

ECO FRIENDLY POLYMER SYSTEMS BASED ON POLYVINYL ACETATE AND SACCHARIDES

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Abstract

The work is focused on the synthesis of aqueous polymeric dispersions based on polyvinyl acetate and D-glucose by emulsion polymerization technique. These polymeric latexes can be used in the field of sustained release fertilizer encapsulation or as an ecological paper glue with subsequent low biological disposal. The main objective of this work was to bond covalently D-glucose into polyvinyl acetate ensure intended feature of these materials is their expected biodegradation of the polymer mainly in the soil environment. Was searched for optimal ratio between the polymer and the simple sugar in the alkaline medium has been investigated so that the resulting latex exhibits good water solubility, sufficient bond strength, and atmospheric humidity stability. Using infrared spectroscopy, binding of D-glucose to the polymer chain of vinyl acetate has been demonstrated.

Keywords: polyvinyl acetate, D-glucose, eco-friendly polymer

Introduction

The consumption of polymeric materials is constantly increasing, that is why the emphasis is on using organic raw materials and also on the recyclability and biodegradability of the final polymeric products. 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. Coalescence is 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 D-glucose.^[2] The potential application can be e.g., encapsulation^[3] of progressive release fertilizers or ecologically gluing of paper. Biodegradable polymeric fertilizer packaging can be subdivided on the basis of the nature of the natural or synthetic polymer, into hydrolyzed hydrophilic polymers and hydrolyzed hydrophobic polymers.^[4] There is a general consensus that hydrolyzed polymers are more biodegradable than the non-hydrolyzed ones due to differences in biodegradation and nutrient release mechanisms.^[5] Based on the distribution mentioned above, D-glucose and polyvinyl acetate-based latexes from the portion saponified to polyvinyl alcohol can be included among the hydrolyzed polymers. It is evident from the literature survey that emulsion polymers with covalently bonded sugar units applied as encapsulation materials for controlled-release fertilizers have not been published so far.^[6]

The common application of polyvinyl acetate latex is gluing of wood and paper substrates. There is one problem with wastepaper recycling – the presence of sticky compounds that are predominantly made up mostly of organic adhesives, including styrene-butadiene rubbers, acrylates, and polyvinyl acetate. When wastepaper containing such adhesives is defibered, the “stickies” are broken down into 0.05- to 0.5-mm particles. These particles in recycled paper reduce its quality and cause paper machine downtime as well. To clean the paper machines, environmentally hazardous solvents are used.^[7] In the case of using polyvinyl acetate polymer adhesive comprising covalently linked D-glucose units, this problem may be avoided. This kind of paper glue exhibits good solubility in water, therefore the glued joints are supposed to be dissolved completely in the washing water during the paper recycling process without the risk of coagulum formation or effluents pollution.^[8]

The synthesis of latexes has been carried out using an emulsion polymerization technique^[9] in the alkaline medium. Because of the alkaline environment, sugars are able to pass into the reactive endiol form^[10,11] which is capable of participating in radical polymerization with vinyl acetate monomer due to the presence of a carbon-carbon double bond (Figure 1). During the polymerization, alkaline hydrolysis of acetate groups also results in

The latexes were prepared under an inert atmosphere of nitrogen in a 700 ml glass reactor at a polymerization temperature 50 °C using a hydrogen peroxide initiator. The 1.2 g of hydrogen peroxide initiator, 2.5 g of sodium carbonate, 10 g of polyvinyl alcohol and the selected amount of D-glucose (Table 1) were dissolved in 150 g of water. Upon heating the reactor at the polymerization temperature, an aqueous monomer emulsion consisting of 150 g of water, 1.2 g of the hydrogen peroxide initiator and 66 g of vinyl acetate was added drop-wise into the reactor at the rate 1.29 ml/min. The polymerization proceeded at 50 °C for 5 hours. The solid polymer content was around 40 % by weight. The D-glucose content of the starting monomer is shown in Table 1.

Table 1: Representation of D-glucose to the initial monomer content.

Sample	Vinyl Acetate (g)	D-glucose (g)
P 0	66	0.0
PG 10	66	6.6
PG 25	66	16.5
PG 50	66	33.0
PG 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 Brookhaven 90 Plus Partical Size (Brookhaven Instruments, USA). DLS measurements were performed at room temperature. The concentration of the polymer dispersion was about 0.05 wt. %, the Zeta-potential was measured using the same apparatus. The minimum film formation temperature (MFFT) was measured using the MFFT-60 instrument (Rhopoint Instruments, UK) in accordance with ISO 2115. The MFFT is defined as the minimum temperature at which the casting from the polymeric dispersion creates a continuous and clear film. 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 a Soxhlet extractor. Approximately 1 g of the dried dispersion sample was transferred to the extraction thimble. After extraction, the thimble was dried in an oven at 75 °C for 6 hours, cooled in a desiccator overnight and the content of insoluble polyvinyl acetate was calculated from the initial and final weight of the thimble, assuming the polymer remained in the thimble.

For the confirmation of covalently linked D-glucose units in the polyvinyl acetate chain, infrared spectroscopy with Fourier Transform (ATR) with diamond crystal was scanned on a FTIR Nicolet iS50 instrument (Thermo Scientific, USA) 32 scans with a spectral resolution of 0.09 cm⁻¹ with unlimited use in the wavelength range 4000 - 500 cm⁻¹. Before these measurements, samples were precipitated in acetic acid and repeatedly washed with distilled water to ensure the isolation of the polymer with a predominant content of vinyl acetate units.

Results and discussions

Polyvinyl acetate latexes with a copolymerized variable content of D-glucose having a minimum amount of coagulum (0.4 – 2%) were prepared by emulsion polymerization technique. All prepared polymer dispersions were stable for only about two weeks, therefore these dispersions are suitable for fast consumption. The latexes were evaluated for their particle size in the aqueous phase, Zeta-potential, viscosity and polyvinyl acetate content relative to the D-glucose concentration. These characteristics are shown in Table 2. The DLS results showed that the size of the latex particles was affected by the amount of D-glucose in the latex, increasing the particle size with increasing amounts of D-glucose. The measured Zeta-potential values ranged from -6.7 – -3.2 mV. These results show low stability of the dispersions and thus explain the relatively rapid coagulation of the system during storage under laboratory conditions. On the other hand, the polymeric systems containing carbohydrate had lower viscosity. All synthesized latexes exhibited MFFT values close to 0 °C, indicating 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 increasing amounts of D-glucose in the latex. It can be

assumed that during the emulsion polymerization in the presence of D-glucose there is a significant saponification of the acetate groups as well as a decrease in the molecular weight appears leading to the formation of low molecular weight polymers and oligomeric products (Figure 3). This phenomenon was described by Takasu et al.^[2] who discussed the biodegradability of emulsion copolymers based on polyvinyl acetate and sugar derivatives.

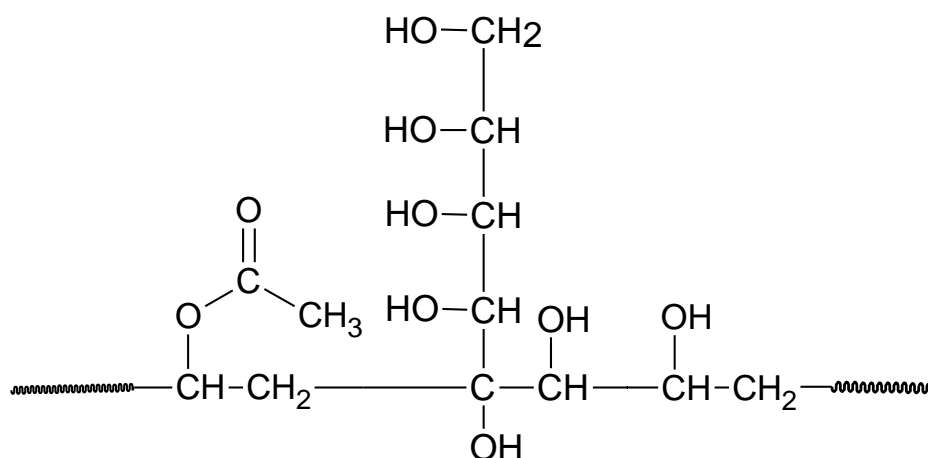


Figure 3: Incorporation of D-glucose into the polymer chain formed by vinyl acetate and vinyl alcohol units.

Table 2: Composition and characteristics of biodegradable latexes based on polyvinyl acetate and D-glucose

Sample	Particle size in the water phase (nm)	Zeta potential (mV)	Viscosity (mPa.s)*	PVAc content (%)	MFFT (°C)
P 0	189.2	-4.8	101.2	51.9	0.9
PG 10	205.6	-5.9	54.6	35.8	0.6
PG 25	465.4	-6.7	39.5	11.5	0.7
PG 50	587.5	-5.4	31.2	3.8	0.3
PG 100	802.3	-3.2	25.7	4.9	1.1

The infrared spectrum of a D-glucose-containing polyvinyl acetate sample is shown in Figure 4. The spectrum shows the absorption band at 1060 cm^{-1} belonging to the carbohydrate units which is characteristic for the glycosidic bond (C-O-C). This band is superimpose in part by a band corresponding to the plane deformation vibration of the C-OH band which in this case is located in the side substitutes of the D-glucose molecule, in the region of $1\ 290 - 1\ 240\text{ cm}^{-1}$. In the spectra, the band corresponding to the carbonyl group (C=O) can also be found in the wavelength range of $1\ 732 - 1\ 729\text{ cm}^{-1}$. It can be argued that vinyl acetate groups have been confirmed in this case since groups whose valence vibration is at the wavelength of $1\ 248\text{ cm}^{-1}$ correspond to an absorption band of the methyl acetate bond (C-O). The polyvinyl alcohol building units are proved because their deuterated alcohol groups exhibit a band in the area of 820 cm^{-1} corresponding to the plane deformation vibration of bond (C-O-D), as deuterated alcohol derivatives that can be found in the spectrum at the wavelength of 820 cm^{-1} . Deuteration shifting the vibration frequency into the region of very low wavelengths and interrupts the interactions with hydrocarbon residue vibrations.^[16] If the polymer system does not contain D-glucose units, the of deformation vibration band at 1060 cm^{-1} disappears (Figure 5).

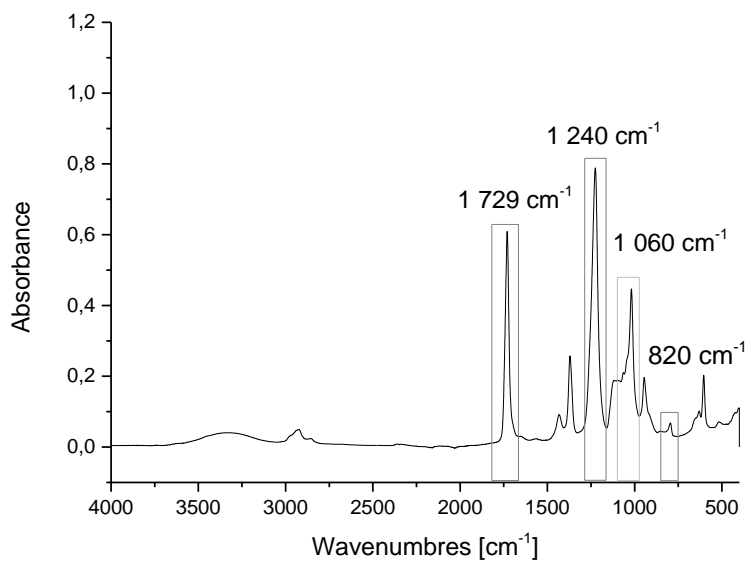


Figure 4: Infrared spectrum for a sample PG 100

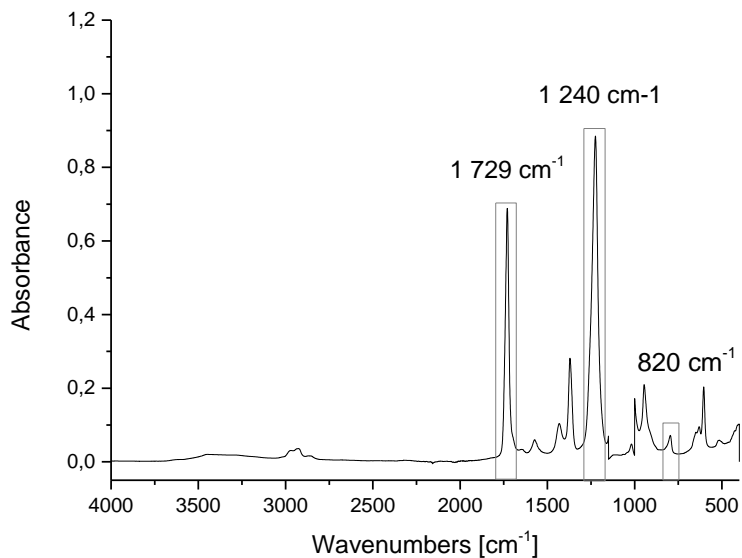


Figure 5: Infrared spectrum for a sample P 0

Conclusion

Latexes based on polyvinyl acetate and D-glucose were prepared by emulsion polymerization as an aqueous dispersion that can be expected to result in faster microbial decomposition. During the synthesis, simple and eco-friendly starting materials were used. The presence of covalently bonded sugar units in polyvinyl acetate polymer chains was confirmed by infrared spectroscopy. Furthermore, the Zeta-potential and size of the polymer particles in the dispersion were measured by dynamic light scattering. These methods confirmed the low latex stability, therefore rapid processing is appropriate this latex. These aqueous dispersions may find their application as adhesives for paper, but also as controlled-release fertilizer packs.

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