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**ECO-FRIENDLY SUCROSE AND POLYVINYL
ACETATE-BASED POLYMERIC SYSTEMS**

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This work is focused on the synthesis of aqueous polymeric dispersions based on polyvinyl acetate and sucrose formed by emulsion polymerization technique. These polymeric latexes can be used in the field of sustained release fertilizer encapsulation or as ecological paper glue with the subsequent biological disposal. The main objective of the work was to bond covalently sucrose into polyvinyl acetate ensuring the effective biodegradation of the respective polymer mainly in the soil environment. We have searched for an optimal ratio between the polymer and the simple sugar in the alkaline medium so that the resulting latex could exhibit good water solubility, sufficient bond strength, and the stability of atmospheric humidity. Using infrared spectroscopy, the process of binding sucrose into the polymer chain of vinyl acetate has been demonstrated.

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Introduction

The consumption of polymeric materials is constantly increasing that is why the emphasis is put on the use of organic raw materials and also on the recyclability and biodegradability of the final polymeric products. The film production from conventional latex coatings is primarily based on the coalescence of thermoplastic polymer particles. The quality of coalescence determines the final mechanical properties of the film being the result of physical coupling of polymer particles [1].

This work focuses on the development of eco-friendly latexes based on polyvinyl acetate (PVAc) and sucrose [2]. A potential application can e.g. be, encapsulation [3] of the progressive release fertilizers or ecologically gluing of paper. Biodegradable polymeric fertilizer packaging can be subdivided based on character of the natural or synthetic polymer, into (i) hydrolyzed hydrophilic polymers and (ii) hydrolyzed hydrophobic polymers [4]. There is a general consensus that hydrolyzed polymers are more biodegradable than the non-hydrolyzed structures due to the differences in biodegradation and nutrient release mechanism [5]. By distinguishing according to the distribution mentioned above, sucrose and polyvinyl acetate-based latexes from the portion saponified to polyvinyl alcohol can be sorted among the hydrolyzed polymers. From the literature survey, it is evident that the emulsion polymers with covalently bonded sugar units applied as the encapsulation materials for controlled-release fertilizers have not yet been published [6].

The common application of polyvinyl acetate latex is a gluing of wood and paper substrates. There is one problem with wastepaper recycling — the presence of sticky compounds that are predominantly built up of the organic adhesives, including styrene-butadiene rubbers, acrylates, and polyvinyl acetate. When wastepaper containing such adhesives is defibred, the “stickies” are broken down into 0.05- to 0.5-mm particles.

In recycled paper, these particles reduce its quality, causing also a paper machine downtime. To clean the paper machines, environmentally hazardous solvents are used [7]. In the case of polyvinyl acetate polymer adhesive comprising the covalently linked sucrose units, this problem can be avoided. This kind of the paper glue exhibits good solubility in water and therefore, the glued joints are supposed to be dissolved completely in washing water during the paper recycling without the risk of formation of coagulum or effluents pollution [8].

The synthesis of latexes has been carried out using an emulsion polymerization technique [9] when choosing the alkaline medium. Because of such environment, sugars are able to pass into the reactive endiol form [10,11] which is capable of participating in the radical polymerization with vinyl acetate monomer due to the presence of a carbon-carbon double bond (see Fig. 1). During the polymerization, alkaline hydrolysis of acetate groups also results in the formation of vinyl alcohol units in the polyvinylacetate chain (Fig. 2) that promote the solubility of the resulting polymer in water [12,13].

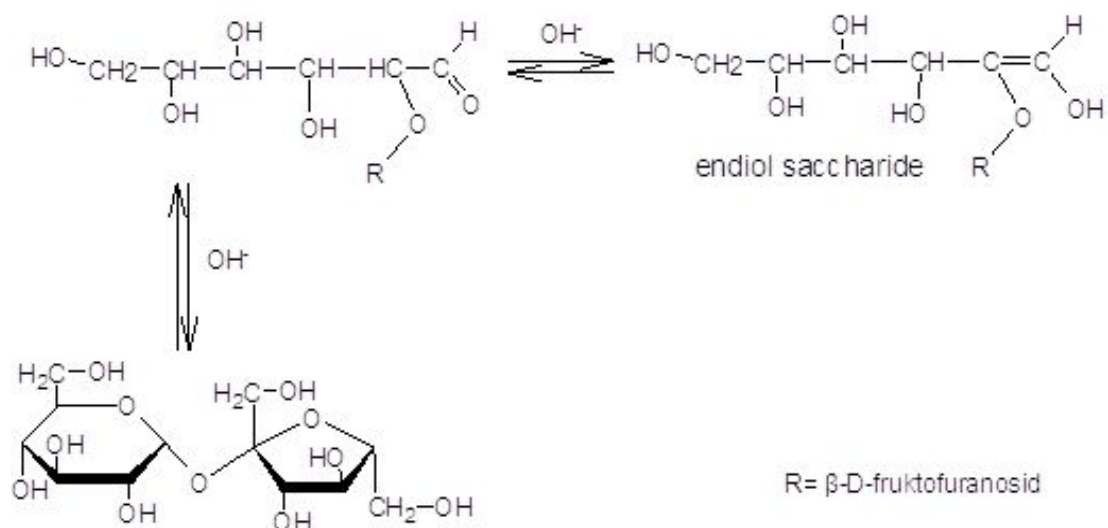


Fig. 1 Scheme of formation of endiol form of sucrose

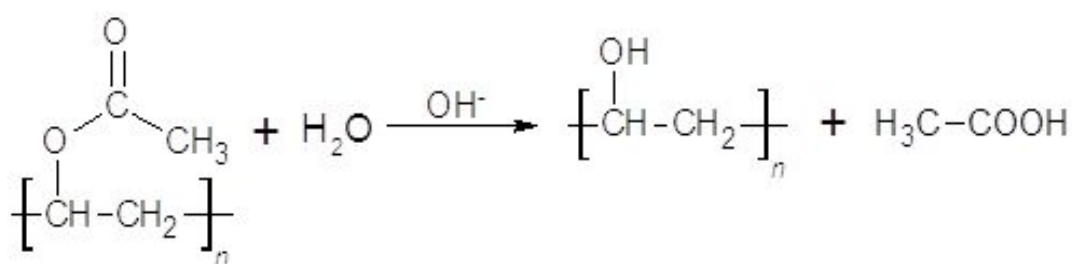


Fig. 2 Alkaline hydrolysis of polyvinyl acetate

Experimental

Materials

Vinyl acetate (VAc) purchased from Sigma-Aldrich was used as the major monomer for the preparation of aqueous polymer dispersions. Polyvinyl alcohol, commercially available as Mowiol 4-88 (Sigma-Aldrich), was used as a protective colloid in the preparation of latexes that led to stability of the polymer particles formed. Anhydrous sucrose obtained from Lach-Ner (Czech Republic) was used to increase the degradation by microorganisms. To adjust the pH during the polymerization, sodium carbonate was purchased from the same company.

Preparation of Aqueous Polymer Dispersions

Polyvinyl acetate latex with a copolymerized variable content of sucrose were prepared by emulsion polymerization technique [14]. Sucrose is soluble in water and introduced as an aqueous solution into the polymer system. The aqueous medium during the polymerization was adjusted to pH 8-9 with sodium carbonate.

Simple saccharides are able to form an enol form in an alkaline environment that can then react with monomers of vinyl acetate in an aqueous medium *via* a radical mechanism. However, this is merely a simplified idea of the ongoing reaction, since it also offers the possibility of forming double bonds during the sugar degradation in an alkaline environment and, subsequently, the possibility of reaction of these degraded products with vinyl acetate. To ensure colloidal stability of latexes during polymerization, polyvinyl alcohol (PVA) was used to prevent the coagulation of latex particles instead of a conventional emulsifier [9,15].

The latexes were prepared in the inert atmosphere of nitrogen in a 700 ml glass reactor at the temperature of polymerization (35 °C) when using a redox initiator [16] consisting of sodium bisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) and ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ at the 1 : 1 stoichiometric ratio. A portion of 0.66 g redox initiator, 2.5 g sodium carbonate, 10 g polyvinyl alcohol and the selected amount of sucrose (see Table I) were dissolved in 150 ml water. Upon heating the reactor at the polymerization temperature, an aqueous monomer emulsion consisting of 150 g water, 0.66 g redox initiator and 66 g vinyl acetate was added drop-wise into the reactor at a rate of 1.29 ml min^{-1} . The polymerization proceeded at 35 °C for 5 hours and the resultant solid polymer was about 40 % (w/w) of the total content. The data characterizing the starting monomer for preparation of sucrose are gathered in Table I.

Table I Representation of sucrose to the initial monomer content

Sample	Vinyl acetate, g	Sucrose, g
R 0	66	0.0
RS 10	66	6.6
RS 25	66	16.5
RS 50	66	33.0
RS 100	66	66.0

Characterization of Aqueous Polymer Dispersions

The average size of the polymer particles in the aqueous phase was obtained by dynamic light scattering (DLS). DLS experiments were performed using a 90 Plus Partical Size apparatus (Brookhaven Instruments, USA); all the measurements being performed at room temperature. The concentration of the polymer dispersion was about 0.05 wt. %, the Zeta-potential was measured using the same device. The minimum film formation temperature (MFFT) — i.e., a minimal temperature at which the casting from the polymeric dispersion forms a continuous and clear film — was measured using a MFFT-60 instrument (Rhopoint Instruments, UK) in accordance with the ISO 2115. The content of polyvinyl acetate in the emulsion copolymer, which is a water-insoluble polymeric fraction, was determined by the extraction in distilled water for 24 hours in the Soxhlet extractor (Fisher Scientific, CZ). Approximately 1 g of the dried dispersion sample was transferred into the extraction thimble. After extraction, the thimble was dried in an oven at 75 °C for 6 hours, cooled down in a desiccator overnight and the content of the insoluble polyvinyl acetate was calculated from the initial and final weights of the thimble, assuming that all the polymer remained in the thimble.

For the confirmation of covalently linked sucrose units in the polyvinyl acetate chain, infrared spectra processed with Fourier Transform (ATR) were scanned on a FTIR instrument (model Nicolet iS50 with diamond crystal; Thermo Scientific, USA) in 32 replicates (scans) with a spectral resolution of 0.09 cm⁻¹ with the unlimited use within wavelength range of 4 000-500 cm⁻¹. Before these measurements, samples were precipitated in acetic acid and repeatedly washed with distilled water in order to ensure the isolation of the polymer with a predominant content of the vinyl acetate units.

Results and Discussion

Polyvinyl acetate latexes with copolymerized variable content of sucrose and having a minimum amount of coagulum (0.4-2 %) were prepared by emulsion polymerization technique. All the polymer dispersions prepared were stable for only about two weeks; therefore, these dispersions were suitable for fast consumption. The latexes were evaluated for their particle size in the aqueous phase, Zeta-potential, viscosity, and the polyvinyl acetate content relative to the sucrose concentration. These characteristics are listed in Table II. The DLS results had shown that the size of the latex particles was affected by the amount of sucrose in the latex, increasing the particle size with the increased amounts of sucrose. The measured Zeta-potential values have ranged from -6.0 to -3.8 mV, which indicates a low stability of the dispersions and may thus explain a relatively rapid coagulation of the system during storage under laboratory conditions. On the

other hand, the polymeric systems containing carbohydrate had a lower viscosity. All synthesized latexes exhibited the MFFT values close to 0 °C, revealing good film-forming properties. This can be explained by the presence of higher amounts of low-molecular polymer fractions that plasticize the polymer in the coalescence phase of latex particles. The content of polyvinyl acetate in the emulsion polymer decreased significantly by the increased amounts of sucrose in the latex. It can be assumed that during emulsion polymerization in the presence of sucrose, there is a significant saponification of the acetate groups, as well as a decrease in the molecular weight. This appears to lead to the formation of low molecular weight polymers and oligomeric products (Fig. 3). This phenomenon had been described by Takasu *et al.* [2] who discussed the bio-degradability of such emulsion copolymers based on polyvinyl acetate and sugar derivatives.

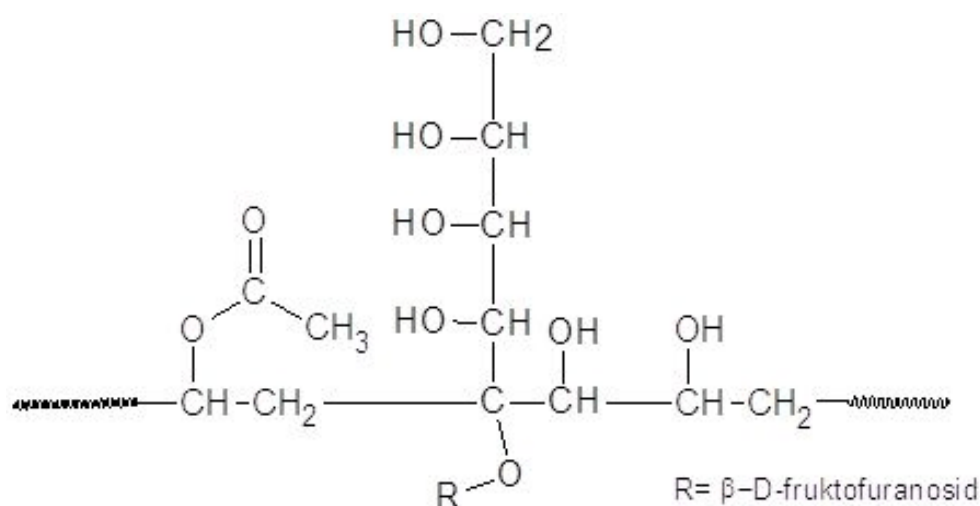


Fig. 3 Incorporation of sucrose into the polymer chain formed by vinyl acetate and vinyl alcohol units

Table II Composition and characteristics of biodegradable latexes based on polyvinyl acetate and sucrose

Sample	Particle size in the water phase, nm	Zeta potential mV	Viscosity mPa s	PVAc content %	MFFT °C
R 0	197.1	-4.7	76.2	63.5	1.1
RS 10	223.5	-5.3	35.8	47.6	0.8
RS 25	453.6	-6.1	42.3	15.2	0.5
RS 50	577.3	-4.9	29.5	5.3	0.7
RS 100	780.7	-3.8	23.9	6.7	1.0

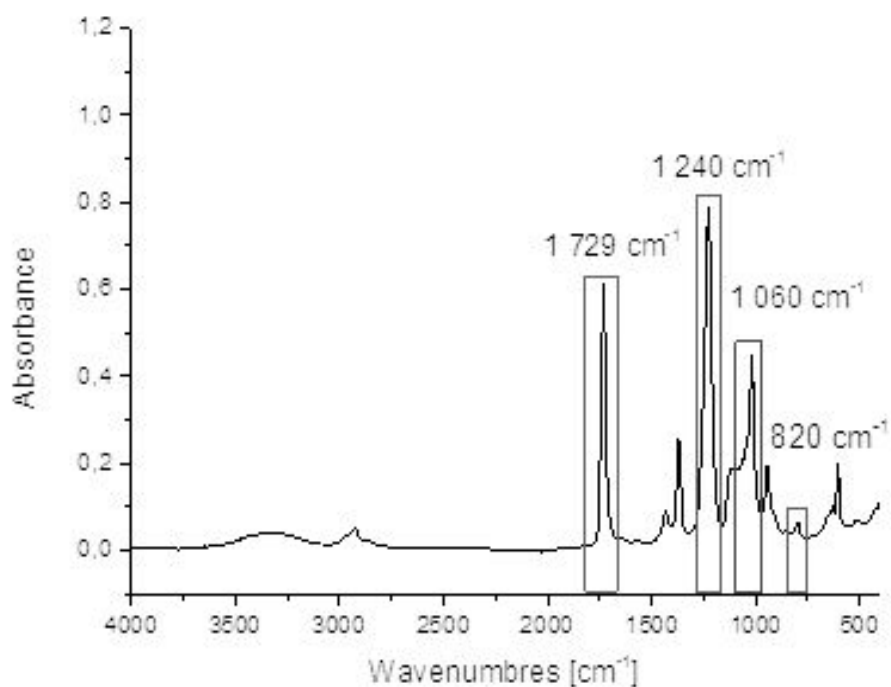


Fig. 4 Infrared spectrum for a sample RS 100

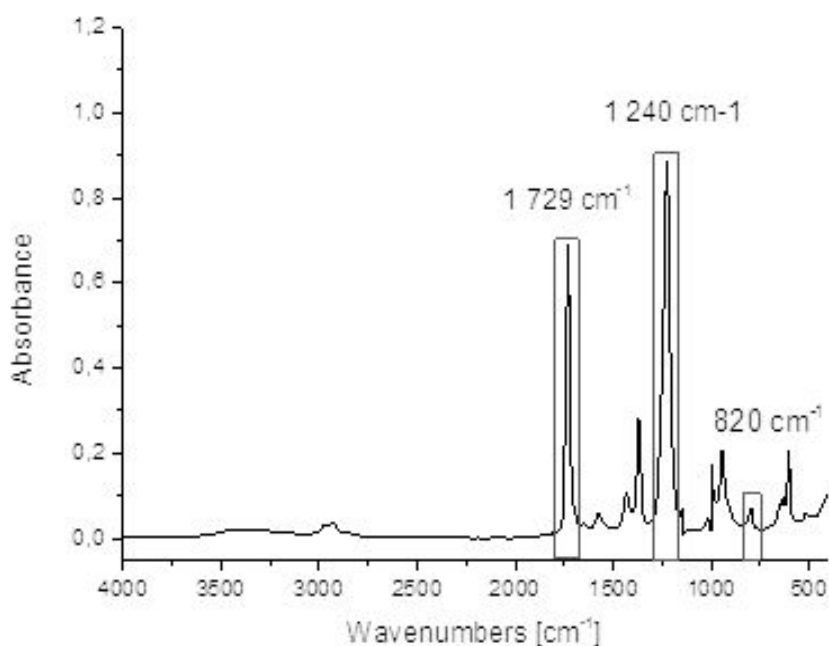


Fig. 5 Infrared spectrum for a sample RS 0

The infrared spectrum of a sucrose-containing polyvinyl acetate sample is illustrated in Fig. 4. The spectrum shows the absorption band at 1060 cm^{-1} belongs to the carbohydrate units, which is characteristic for the glycosidic bond (C–O–C). This band is partly superimposed by a band corresponding to the plane deformation vibration of the C–OH band that, in this case, is located in the side

substitutes of the molecule of sucrose; namely, in the region of 1 290-1 240 cm^{-1} . In the spectra, at the wavelength range of 1 732-1 729 cm^{-1} , the band corresponding to the carbonyl group (C=O) can be found as well. Here, one can argue that the vinyl acetate groups have been confirmed since the structures whose valence vibration is at the wavelength of 1 248 cm^{-1} correspond to the absorption band of the methyl acetate bond (C–O). The polyvinyl alcohol building units are proved too, because their deuterated alcohol groups exhibit a band in the area of 820 cm^{-1} that can be ascribed to the plane deformation vibration of bond (C–O–D), as deuterated alcohol derivatives found in the spectrum at the wavelength of 820 cm^{-1} . Deuteration shifts the vibration frequency into the region of very low wavelengths and hence, it interrupts the interactions with the vibrations of hydrocarbon residue [17]. If the polymer system does not contain the sucrose units, a notable deformation of the vibration band at 1060 cm^{-1} disappears as documented in Fig. 5.

Conclusion

Latexes based on polyvinyl acetate and sucrose were prepared by emulsion polymerization as an aqueous dispersion that can be expected to facilitate the microbial decomposition. During the synthesis, simple and eco-friendly starting materials were used. The presence of the covalently bonded sugar units in polyvinyl acetate polymer chains was confirmed by infrared spectroscopy. Furthermore, the Zeta-potential and the particle size of the resultant polymer in dispersion were measured by dynamic light scattering. These methods have confirmed a low latex stability; therefore, a rapid processing is typical for this latex. The aqueous dispersions concerned in this study can be applied as adhesives for paper, but also as the controlled-release fertilizer packs.

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