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Physical behaviour of water dispersion glue system modified with organic wastes

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A new approach to the utilization of organic wastes discharged after biofuel production is proposed. Different amounts of glycerol-containing poly(vinyl acetate) glue samples were prepared and tested in order to examine the mechanical, rheological properties and stability to freeze / thaw cycles. Small amounts (up to 5%) of crude glycerol were found to improve freeze / thaw stability of dispersion and the elasticity of films. Samples containing up to 15% of crude glycerol fulfil D2 class requirements according to EN 204 and could be further used as a wood adhesive.

Introduction

During the last decade, environmental aspects of chemical industry have received much attention. The necessity to utilize by-products came along with strict governmental regulations on the handling of production wastes. In industry, biodiesel fuels are described as fatty acid methyl or ethyl esters from vegetable oils or animal fats, and they are used as fuel in diesel engines and heating systems [1, 2]. For every ton of biodiesel made from vegetable oil, 100 kg of crude glycerol is produced as a by-product. The annual 6.8 billion litres of biodiesel production in the EU yields around 680,000 tons of crude glycerol [3]. Regarding purification costs, crude glycerol is rather a waste than a raw material, because it cannot be disposed of in the environment. In recent years, some studies were published regarding crude glycerol utilization via fermentation process in order to produce hydrogen, ethanol [4], 1,3-propanediol as a basic ingredient of polyesters [5].

Pure glycerol is a well-known additive in cosmetics formulations, which improves the freeze / thaw stability of emulsion systems [6], and as a polymer plasticizer [7]. Thus, it should be possible to use crude glycerol as a cheap glycerol source in dispersion system modifications. The aim of the present investigation was to compare the properties of a plain poly(vinyl acetate) dispersion sample to samples modified with pure and crude glycerol.

Experimental

Poly(vinyl acetate) dispersion, modified with approx. 10% of plasticizer (“Lipalas DP51/10”) was purchased from SC “Achema” (Lithuania) and used as received. Crude glycerol as a byproduct of methyl ester production was provided by UAB “Mestilla”. The quality of crude glycerol is presented in Table 1. Pure glycerol (99%) was purchased from “Lachner” (Czech Republic) and diluted with distilled water to a concentration of 81.09% before use.

Table 1. Quality of crude glycerol

Parameters	Test method	Units	Results
Glycerol content	BS 5711-3	% (m/m)	81.09
Density at 20 °C	LST EN ISO 12185	kg/m^3	1260.2
Water	LST EN ISO 12937	% (m/m)	12.62
Methanol content	LST EN 14110	% (m/m)	0.05
Sulphated ash content	ISO 3987	% (m/m)	4.93
MONG (Matter Organic Non-Glycerol)	Calculated	% (m/m)	1.36

The samples were prepared by mixing poly(vinyl acetate) dispersion with 5, 10 and 15% by weight of pure and crude glycerol (Table 2). An IKA Yellowline OST 20 basic (Germany) lab mixer was used (rotation speed 200 rpm, mixing time 30 min).

Table 2. Composition of samples

Marking of composition	Dispersion modifying substances
1	Unmodified poly(vinyl acetate) dispersion
2	Poly(vinyl acetate) dispersion modified with 5% pure glycerol
3	Poly(vinyl acetate) dispersion modified with 10% pure glycerol
4	Poly(vinyl acetate) dispersion modified with 15% pure glycerol
5	Poly(vinyl acetate) dispersion modified with 5% crude glycerol
6	Poly(vinyl acetate) dispersion modified with 10% crude glycerol
7	Poly(vinyl acetate) dispersion modified with 15% crude glycerol

VISCOSITY MEASUREMENTS. The viscosity of the prepared samples was determined with a *Brookfield DV-I* (Brookfield, USA) viscosimeter, RV disc type spindle number 3, test temperature 25 ±1 °C. The shear rate and shear stress values were calculated by Mitschka' method [8]. The yield was calculated by Brookfield' method [9].

FREEZE / THAW CYCLES. The test was carried out according to the ISO 1147 standard. One freeze/thaw cycle consisted of 16 hours of freezing at -20 ±1 °C and the further keeping for 8 hours at 23 ±1 °C.

MECHANICAL PROPERTIES. Sample films were made by casting glue on a flexible plastic polyester sheet. The film thickness was obtained after drying for 10 days at room temperature. Test specimens were prepared by cutting strips (80 × 10 mm). Specimens were tested with a *Zwick/Roell BDO-FB 0,5TH* (Germany) machine. The speed of the crosshead was maintained at 100 mm/min. Specimens were tested for tensile strength (F_{max}), elongation (ε_R) and tensile stress (σ_B).

FILM HARDNESS. The film hardness was examined using a *Pendulum Hardness Rocker Ref.707* hardness tester (Sheen Instruments Ltd, England) by the Persoz method (12^o to 4^o).

Results and discussion

The impact of glycerol content on the initial dispersion viscosity is presented in Figure 1. Significant quantities of glycerol determine a high viscosity drop. The effect of pure and crude glycerol on dispersion viscosity behaviour was rather similar. A greater amount of glycerol shows a slight shear-thinning behaviour (very close to Newtonian fluid). However, small amounts of glycerol in a sample display a strong shear-thinning behaviour.

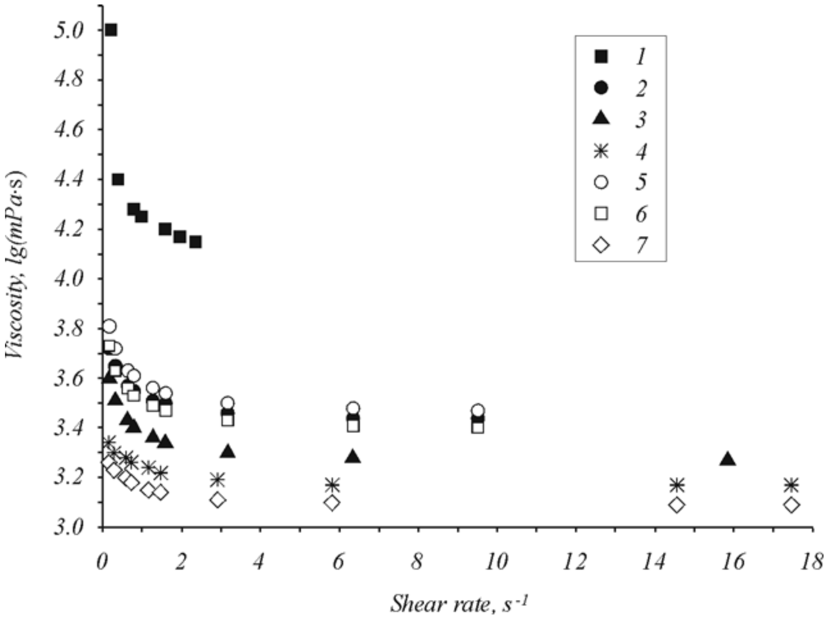

Fig. 1. Initial viscosities of prepared poly(vinyl acetate) samples

Dispersion viscosity increased dramatically after freeze/thaw cycles (Fig. 2). Nevertheless, samples modified with glycerol showed a better resistance to freeze in comparison with an unmodified sample. Sample condition after 9 freeze / thaw cycles is presented in Figure 3. The slightly brownish colour of samples 6 and 7 was determined by the crude glycerol colour. Crude glycerol is a brown liquid. An unmodified sample (1) looks like curd. Other samples have a consistence of the concentrated dispersion.

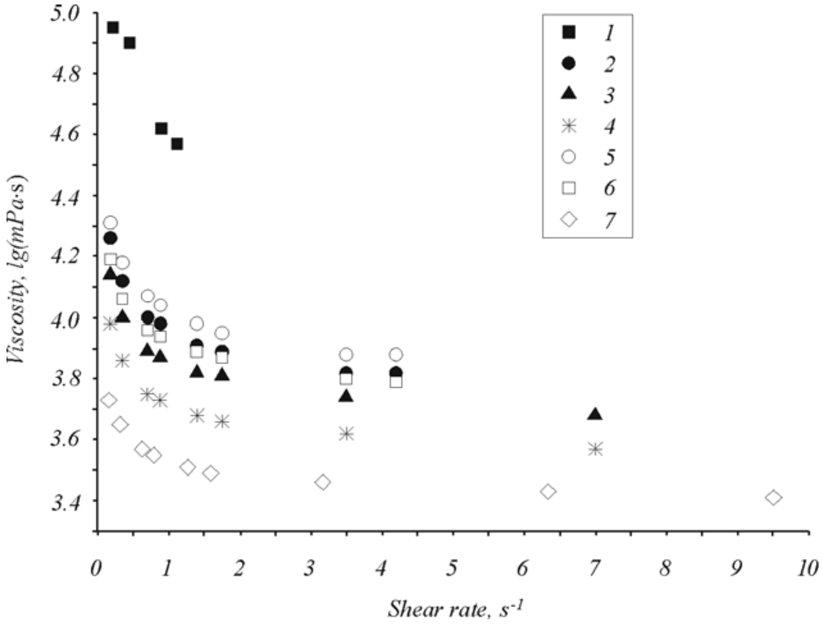

Fig. 2. Viscosities of prepared poly(vinyl acetate) samples after 9 freeze / thaw cycles

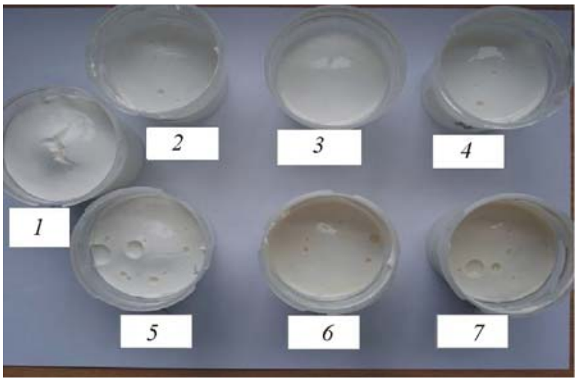

Fig. 3. Samples after 9 freeze / thaw cycles

Both crude and pure glycerol showed rather similar results. The higher viscosity after cycles could be explained by polymer structure changes. We found that the freeze / thaw cycles could determine the branching reaction of the polymer [10]. Glycerol in this case had a positive effect and reduced the branching reaction due to the lower freezing point of a watered system.

Some fluids behave much like a solid at a zero shear rate. They will not flow until a certain amount of force is applied, at which time they will revert to fluid behaviour. This force is called “yield value”. Figure 4 demonstrates a high dependence of the yield value on glycerol content in a poly(vinyl acetate) composition as well as on freeze / thaw cycles.

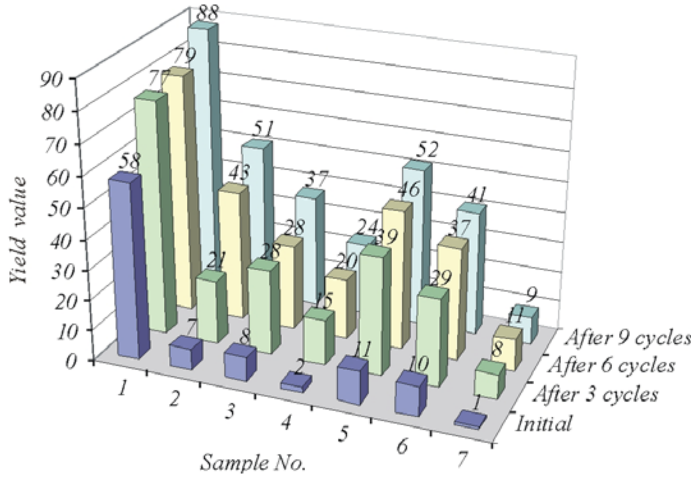

Fig. 4. Yield value dependence of the samples on freeze / thaw cycles

Yield value reduction at higher amounts of glycerol was obtained. This could be due to a lower aggregation of particles in the presence of glycerol which works in this case as a non-ionic surfactant. Thus, a lower force is required to dissipate the agglomerated components of the dispersion.

The mechanical behaviour of polymer films was investigated. Film hardness changes of the initial samples and after 9 freeze / thaw cycles are presented in Figure 5. Glycerol was found to reduce film hardness. However, no obvious differences between samples modified by crude and pure glycerol were detected. The influence of freeze / thaw cycles on the unmodified film was approx. twice higher in comparison with the film modified with glycerol. In both cases the freeze / thaw cycles determine formation of a greater mechanical strength of films, and this proves the presumption of the branching reactions that proceed during freeze / thaw cycles. Furthermore, the branching reaction proceeds much slower when glycerol is added to a glue system.

The tensile strength and tensile stress of prepared films are presented in Figures 6 and 7. The effect of glycerol (up to 5%) on film tensile strength was rather insignificant. Nevertheless, greater amounts of glycerol reduced film strength significantly. Films prepared after 9 freeze/thaw cycles showed a higher tensile strength and tensile stress values in comparison with films of initial samples.

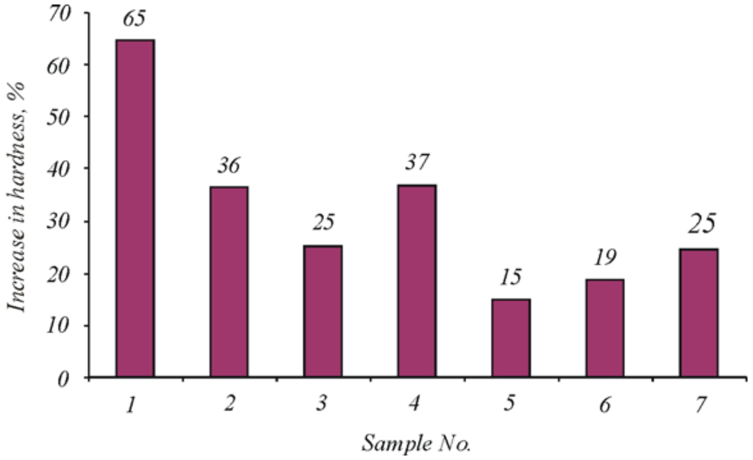

Fig. 5. Increase in hardness after 9 freeze / thaw cycles

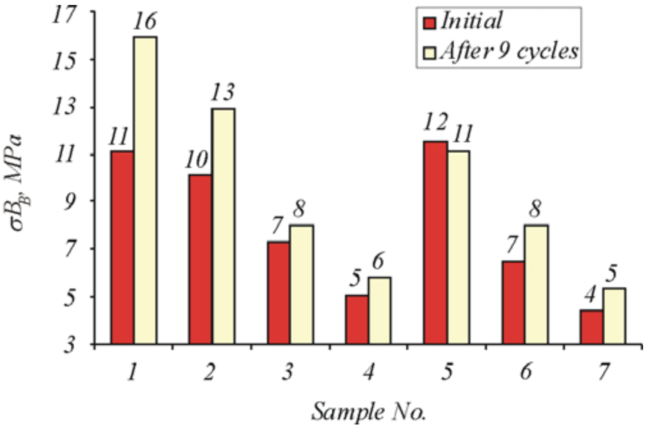

Fig. 6. Tensile strength of the films

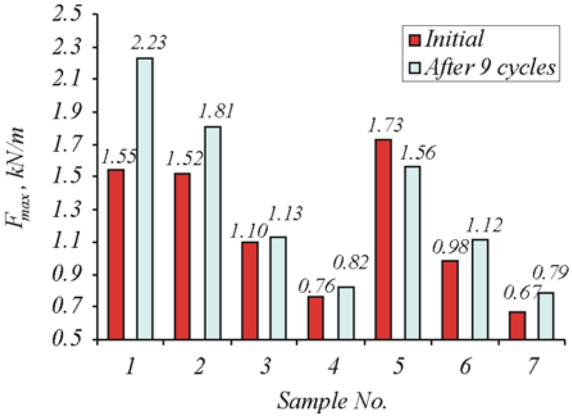

Fig. 7. Tensile stress of the films

As shown in Figure 8, small amounts of glycerol (up to 5%) improved the elasticity of films and worked as a plasticizer. However, a higher than 5% glycerol content reduced the mechanical properties of the film. Poor mechanical properties could be explained by la weak interaction among the particles (cohesion) during film formation. High amounts of water-soluble surfactants can decrease the water resistance and mechanical properties of the film. Thus, they should be used at minimal concentrations [11].

Bond strength and its water resistance were assessed in accordance with the European standards EN 204 [12] and EN 205 [13]. Tests with beech timber were carried out according to the first and second (resistant to moisture) series of the EN 204 standard. The effect of pure and crude glycerol on bond strength and on freeze / thaw cycles was determined. The results are presented in Figures 9 and 10.

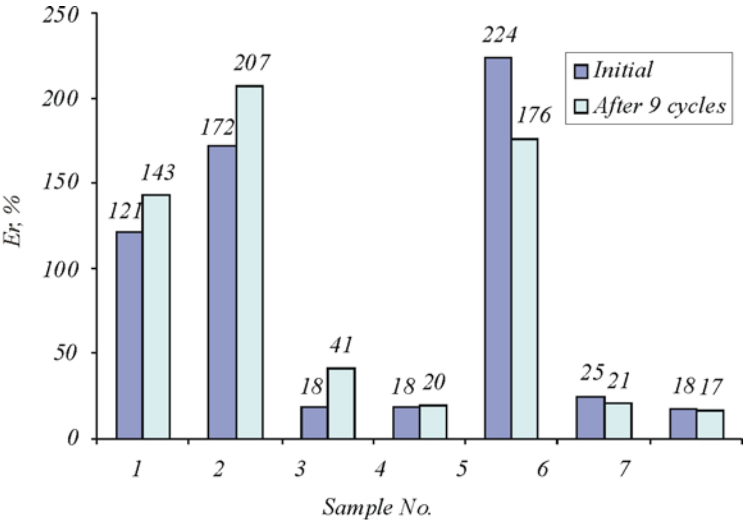

Fig. 8. Elongation at break of films – initial and after 9 freeze / thaw cycles

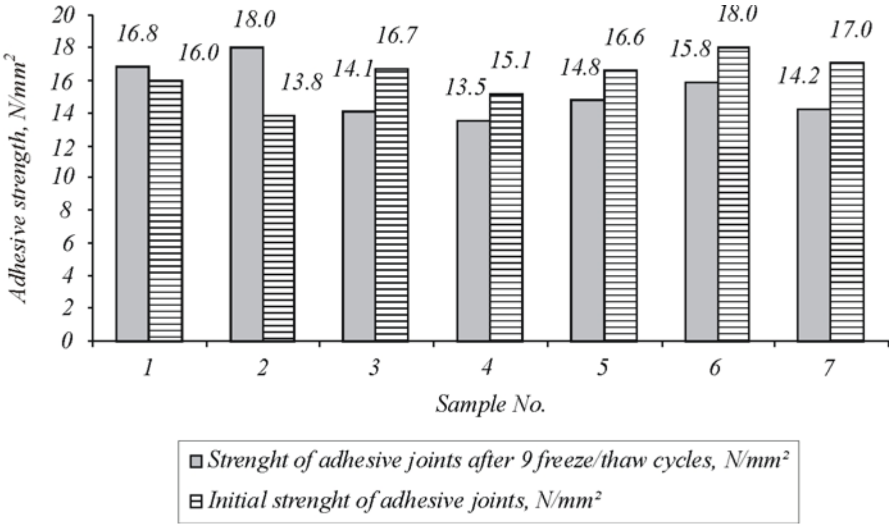

Fig. 9. Dependence of adhesive joint strength according to conditioning sequence No.1 on the amount of pure and crude glycerol and on freeze / thaw cycles

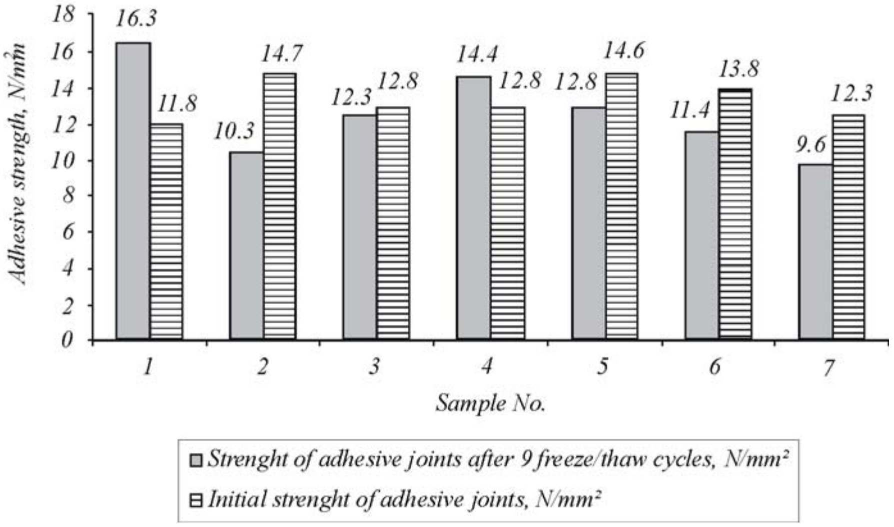

Fig. 10. Dependence of adhesive joint strength according to conditioning sequence No.2 on the amount of pure and crude glycerol and on freeze / thaw cycles

According to results presented in Figures 9 and 10 the effect of glycerol amount on bond strength was rather low. Because of a great variation of test results, no reliable dependence of glycerol content in the sample on bond strength was defined. All samples with a different glycerol content fulfilled D2 class requirements of the European standard EN 204.

Conclusions

1. Crude glycerol could be used for viscosity control in poly(vinyl acetate) glue compositions. However, greater amounts of glycerol could determine the poor mechanical properties of films. Thus, the optimal content of glycerol should not exceed 5%.
2. Both crude and pure glycerol improved freeze / thaw stability of the final product. The polymer branching reaction proceeded slower in glycerol-modified samples.
3. No significant effect of glycerol content on wood glued-bond strength was observed. All samples fulfilled D2 class requirements of the European standard EN 204 and could be further used as a wood adhesive.

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VANDENS DISPERSINIŲ KLIJŲ, MODIFIKUOTŲ ORGANINĖMIS ATLIEKOMIS, FIZINĖS SAVYBĖS

Santrauka

Organinės atliekos, susidarančios biokuro gamybos metu, buvo panaudotos vandens dispersinių klijų modifikavimui. Polivinilacetatinės dispersijos buvo sumaišytos su skirtingu kiekiu organinių atliekų, kurių pagrindinis komponentas yra glicerolis. Ištirtos kai kurios mechaninės, reologinės ir atsparumo šaldymo / šildymo ciklams savybės. Mažas kiekis (iki 5 %) atliekinio glicerolio padidina dispersijos atsparumą šaldymo / šildymo poveikiui bei plėvelių, gautų iš šių dispersijų, elastingumą. Dispersijos, kuriose glicerolio priedo kiekis ne didesnis kaip 15 %, atitinka EN 204 standarto D2 klasės klijams keliamus reikalavimus ir gali būti naudojamos kaip klijai medienai.

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