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Sugar Latexes as a New Type of Binder for Water-Based Paint and Coating

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Summary: Sugar latexes based on saccharid derivatives, such as 3-MDG, 1- or 3-MDF and ITDF, have been synthesized in batch and semi-continuous emulsion polymerization. The polymerizations were carried out at 60 or 70°C, initiated by potassium peroxodisulfate, (KPS), in the presence of either ionic or non-ionic surfactant. The effect of the type and concentration of the surfactant and the type of polymerization process on the colloidal and rheological properties was studied. It was found that the particles size increased with using a non-ionic surfactant. Monodisperse particles were obtained by using SDS below its CMC, and smaller polydisperse latexes were observed when the SDS conc. was above the CMC. The latexes exhibit different non-Newtonian flows depending on the solid content and on the additives.

Keywords: sugar monomers; emulsion polymerization; sugar latexes; rheology

Introduction

Water polymer dispersions based on renewable present a new type of binders for a wide range of applications especially for paint and coating. From point of view of environment protection, sustainable development and also new properties, we believe that these polymer dispersions present a high challenge for chemists and industries. Furthermore, they offer a serious alternative for limited petrochemical resource.

Low molecular carbohydrates such as Saccharose (from sugar beet), D-glucose (from starch) and D-fructose (from innulin), are available in a large industrial scale, low cost, exhibit high pure grades quality and permanent reproducibility. They are suitable as sources for sugar monomer synthesis. Figure 1 shows some examples of sugar (meth)acrylates such as 3-MDG, 1-MDF, 3-MDF and itaconic ester, ITDF.

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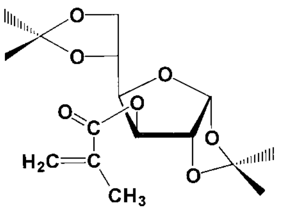
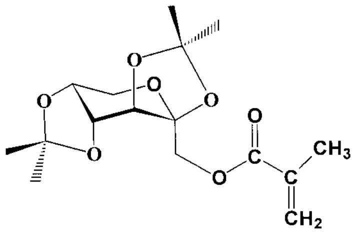
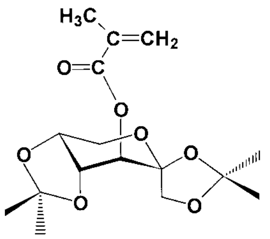


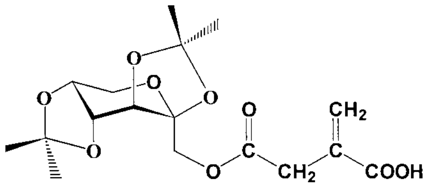
3-*O*-Methacryloyl-1,2:5,6-di-acetone-glucose (3-MDG)



1-*O*-Methacryloyl-2,3:4,5-di-acetone-fructose (1-MDF)



3-*O*-Methacryloyl-1,2:4,5-di-acetone-fructose (3-MDF)



Itaconic- 4-(2,3:4,5-di-*O*-isopropylidene-ß-D-fructopyranose)ester (ITDF)

Figure 1. Sugar monomers based on monosaccharides.

As comonomers for radical emulsion polymerization either the commercially available petrochemical monomers, such as butyl and 2-ethyl hexyl (meth)acrylate, or comonomer based on fats and oils, such as fatty alcohol (meth)acrylate or vinyl esters, could be choice for tailor made polymeric materials.

The use of such renewable based monomers in free radical emulsion polymerization, using various processes such us batch, semi-continuous or seed polymerization, lead to new tailor made polymer dispersions with various structures and morphologies. These nanoparticles exhibit interesting thermal, mechanical and rheological properties.[1-4] Example of copolymer latexes with different colloidal, chemical and physical properties are discussed.

Batch emulsion copolymerization

Batch emulsion copolymerization of 3-MDG and butyl acrylate (BA) was investigated at 70°C. First, the monomer reactivity ratios, $r_{(3\text{-MDG})}$ and $r_{(BA)}$, were determined at 10 wt.-%

solid content, using 0.5wt.-% potassium persulfate (KPS), and 5 wt.-% sodium dodecyl sulfate (SDS). The emulsion copolymerizations were carried out using different mixture of 3-MDG and BA in feed. The reactions were quenched at low-conversion, the copolymer composition were determined from ^{1}H NMR and the monomer reactivity ratios were calculated. The values were found to be $r_{(3\text{-MDG})} = 2.01$ and $r_{(\mathrm{BA})} = 0.54$.[3] In that case, 3-MDG is more reactive than the BA and consequently the polymer particles are richer with the harder segment (3-MDG) on the interior and the softer segment (BA) on the exterior. The Figure 2 shows the schematic structure of the copolymers.

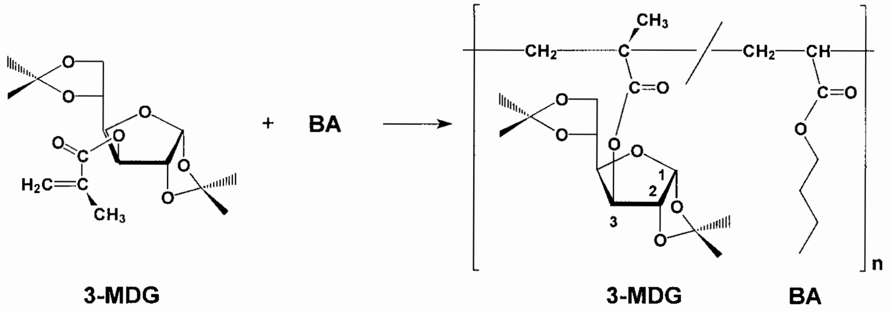


Figure 2. Schematic presentation of 3-MDG/BA copolymer.

Sugar latexes were synthesized using other comonomers than alkyl (meth)acrylate. Itaconic esters derived from fatty alcohols and itaconic acid were used as comonomers. The influence of the aliphatic structure of fatty alcohol esters on the rate of polymerization was studied. The emulsion polymerization of 3-MDG and itaconic acid pentyl ester (ITSPE) was carried out at 70°C, at 15 wt.-% solid content and using fatty alcohol polyether sulfate as ionic surfactant (Disponil FES® 32 IS, Cognis). The reaction was followed by gas chromatography. Figure 3 shows the monomers and the total conversion versus time. It can be observed that the sugar monomer is more reactive than the itaconic ester. After 6h the polymerization is nearly complete. More than 99% yield was obtained.

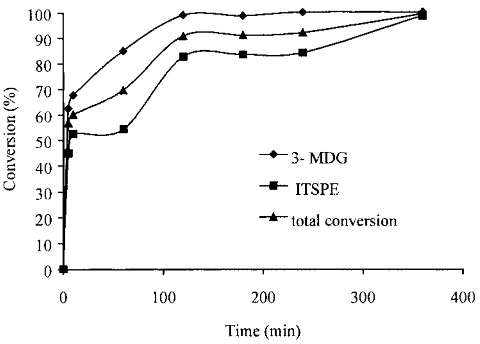


Figure 3. Time-conversion curve of batch emulsion copolymerization of 3-MDG/ITSPE.

Thermal behavior

Figure 4 shows the relationship between glass transition temperature (T_g) of (3-MDG/BA) copolymers and the sugar content in the corresponding copolymers. As expected, a small quantity of glucose units in the copolymer is sufficient to enhance obviously the glass temperature. Furthermore, from the plot it can also be observed that the glass temperature of the copolymers is strongly dependent on the polymer composition. The T_g increased nearly linearly with increasing the sugar moieties up to 100 mol-% in the copolymers Due to the rigidity of the sugar units as cyclic structure, it is though that saccharide moieties affect the flexibility of the polymeric chain and consequently enhance the T_g.

Semi-continuous emulsion copolymerization

Four experiments were carried out with different monomer addition rates (R_m) in order to study the effect of addition rate on the polymerization rate. The solid content was 20 wt.-% and SDS was used as an ionic surfactant with a concentration of 5 g/L. The reaction was carried out at 70°C under mild agitation. A two titrating pumps were used to feed separately the monomer mixture (3-MDG/BA; 35/65 mol%) and the initiator solution. The flow rates of these streams were in the range from 0.12 to 0.44 g/min and were kept constant during all the polymerization. The monomer feed was low enough to ensure monomer starved conditions.

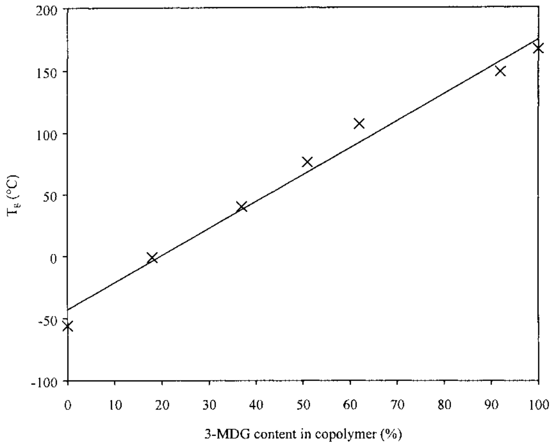


Figure 4. Effect of the sugar content in the (3-MDG/BA) copolymers on the glass transition temperature T_g.

Figure 5 shows the conversion-time curves at different monomer addition rate. The reaction rate in batch process is very high, more than 95% total conversion was reached after only 15 min. In semi-continuous reaction, the polymerization rate (R_p) is strongly depending on R_m. Under these conditions, R_p increases with increasing R_m. At the beginning of the addition of monomer, a finite time is required before the steady-state value of $[M]_p$ is reached. Initially, therefore, there is a gradual increase in R_p as the value of $[M]_p$ increase to its steady-state. R_p was calculated experimentally from the slopes of the nominally linear regions of the total conversion. It was found that the monomer addition rate (R_m) and the calculated reaction rate (R_p) are the same, which means all the reactions were in starved-feed condition.

Effect of the type and concentration of surfactant

The effect of the type and the amount of surfactant on colloidal characteristics, namely particle size (D) and particle size distributions (PSD) and rheological properties of the sugar latexes were investigated. Different anionic surfactants such as sodium dodecyl sulfate (SDS, Merck), sodium lauryl ether sulfate (SLES, Henkel), sodium alkylphenyl polyglycol ether sulfate (NOS10, Wittco) as well as the non ionic surfactant nonylphenyl polyglycol ether (HV25, Wittco) were used above their critical miccellar concentration (CMC). It was found that the surfactant type has a little influence on the reaction rate. Nevertheless, the number of particles and the particle size (*D*) are strongly related to the type of surfactant.

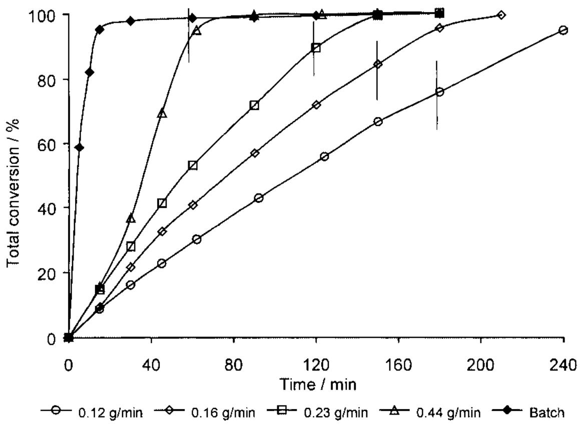


Figure 5. Effect of the monomer addition rate on the total conversion against time for batch and semi-continuous emulsion copolymerization of (3-MDG/BA) at 70°C.

By using anionic surfactants, the particles size slightly enhances during the reaction (Figure 6). The *D* are smaller by using ionic surfactants than that of the case of non ionic surfactant HV25. This is due to the art of particles stabilization, which could be ionically or sterically nature. The ionic stabilization of the formed particles results from the negatively head charge of the surfactant as well as from the sulfate charge, which arises from the initiator derived polymers end-group. This leads to the increasing of the surface charge density of the particles and allowed a high stability through greater mutual repulsion forces. In the case of HV25, in which the polymer particles are stabilized sterically, the *D* increased drastically during the polymerization reaction. This could be due to the poor stability of the polymer particles. These are not enough stabilized by the non ionic surfactant to counteract the increase in the ionic strength. It is also conceivable that this increase in particles size may cause the burial of more HV25 surfactant within the particles. As consequence coagulation takes place and the size of particles increases.

Furthermore, the concentration of the surfactant has a great effect on the particles size (D) and their distributions (PSD). Two sugar latexes have been synthesized by semi-continuous emulsion copolymerization, using SDS as ionic surfactant at two different concentrations, above and below the CMC. Figure 7 clearly shows this effect on the particle size and the PSD

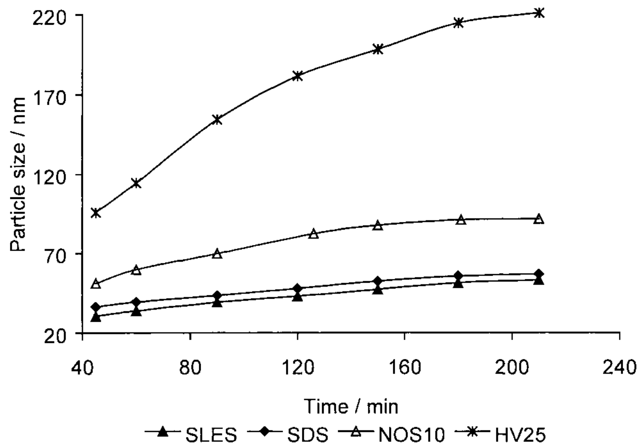


Figure 6. Effect of the surfactant type on the particle size (*D*) against time for semi-continuous polymerization of (3-MDG/BuA); SDS, SLES, NOS10 and HV25 were used as surfactant with a concentration 5 g/L.

measured by transmission electron microscopy (TEM). Below the CMC, monodisperse particles were obtained with D of 120 nm and a PSD of 0.04. Above the CMC, the particles are smaller (D= 61 nm) and polydisperse (PSD = 0.07).

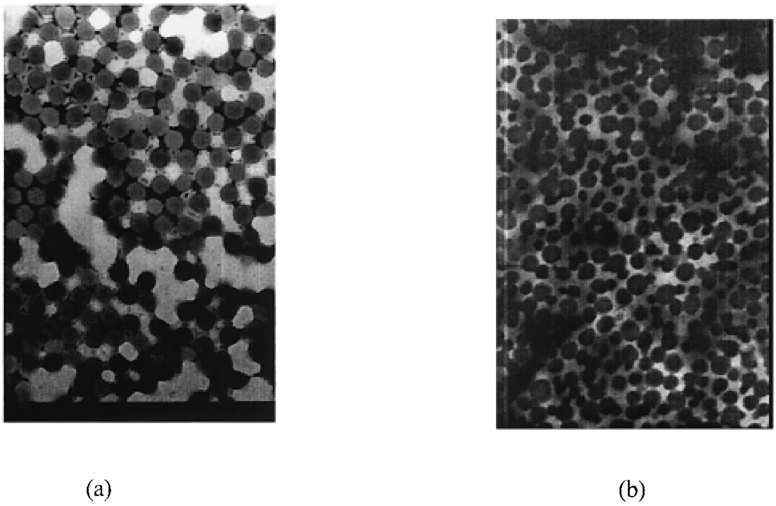

(a) (b)

Figure 7. TEM of (MDG/BA) latex synthesized by semi-continuous emulsion polymerization; (a) [SDS]<CMC, D = 120 nm and PSD= 0,04 ; (b) [SDS]>CMC, D = 61 nm and PSD = 0,07.

Rheological properties

It is well known that the rheological properties of the latexes are strongly dependent on the particle size, the particle size distribution, the solid content and from other factors such as the functional groups on the particle surface. The effect of these parameters on the rheological behavior of latexes is of great practical importance. The flow behavior of (3-MDG/BA) latexes, synthesized by batch emulsion polymerization at 30 wt.-% solid content, with 5 wt.-% acrylic acid (AA), was investigated. The shear stress-shear rate curves of the sugar latexes at room temperature are shown in Figure 8 a and b. Both latexes exhibit non-Newtonian flow. Before and after neutralization, the shear stress (τ) and shear rate ($\dot{\gamma}$) are not linearly related. Before neutralization, the curve flow shows that the shear stress increases by increasing the shear rate and the viscosity increases with increasing shear rate (Figure 8a). After neutralization, τ increases by increasing $\dot{\gamma}$ rate and the viscosity decreases with increasing shear rate (Figure 8b).

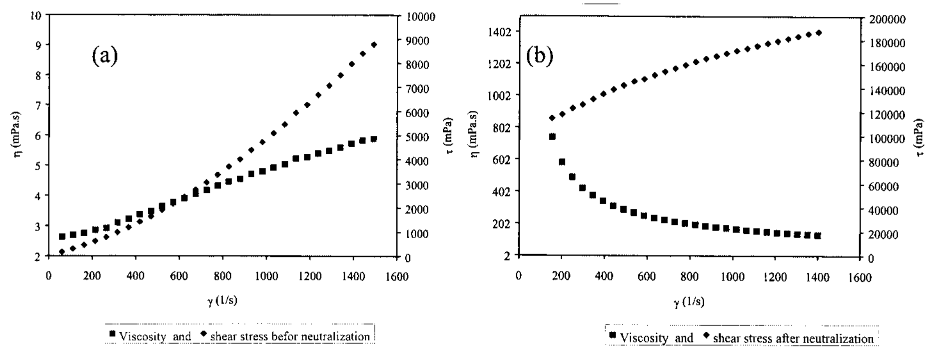


Figure 8. Evolution of shear stress (τ)-viscosity (η) versus shear rate ($\dot{\gamma}$), for a sugar latex at 25 wt.-% solid content. 3-MDG and BA were polymerized with 5wt.-% AA. Measurements were carried out at room temperature. (a) before neutralization; (b) after neutralization.

It can be assumed that in the first case, the behavior characterizes pseudoplastic flow or shear thinning and in the second case, a shear thickening flow (dilatent).

The flow behavior of sugar latexes at different solid contents (Ts) was investigated at room temperature. Figure 9 shows the different flow behaviors at 20 and 50 wt.-% solid content. At low solid content the sugar latex exhibits a Newtonian flow and the measured latex viscosity at the shear rate 1000 s^{-1} was 3.5 mPa.s. At higher solid content (50%), the sugar latex exhibits a non-Newtonian flow, e.g. shear thinning, in which the viscosity decreases with increasing shear rate. The constant, minimum value of the latex viscosity was 150 mPa.s at the shear rate of 1000 s^{-1}.

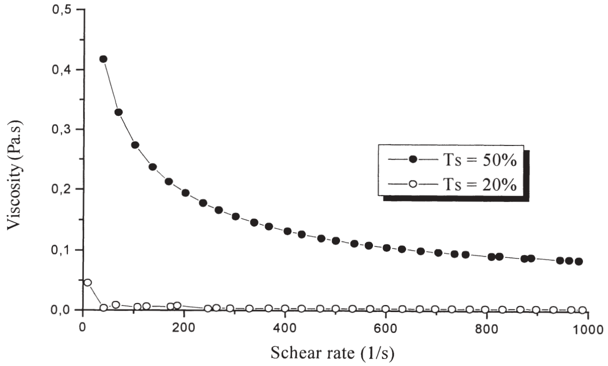


Figure 9. Evolution of the viscosity (η) versus shear rate ($\dot{\gamma}$), for two sugar latexes at 20 and 50 wt.-% solid content. Measurements were performed at room temperature.

Conclusions

It has been shown that the sugar monomer polymerized much faster than the BA and ITSPE. The glass transition temperature of the copolymers are linearly related to the monomer mixture in feed. The particle size and particle size distribution of the sugar latexes were strongly dependent on the type and concentration of the surfactant and on the type of polymerization process (batch or semi-continuous). The investigation of the rheological properties showed that the sugar latexes exhibit a non-Newtonian flow, e.g. shear thinning, at high solid content. Furthermore, two different non-Newtonian flows were observed depending on the pH of the latex solution when acrylic acid is used. Shear thickening flow and pseudoplastic flow or shear thinning were obtained before and after neutralization respectively.

References

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