXPERIMENTAL

Butyl acrylate (BA) and 2-ethylhexyl acrylate (EHA) manufactured by Sigma Aldrich, Germany, were used as monomers for the synthesis of the acrylate emulsion. Methyl methacrylate (MMA) manufactured by Triplex Hot, Ivoclarvivadent, Great Britain, was employed to improve the mechanical properties of the acrylate films. The surfactants used were sodium lauryl sulfate by Sigma Aldrich (SLS) and Emulsogen LCN, series 200 (ELCN),

manufactured by Clariant, Switzerland. Potassium persulfate (PPS) provided by Centrohem, Serbia, was used as the initiator. Crosslinking of the samples was achieved by adding styrene (S) manufactured by Sigma Aldrich, Germany.

The sample preparation involved preparing a 30wt% polymer emulsion with water, used as the solvent. The adequate amount of the monomer (BA) was first measured, followed by the addition of water and surfactants. The amount of the surfactant was the same, measuring 1wt% of the monomer. After this mixture was prepared, the monomer EHA was added in the same amount as that of BA, and the initiator, in the amount of 5 wt% of the total mass of the monomer. In order to investigate the effect of MMA on the properties of synthesized acrylate emulsions, several series of samples were synthesized with the MMA content that was varied from 10-50 wt% of the total mass of BA and EHA. Table 1 shows the composition and labels of the samples.

The emulsions were applied to a paper using an acrylic paint brush and the analyses of water and oil resistance of the coated paper were conducted.

The identification of materials was carried out using the Fourier Transform Infrared Spectroscopy (FTIR) method, since this is an absorption spectroscopy technique based on the concept that molecules and atoms absorb specifically the radiation which corresponds to the frequencies of the vibrations of the bonds within the material. In other words, the absorption peak positions in the IR spectra correspond actually to the vibration (oscillation) frequencies of the molecules and functional groups in the material. Position, intensity, number and shape of absorption maximums (absorption bands) are directly determined by the structure of the material.

Table 1. Composition and labels of the samples prepared

Sample label	BA (g)	EHA (g)	SLS (g)	ELCN (g)	MMA (g)	Water (ml)	PPS (g)
BA_EHA	1.35	1.33	0.0268	0.0268	0	6.25	0.134
BA_EHA_MMA_10	1.35	1.33	0.0295	0.0295	0.268	6.87	0.147
BA_EHA_MMA_20	1.35	1.33	0.0322	0.0322	0.536	7.50	0.161
BA_EHA_MMA_30	1.35	1.33	0.0348	0.0348	0.804	8.13	0.174
BA_EHA_MMA_40	1.35	1.33	0.0375	0.0375	1.072	8.75	0.188
BA_EHA_MMA_50	1.35	1.33	0.0402	0.0402	1.34	9.38	0.201

The thermal properties of the dry films of acrylate emulsions were analyzed using the DSC method (model DSC Q20 TA Instruments).

Mechanical characterization of dry acrylate films was carried out using a Shimadzu ez-test LX device. The emulsion was applied to a paper using a

brush, first in one direction, and then in the opposite direction. When the sample became dry and the acrylate film was formed on one side of the paper, the emulsion was applied on the other side of the paper also in both directions. When the samples became totally dry, their mechanical properties were

tested on a universal testing machine. The parameters tested were tensile strength and elongation at break, and the tests were performed at the cross head speed of 1 mm/min.

3. RESULTS AND DISCUSSION

The acrylate emulsion was spread with a brush on the paper in one direction for every sample, and when the samples dried, a drop of water and a drop of oil were added on each sample. The permeability of the emulsion coated on the paper was tested after 1 hour and 2 hours respectively. Figures 1 and 2 show the samples with oil and water after 1 hour (Figure 1) and after 2 hours (Figure 2).

Figures 1 and 2 show that no emulsion was permeated either by water or by oil after 1 hour or after 2 hours. However, on the samples containing MMA the coating is less sticky after curing and the stickiness decreased with the increase of the content of MMA.

FTIR spectra were recorded in the 400 to 4000 cm^{-1} wave number range. The results of the FTIR analysis are one of the best indicators of

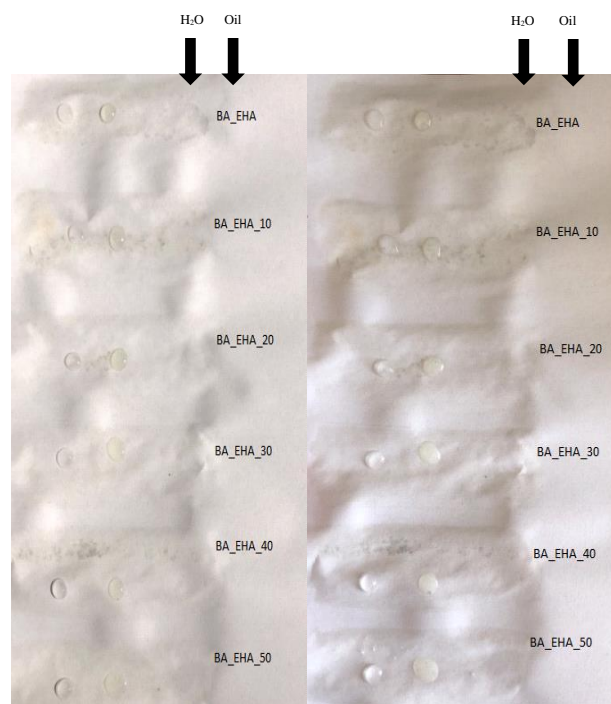acrylate monomer polymerization. Figures 3–8 display the FTIR spectra of the investigated samples.

Figure 1. Paper sample after 1 h
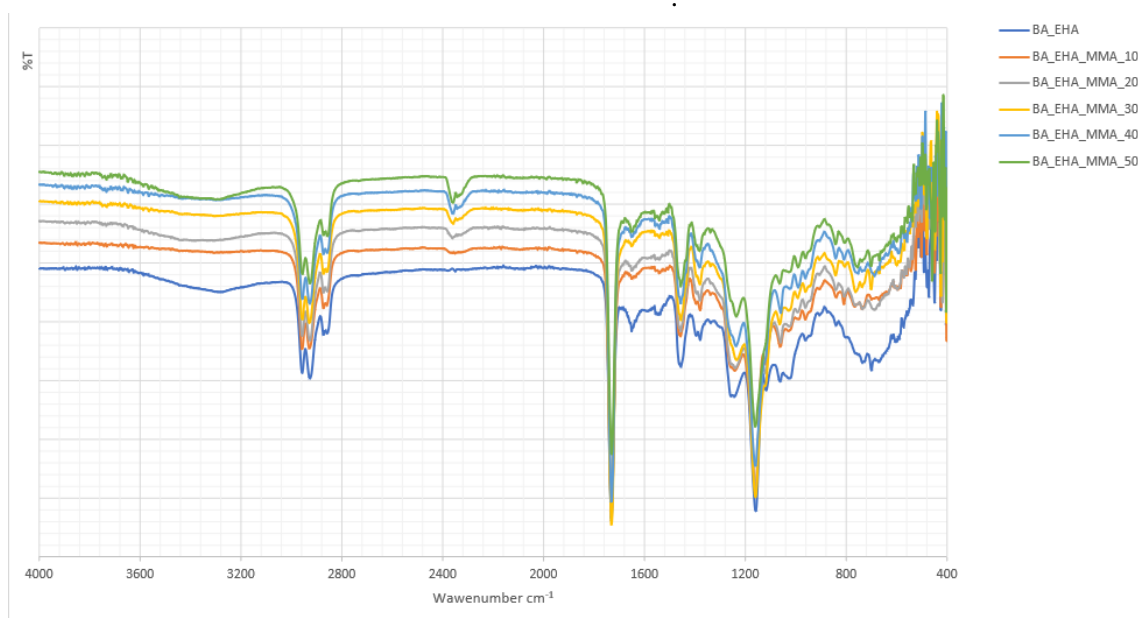
Figure 2. Paper sample after 2 h

Figure 3. FTIR spectrum for samples of BA_EHA without and with MMA

Figure 3 shows the FTIR spectrum of BA_EHA sample, where it can be observed that polymerization has occurred since there are no visible vibrations of any residual monomer functional groups. The absorption peak which occurs at 2900-2980 cm^{-1} originates from C-H groups. The

peaks occur at 2850-2929 cm^{-1} are from an asymmetric CH_2, CH_3 stretching. The peak occurring at 2250cm^{-1} represents C-C stretching. The next intense peak which occurs in all samples at the 1750 cm^{-1} wave number comes from ester groups. The peak at 1650cm^{-1} represents an aromatic C=C bond

coming from styrene. The peak at 1370 cm^{-1} represents the CH$_3$ group bending. The peaks at 1450 cm^{-1} come from CH$_2$ vibrations, whereas the peak at 1250 cm^{-1} and the pronounced peak at 1156 cm^{-1} are attributed to the vibrations of the strong C-O-C bonds which come from acrylate. As the proportion of methyl methacrylate increases, it can be observed that the peak intensity decreases to 1650 cm^{-1}, which is the peak of the aromatic C=C group. It is also observed that with increasing methyl methacrylate content a peak occurs at 2350-2360 cm^{-1}, which becomes more intense with increasing methyl methacrylate content, this peak originates from Alkynes groups C ≡ C resulting from dehydrogenation reactions absorbed in IR.

The analysis of the thermal properties of acrylate films was carried out by distributing samples into pan and placing them into the device containing the referent pan and heat with the heating rate of 10°C/min in the temperature range of -90°C do 220°C.

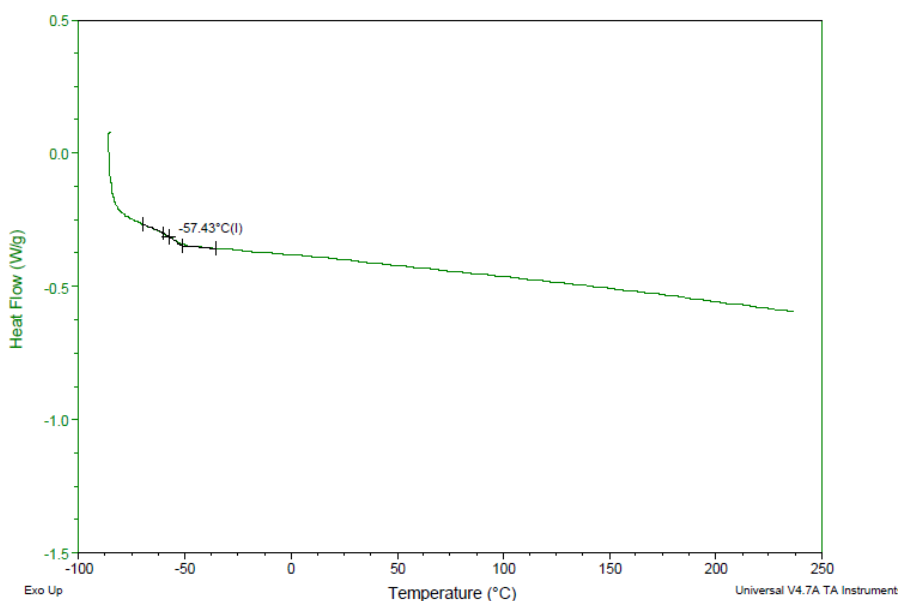Figures 4, 5, 6, 7, 8 and 9 show the DSC thermograms of the samples.
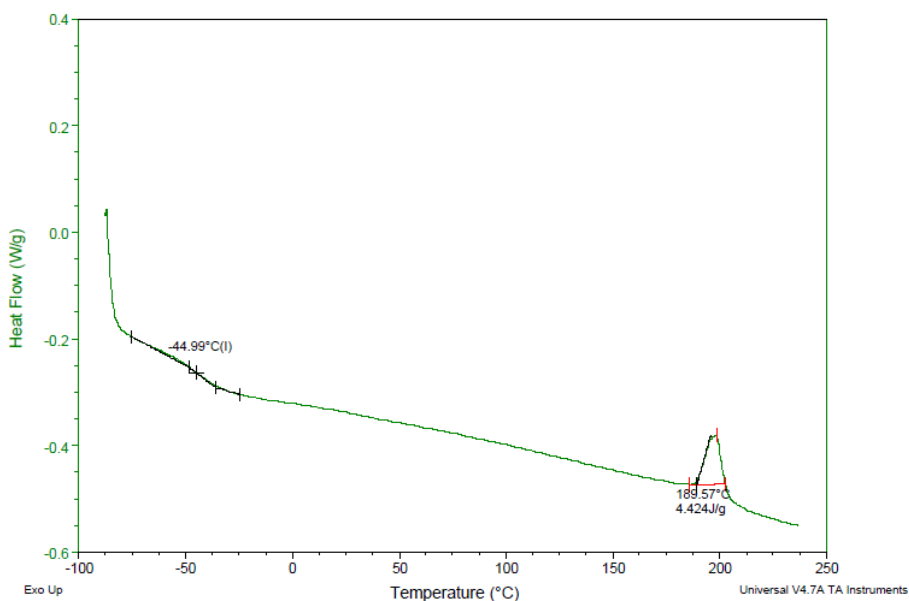

Figure 4. DSC thermogram of BA_EHA

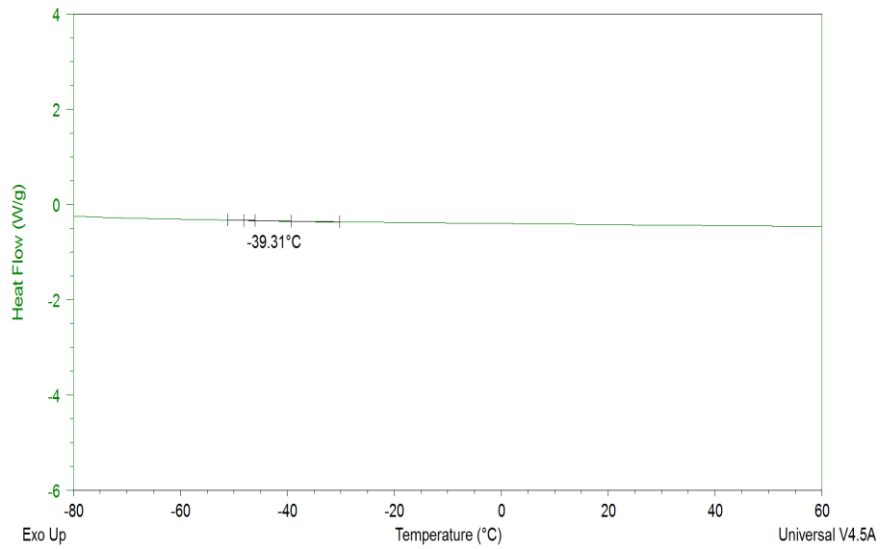*Figure 5. DSC thermogram of BA_EHA_MMA_10*

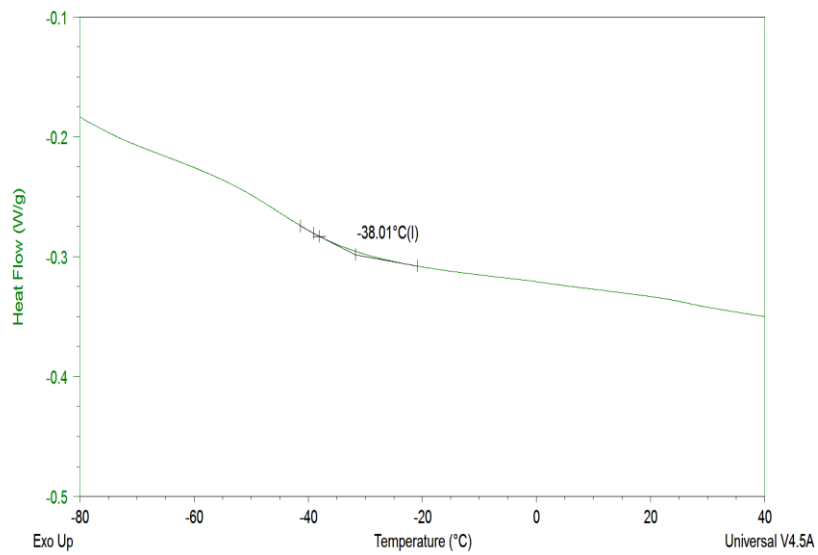*Figure 6. DSC thermogram of BA_EHA_MMA_20*
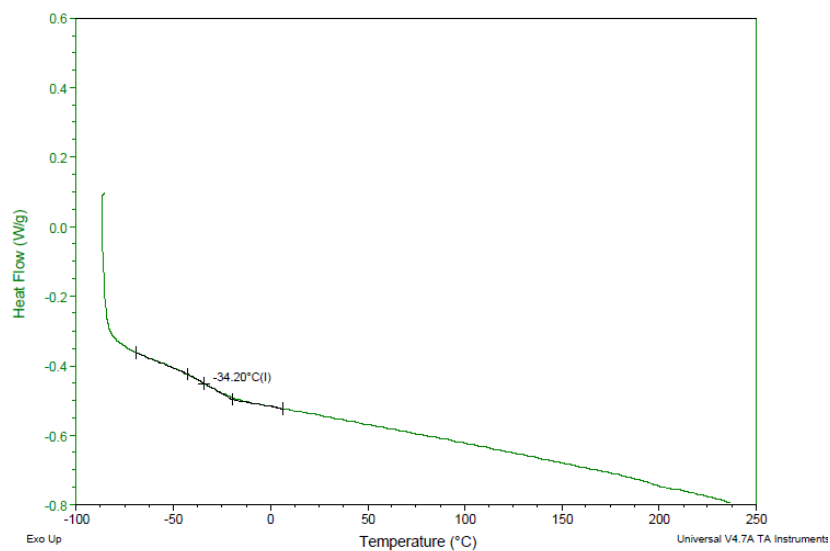

Figure 7. DSC thermogram of BA_EHA_MMA_30

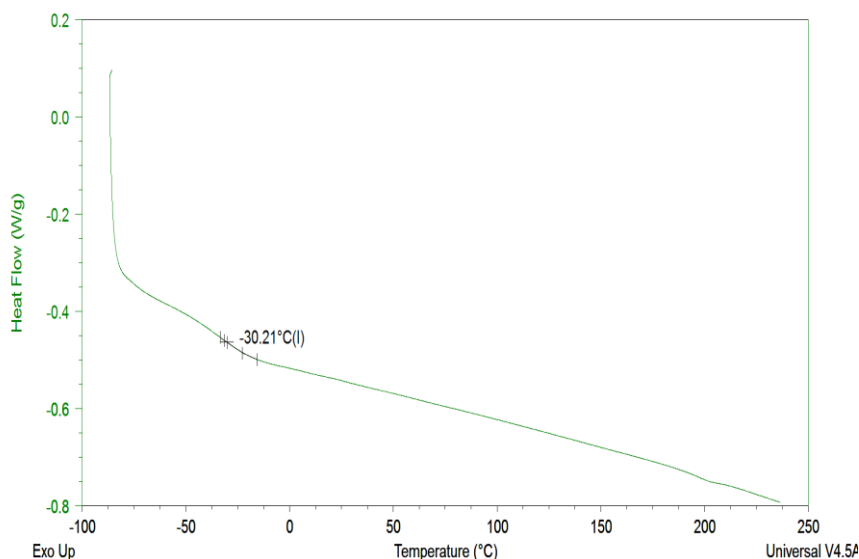*Figure 8. DSC thermogram of BA_EHA_MMA_40*

Figure 9. DSC thermogram of BA_EHA_MMA_50

The data shown in Figure 4 are indicative of only one effect, namely glass transition at -57.43°C, whereas with further heating, the sample remains stable [18]. Figure 5 shows an exothermic peak at 189 °C, which indicates the subsequent crosslinking reaction of the acrylate film. Glass transition temperature occurs at temperature -44.99°C. In figure 7 it can be seen that the glass transition temperature is at -38,01 °C. Figure 8 shows that during heating, glass transition can be observed -34.20°C, and with further heating, the sample remains stable. Figure 9 shows that the glass transition temperature occurs at temperature -30.21°C. The results of the thermal analyses of dry acrylate films undoubtedly indicate a clear trend in the increase in glass transition temperature with the increase of the MMA content in the structure of the acrylate film. This tendency reflects what was expected considering the rigidity of the MMA structure, and allows for a material to be produced with the desired values of glass transition temperature.

Table 2 gives the results of mechanical analyses.

Table 2. Results of the mechanical analyses of the samples

Sample label		Ultimate tensile strength (kPa)	Relative elongation (%)
Clean paper		0.9	5
BA_EHA	One-sided coating	1.02	12
BA_EHA_MMA_10		1.21	21
BA_EHA_MMA_20		1.26	43
BA_EHA_MMA_30		1.42	57
BA_EHA_MMA_40		1.52	49
BA_EHA_MMA_50		1.76	48
BA_EHA	Double-sided coating	1.26	17
BA_EHA_MMA_10		1.47	22
BA_EHA_MMA_20		1.86	58
BA_EHA_MMA_30		1.98	92
BA_EHA_MMA_40		2.14	56
BA_EHA_MMA_50		2.48	36

The results shown in Table 2 indicate that applying acrylate emulsion on the paper increases its tensile strength and elongation-at-break compared to the paper without the coating. The tensile strength varied from 0.9 to 2.48 kPa, and increased proportionately with the increased content of MMA in the emulsion sample. The values of relative elongation were in the range of 5 to 92% depending

on the type of emulsion applied. The samples containing 30% MMA exhibited the highest relative elongation. Further increase in the MMA content decreased the values of relative elongation, which is the result of the formation of a more rigid structure characteristic of polymethylmethacrylate [7].

4. CONCLUSION

The paper presents a successfully developed procedure for producing acrylate-based emulsion coatings which can be applied to improve the properties of paper used as a wrapping material. Acrylic coatings were synthesized from butyl acrylate and 2-ethylhexyl acrylate with the addition of methyl methacrylate to improve the mechanical properties of the final coating. The FTIR analysis confirmed that using the given ratios of the components causes a quantitative reaction in which acrylic materials are formed. When applied to paper, all emulsions gave water- and oil-impermeable, or stable films. As expected, the introduction of methyl methacrylate improves the mechanical and thermal properties; due to different individual requirements, however, special attention must be paid in order to determine accurately the necessary amount of methyl methacrylate for each specific purpose. The acrylic materials with the addition of methyl methacrylate exhibit increased glass transition temperatures. Mechanical analyses of the properties of paper after the application of emulsion coatings show that the introduction of methyl methacrylate increases elongation to the optimal value, and the most effective content proves to be 30wt% of BA and EHA. The introduction of methyl methacrylate above the given amount causes the decrease in elongation, whereas the tensile strength increases with the increase of the content of methyl methacrylate in the samples.

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УТИЦАЈ МЕТИЛ МЕТАКРИЛАТА НА СВОЈСТВА СИНТЕТИСАНИХ АКРИЛАТНИХ ЕМУЛЗИЈА

Сажетак: У раду је извршено испитивање утицаја додатка метал метакрилата (ММА) на својства синтетисаних акрилатних емулзија. Синтетисане су серије емулзија са додатком ММА од 10 до 50 масе % у односу на укупну масу бутилакрилата (БА) и 2-етилхексилакрилата (ЕХА). Инфрацрвеном спектроскопијом са Фоуријеовом трансформацијом (ФТИР) анализирана је молекулска структура синтетисаних акрилатних емулзија и потврђено је да долази до квантитативне реакције полимеризације. Анализом топлотних својстава показано је да са додатком метилметакрилата долази до повећања вредности температуре преласка у стакласто стање филмова добијених сушењем синтетисаних емулзија. Напон истезања и прекидно издужење повећавали су се сразмерно повећању удела ММА у узорцима синтетисаних емулзија. Добијени акрилатни материјали могу се користити за побољшање водне пропустивости папира и других материјала. Зато су на папир наношене емулзије (у танком слоју) и испитана је отпорност папира са премазом на воду и уље. Примећено је да ниједна емулзија није пропустила ни воду ни уље.

Кључне речи: емулзиона полимеризација, акрилни премази, синтеза, метилметакрилат.

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