SYNTÉZA BIODEGRADABILNÍHO POLYMERNÍHO SYSTÉMU NA BÁZI POLYVINYLACETÁTU A JEDNODUCHÝCH CUKRŮ

SYNTHESIS OF BIODEGRADABLE POLYMER SYSTEM BASED ON POLYVINYL ACETATE AND SIMPLE SACCHARIDES

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Summary

The aim of the research is to find the ideal balance and process for polymerizing sugar units in the chain of polyvinyl acetate and thus improve biodegradation, primarily in the soil environment. The product is in the form of an aqueous dispersion which can be applied as biodegradable glue or as a micro-container for gradually releasing fertilizers.

Key words: polyvinyl acetate, simple sugars, biodegradable polymer

Introduction

The consumption of polymeric materials is constantly growing, therefore their production emphasizes on the use of ecological materials and also on recyclability and biodegradability of the final polymer product. This work is focused on completely biodegradable latex, based on polyvinyl acetate and saccharides [1]. Its potential application may be e.g. the encapsulation [2] of controlled released fertilizers, environmentally friendly paper glues and others. The preparation of lattices is carried out using the technique of emulsion polymerization [3] in an aqueous medium with the addition of sodium carbonate to provide an alkaline pH. Thanks to the basicity of the medium, the sugars are transferred to endiol reactive form (Fig. 1) that is able to participate in a radical polymerization with the vinyl acetate monomers. During the polymerization, alkaline hydrolysis of the acetate groups also occurs resulting in vinyl alcohol units in the polyvinyl acetate chain (Fig. 2).

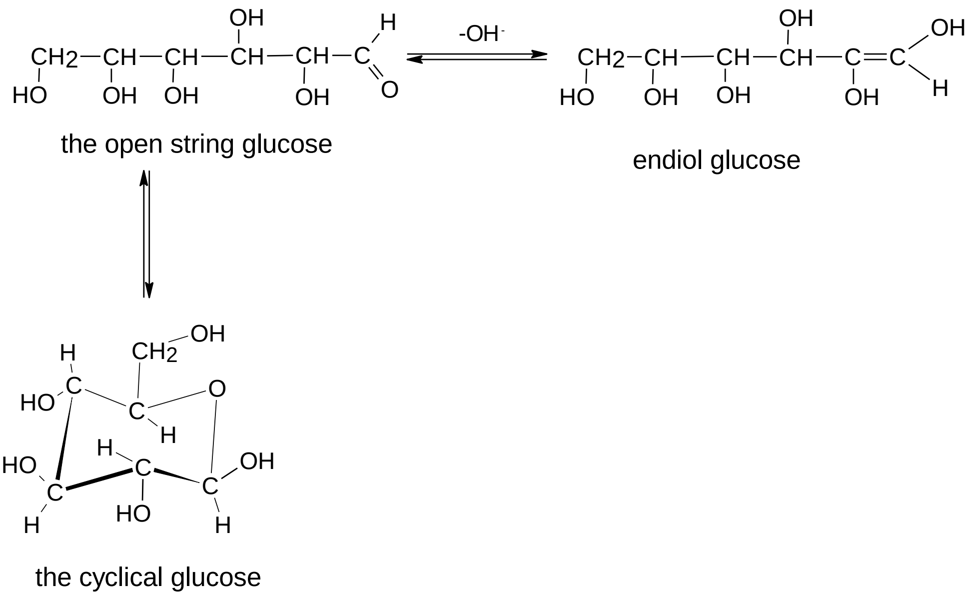

Figure 1: Scheme showing the creation of endiol form of glucose

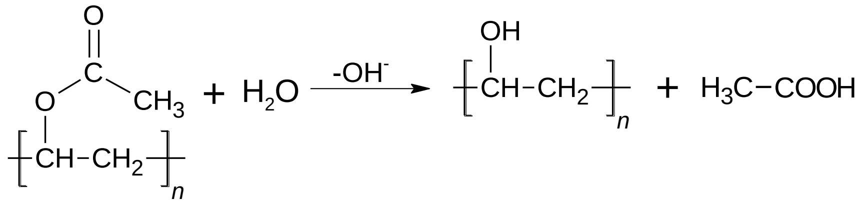

Figure 2: Alkaline hydrolysis of polyvinyl acetate

Experimental methods

The emulsion polymerization of vinyl acetate is usually carried out at temperatures around 80 °C. Two series of latexes using two types of saccharides, namely D-glucose and sucrose were prepared. The concentration of the saccharides in the reaction mixture was 100, 50, 25 and 10 wt. % based on the initial amount of vinyl acetate. As the protective colloid, polyvinyl alcohol was used in the amount of 15 wt. % based on the initial amount of vinyl acetate. To prevent degradation of saccharide molecule during the polymerization, the redox initiator [4] based on ammonium persulfate and sodium bisulfite was used. In this case, the polymerization was carried out at 35 °C for a total time of 6.5 hours. In another series of experiments, hydrogen peroxide was used as the initiator. In this case, the polymerization was conducted at 50 °C for a total time of 4.5 hours. To ensure the environment is alkaline, liquid sodium carbonate was added at the beginning and also during the polymerization. In the presence of both types of saccharides, a saponification of the acetate groups is significant as well as a decrease in the molecular weight, leading to the formation of low molecular weight polymers or even oligomer products (Fig. 3). This phenomenon was well described by Takasu et al.[1] who discussed the biodegradability of emulsion copolymers based on polyvinyl acetate and saccharide derivatives. In the case the series of polymerizations initiated by the redox initiator system, a significant decrease in conversion occurred. For this reason, a thorough attention was focused on the series of lattices based on the initiation by means of hydrogen peroxide in later studies.

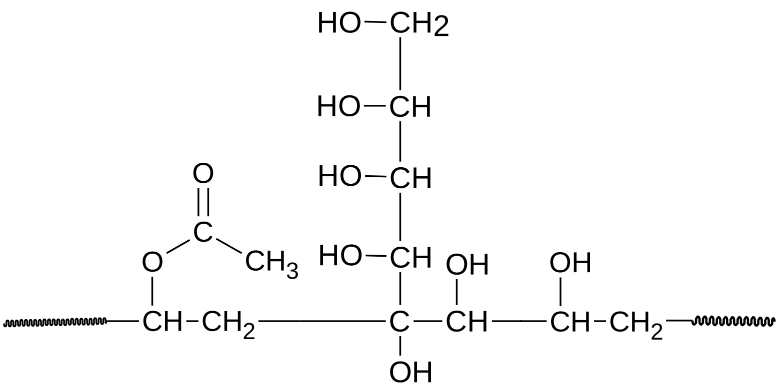

Figure 3: The attachment of glucose in a polymer chain composed of vinyl acetate and vinyl alcohol units

Results and Discussion

To prove the appearance of the saccharide units in the polyvinyl acetate chains, the infrared spectroscopy using the FTIR Nicolet 6700 instrument with a spectral resolution of 0.09 cm^{-1} with unlimited use in distant, intermediate and near infrared region of wave numbers length of 27 000 to 10 cm^{-1} was used. For separating the water-dissolved saccharide and lower-molar-mass polyvinyl alcohol (protective colloid) and thus ensuring the proper measurements of the prepared polyvinyl acetate polymer bearing saccharide units, the samples were precipitated in tetrahydrofuran and washed repeatedly with distilled water to give the polyvinyl acetate polymer portion which was analyzed by the aforementioned method.

Figure 4 is IR spectrum for the polyvinyl acetate sample containing sucrose. As indicated in the spectrum, saccharide units are located in the region of 1 000 – 1 100 cm^{-1}. Furthermore, absorption peaks of acetate groups and hydroxyl groups can be seen as well. Due to the alkaline hydrolysis of the acetate groups, not only alcohol, but also sodium acetate arises during the polymerization, which was also detected in the spectrum. For the comparison, Figure 5 shows an infrared spectrum of the polyvinyl acetate sample containing no saccharide units. This can be seen in the region of 1 000 – 1 100 cm^{-1} where no absorption peak was recorded. The spectrum shows the presence of vinyl acetate and vinyl alcohol units.

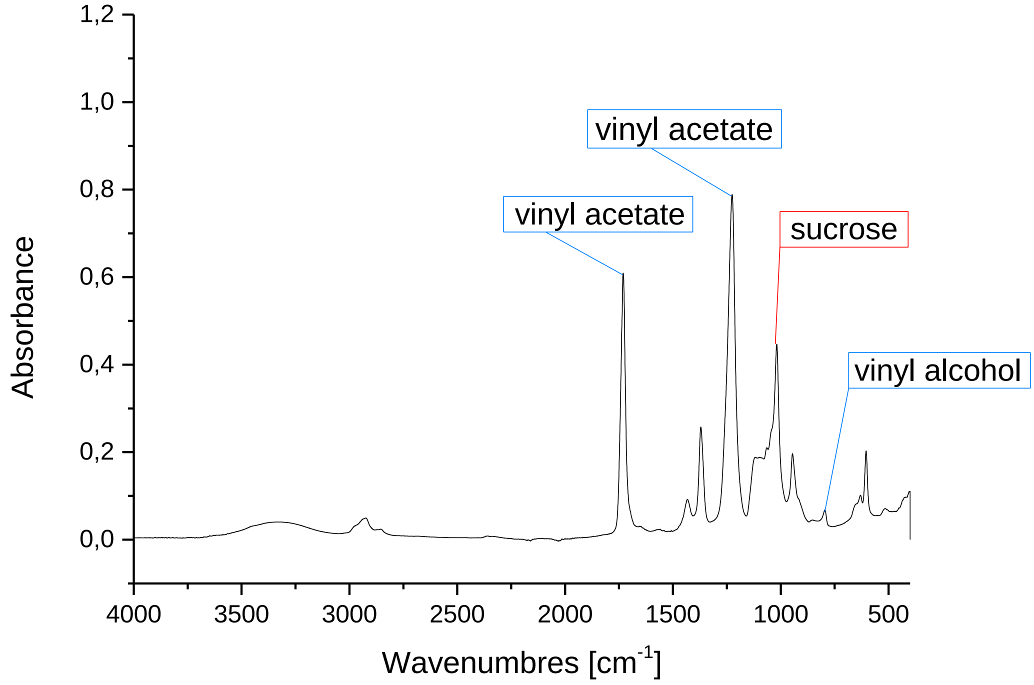

Figure 4: The infrared spectrum of a resulting polymer produced via the hydrogen peroxide-initiated polymerization of vinyl acetate and sucrose (the starting ratio of vinyl acetate and sucrose was 1/1)

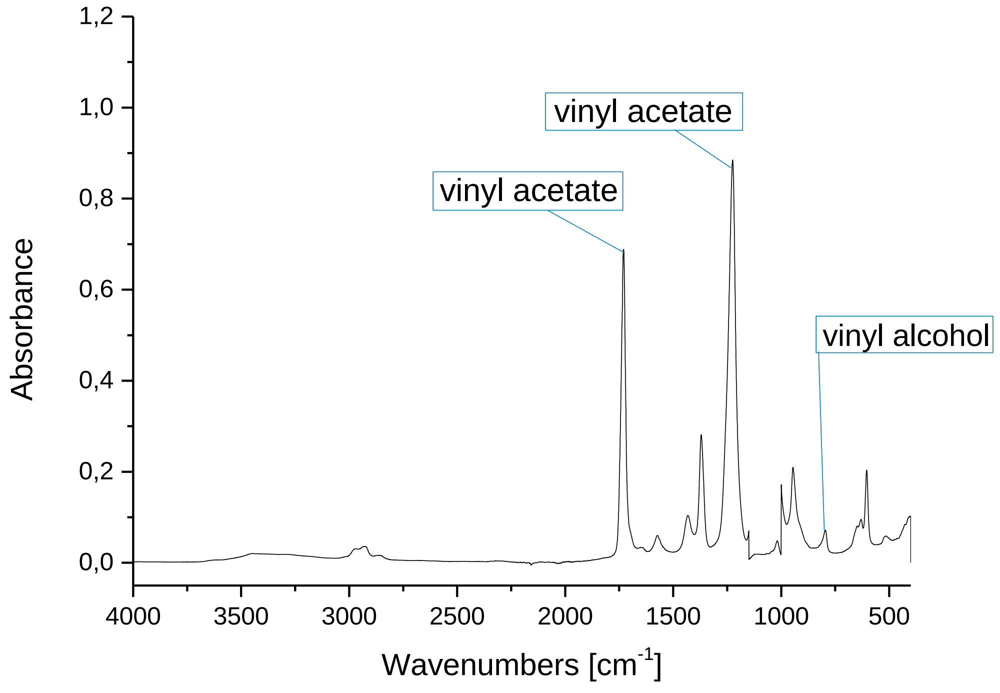

Figure 5: The infrared spectrum of a resulting polymer produced via the hydrogen peroxide-initiated polymerization of vinyl acetate

Conclusion

Currently, the biodegradability of the prepared materials is being tested according to CSN EN ISO 14855-1 based on the monitoring of CO_2 evolution measured by means of gas chromatography. This standard method is aimed to be confronted with the results of the degradability testing from the point of view of bacterial decomposition of inoculum (compost). The results of the latter test will be compared with international standards, the Organization for Economic Cooperation and Development (OECD). The tests are divided into two parts, the biological decomposition in the ground aerobic and anaerobic disintegration and a section of the substance in aqueous medium.

Reference

[1] A. Takasu, M. Baba, T. Hirabayashi; Preparation and biodegradation of sugar-containing poly(vinyl acetate) emulsions, *Macromolecular Bioscience* 2008, *8*, p193 – 198

[2] A. K. Patra, S. Dahiya; Microencapsulation – technique and applications, *Man-made in India*, 2009, *52*, p224 - 232

[3] J. Machotová, J. Šňupárek, L. Prokůpek, T. Rychlý, P. Vlasák; Effect of functionalized core-shell microgels prepared by emulsion polymerization on acrylic coatings properties, *Progress in Organic Coatings* 2008, *63*, p175 - 181

[4] I. D. Sideridou, D. S. Achilias, O. Karava; Reactivity of benzoyl peroxide/amine system as an initiator for the free radical polymerization of dental and orthopaedic dimethacrylate monomers: effect of the amine and monomer chemical structure, *Macromolecules* 2006, *39*, *p*2072 - 2080