Oxypropylation of sugar beet pulp. 1. Optimisation of the reaction

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Abstract

An oxypropylation reaction was carried out by suspending sugar beet pulp in propylene oxide in the presence of a basic catalyst and heating the resulting mixture under pressure. Optimisation of the conditions (pulp granulometry, type and amount of catalyst, relative proportion of pulp with respect to propylene oxide, amount of residual moisture and temperature) allowed quantitative conversion of the pulp into polyols possessing different viscosities and OH numbers. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The purpose of this investigation was to find a useful industrial application for sugar beet pulp (SBP) which is a waste product left after the extraction of sugar from the beet. Usually, this product is returned to the farmers to be used as feed for ruminants. In recent years, however, research has started in order to find new uses for SBP (Vogel, 1990; Dinan et al., 1996). In those papers, the constituents of the pulp were separated in order to use them as such (e.g. microfibrils) or as a source of chemicals (e.g. ethanol through biotechnology). To the best of our knowledge, no corresponding work has been published on the global chemical modification of SBP. We sought this research because the polysaccharide nature of SBP (rich in hydroxy groups) seemed a potential property to exploit as a whole, without the burden of separating its components and with the additional advantage of using this waste without creating another one. The problem was then how to convert all its various solid components into a homogeneous liquid product, soluble in common solvents and bearing a high content of accessible OH groups. Such a product would obviously be a suitable candidate for use as a typical polyol in the manufacture of polyurethanes. Oxypropylation appeared as the most promising procedure to achieve this goal.

The reaction of oxypropylation has been extensively applied to renewable resources and more
particularly to various types of saccharides, including monomers, oligomers and polymers. The main scope of these chemical modifications of natural substances is to obtain polyols, in the form of viscous liquids, which can be interesting comonomers in the manufacture of polyurethanes. The large number of OH groups available per saccharide molecule makes them attractive and a cheap potential substitute for petroleum-derived counterparts. Thus, natural polymers, such as starch from rice (Seow and Thevamalar, 1993), potato (Hjermstad and Rapids, 1971; Kim et al., 1992; Lammers et al., 1993), maize (Wootton and Manatsathit, 1983), cellulose (Patton, 1971; Lee and Perlin, 1982), chitosan (Velasquez-Morales et al., 1998) and simple sugars such as sorbitol (Woods, 1987), but also glycerol (Pruitt et al., 1960; Yost et al., 1967), have been submitted to oxypropylation in this context. Other vegetable renewable resources such as lignins from various biomass refinery processes (Hsu and Glasser, 1975, 1976; Wu and Glasser, 1984; Yoshida et al., 1987) have also been investigated with respect to this reaction. In all instances, the basic object of this exercise was to move the OH groups outside the main molecular core of the substrate and thus render them much more accessible to the terminal NCO groups in the polycondensation reactions leading to polyurethanes. Moreover, organised structures associated with both small and large molecules, particularly unreactive because of their crystalline morphology, are in this way converted into liquid polyols possessing the same aptitude to react with NCO functions as their originally amorphous homologues.

A variety of experimental conditions have been applied to the oxypropylation of these natural products. Most of the work has been carried out using Brønsted and Lewis bases as catalysts (De Groote, 1953; Hsu and Glasser, 1975, 1976; Hornof and Hombek, 1990), but acids have also been tested (Glasser and Hsu, 1977; Glasser et al., 1981; Still et al., 1986). These catalysts were added either as solid pellets or as solutions in a specific solvent or, whenever possible, in the substrate. Reactions have been conducted both in bulk or using a solvent ranging in polarity from water (Hjermstad and Rapids, 1971; Leegwater and Luten, 1971; Wootton and Manatsathit, 1983) to toluene (Glasser and Hsu, 1977; Glasser et al., 1983). A wide range of reaction temperatures has been explored, going from ~40°C (Hjermstad and Rapids, 1971; Leegwater and Luten, 1971; Wootton and Manatsathit, 1983; Kim et al., 1992; Lammers et al., 1993) all the way to 250°C (Glasser and Hsu, 1977; Kang et al., 1980), depending on the specific system. These reactions were usually carried out in an autoclave and the progressive decrease in the pressure of propylene oxide was a convenient means of following the rate of its consumption. The propylene oxide was added in one or several steps depending on the study.

It is stressed that the numerous papers and patents which cover the present topic are typically quite empirical in their approach and little is available in the published literature about a more rigorous and argumented study on how to optimise the oxypropylation reaction for a given substrate.

2. Experimental

2.1. Starting materials and reagents and reactor

Sugar beet pulp, used as the initial product, was a solid, partly crystalline, mixture of oligomeric and polymeric pentoses and hexoses (Vogel, 1990). Its actual composition in organic matter was 23% cellulose, 31% hemicelluloses, 18% pectines, 5% sucroses, 4% lignin and 8% proteins. The average OH molecular functionality was therefore high. This product was insoluble in all common solvents and therefore its thorough characterisation was difficult.

The propylene oxide, catalysts and solvents used in this study were high-purity commercial products.

Reactions were carried out in a 1-l stainless steel autoclave equipped with a mechanical stirrer and a manometer. Its contents were heated by a silicone oil bath whose temperature was constantly monitored.
2.2. Operating procedure

The typical procedure adopted to conduct the oxypropylation of SBP is summarised as follows. The pulp, catalyst and propylene oxide (PO) were placed in the reactor. The catalyst was then added as pellets, in the case of KOH or NaOH, or as a liquid, in the case of tertiary amines. The reactor was closed and its contents heated at temperatures from room temperature up to ~170°C. The reaction was followed by monitoring the pressure inside the reactor (which never exceeded 8 bar when 100 ml of PO were used) and was considered finished when the pressure returned to atmospheric levels or stabilised with time. The reactor was then cooled and the product recovered.

The basic catalyst was neutralised by adding the required amount of a solution of tartaric acid in ethanol.

The whole mixture was stirred with a large excess of dichloromethane. In certain instances, this operation resulted in partial dissolution, in others, complete dissolution occurred. In the former case, the suspension was filtered and both parts were vacuum dried to constant weight, whereas in the latter case, the solvent was simply eliminated in a rotary evaporator and the resulting polyol vacuum dried to constant weight. In other words, in these isolation procedures, only the volatile components of the mixtures were eliminated, i.e. any residual PO and the solvents. The product thus contained unreacted SBP (if any), oxypropylated SBP (viz. a mixture of polysaccharides bearing different initial structures and molecular weights and different extents of oxypropylation in terms of both degree of substitution (DS) and length (DP) of grafts), PPO homopolymer and the salts arising from the neutralisation of the basic catalysts.

Given the heterogeneous nature of the oxypropylation reactions we studied, reproducibility was poor. In order to obtain reliable data, any given reaction was repeated twice or several times and the results reported below reflect the corresponding average values. However, the scatter in these figures were modest, never exceeding 10%.

2.3. Characterisation

The products obtained in the different reactions were characterised by FTIR spectroscopy with a Perkin-Elmer Paragon 1000 spectrometer.

The hydroxy index or OH number \( I_{\text{OH}} \) is obviously an important parameter in the characterisation of polyols used as monomers for polyurethanes. By definition, this parameter is the number of milligrams of potassium hydroxide equivalent to the hydroxy content of 1 g of the polyol. \( I_{\text{OH}} \) was determined following the ASTM D1638 standard, which consists of dissolving a weighed amount of product in pyridine, treating it with a known excess of phthalic anhydride under reflux for 1 h and back-titrating the unreacted mixture of acid and anhydride. The titration of these solutions was carried out using an automatic potentiometric titrator (Mettler DL 21) equipped with a glass DG 111 electrode.

All materials were also characterised by their thermal properties in order to obtain the respective glass transition temperatures (by DSC) and the degradation pattern (by TGA). These measurements were carried out with a Setaram analyser in a stream of helium, scanning at 10°C min\(^{-1}\).

The viscosity of the polyols was determined at 20°C with a cone-plate CSL\(^2\) 500 rheometer from TA Instruments working in a stress-controlled mode, using a 2-cm diameter, 4° top-angle cone.

3. Results and discussion

3.1. Effect of SBP granulometry

Three sets of identical reactions were carried out in which the only variable was the granulometry of the SBP, namely ground pulp (average particle diameter 0.5 mm), crude pulp (large fibrous dispersion, ranging in length from a few mm to a few cm and with a diameter of ~1 mm) and pulp in pellets (cylinders 1 cm in diameter and a few cm in length). A total of 100 ml of PO was added to 10 g of SBP and 2 g of potassium hydroxide. After 4 h, the reactions had stopped and the products showed a marked difference in
aspect, related to the progressive difficulty of attack by the PO as the SBP gained in coarseness. This observation was corroborated by the fact that the extent of product insoluble in methylene chloride increased from 0 to \( \sim 60\% \) when going from the ground SBP to the pellets.

Clearly, the fundamental difference among these reactions arose from the variable steric hindrance related to the availability of the OH groups: those in the ground pulp were the most accessible to PO, whereas those in the pellets had the lowest reactivity. The insoluble residue from the latter substrate showed indeed that the fibrous structure had only been attacked superficially.

The viscosity of the soluble fractions of each reaction product confirmed that the extent of oxypropylation had been the highest in the case of the ground pulp (49 Pa·s), lower with the crude samples (9.5 Pa·s) and lowest with the pellets (4 Pa·s).

The ground pulp (GP) was therefore adopted as our standard substrate for the rest of the study.

3.2. Effect of the nature of the catalyst

A total of 10 g of GP, 2 g of catalyst and 100 ml of propylene oxide were introduced into the reactor. Then four different catalysts were used in order to compare their activity under the same experimental conditions, viz. KOH, NaOH, triethylamine and 1,4-diazobicyclo[2.2.2]octane (DABCO).

The most important difference among these reactions was the time and the yield. The two hydroxides appeared to be the best catalysts, KOH being slightly superior. In fact most of the pulp was transformed into a soluble viscous polyol with them. Between the two tertiary amines, DABCO gave better results, as shown by the higher percentage of soluble product, but both reactions were slow and the pressure of PO did not drop to low values, suggesting that they had lost activity during the reaction.

The above results determined our choice of KOH as the best catalyst, which was thereafter used for all experiments.

3.3. Effect of the amount of KOH

In this series of four different reactions, the percentage of KOH ranged between 1 and 30 by weight in relation to the amount of GP (here 10 g). The quantity of propylene oxide added was 100 ml. All oxypropylations reached completion and gave entirely soluble products, except for those conducted with 1% KOH which left about 10% residue.

The viscosity of the soluble fraction of each reaction product showed that the optimal percentage of KOH was 10%, as shown in Fig. 1. The
criterion chosen to assess this choice was based on the fact that for the three reactions which had given totally soluble products, the decrease in viscosity of the product must have been related to a corresponding increase in the proportion of homoPPO, which is the product having by far the lowest molecular weight in these systems (Pavier and Gandini, 1999a). In other words, too high proportions of catalyst seem to favour the homopolymerisation of PO to the detriment of the grafting of polysaccharide chains by oxypropylation.

The concentration of KOH adopted for the pursuit of this study was therefore 10% w:w with respect to the GP.

3.4. Effect of the percentage of GP

The following series of eight experiments involved a progressive change in the GP w:w percentage with respect to GP + PO, from 10 to 55%, using 100 ml of PO.

The viscosity of the product’s soluble fraction decreased with increasing pulp percentage (Fig. 2) whilst the corresponding percentage of insoluble fraction increased in a roughly linear fashion (Fig. 2). The glass transition temperature ($T_g$) of the latter fractions remained close to 20°C (Fig. 3) indicating that this was a new product, because the initial sugar beet pulp showed no detectable glass transition and the homoPPO of low DP had a $T_g$ of −85°C. The OH number of the soluble fraction increased with the percentage of GP (Fig. 2) and the $T_g$ of this portion of the reaction product decreased from about −65 to −85°C (Fig. 2).

All this evidence suggests that as the percentage of GP in the initial reaction mixture was increased, the CH$_2$Cl$_2$-soluble product dropped from 100 to ~50% and became progressively richer in PO homopolymer, whereas the correspondingly growing insoluble counterpart reflected the formation of oxypropylated pulp with a decreasing degree of grafting. The latter product was therefore the result of the desired reaction, albeit with branches which became progressively shorter and/or less frequent.

In conclusion, whereas the study of all the previous variables provided an optimum value for each one, here the choice of the relative amount of pulp would depend on the actual application envisaged for the ensuing oxypropylated product.

3.5. Effect of the percentage of water

In many of the publications about oxypropylation discussed above, the catalyst was added as an aqueous solution. The following five experiments
The reaction which forms the PO homopolymer was therefore clearly favoured by the presence of water. In fact, all trends pointed to the formation of a growing amount of low-DP polyol, which obviously was related to the increasing role of PO homopolymerisation (as indeed was confirmed by the low $T_g$ of these products). This feature is entirely compatible with a reaction mechanism involving a growing contribution of initiation of...

Fig. 3. Variation of the glass transition temperatures of the CH$_2$Cl$_2$-soluble and insoluble fractions as a function of the initial percentage of pulp in the reaction mixture.

Fig. 4. Relationship between the viscosity and the OH number of the oxypropylated pulp and the percentage of water present in the reaction mixture.
the anionic polymerisation of PO by OH\(^{-}\) to the detriment of the alternative grafting from alkoxy anions formed by KOH on the polysaccharide chains.

In this series of experiments, ‘0%’ water reflected simply the use of GP with a residual moisture corresponding to its equilibration with ambient air, viz. \(\sim 8\%\) w/w (as determined by Karl-Fischer titration). In order to assess the role of small amounts of residual water on this system, a sixth reaction was conducted in the same conditions, but after submitting the GP to a thorough vacuum drying for 24 h at 100°C and using PO and KOH devoid of moisture. Neither oxypropylation, nor homopolymerisation occurred, indicating that initiation is not possible in the absence of traces of moisture which are necessary to produce the partial solubilisation/ionisation of the catalyst.

In conclusion, the most appropriate way to conduct the oxypropylation of sugar beet pulp consists in using it as such, viz. with its equilibrium moisture. Of course a simple way of reducing the viscosity of the product would call for the addition of a corresponding amount of water to the reaction mixture.

### 3.6. Effect of the reaction temperature

As mentioned above, the oxypropylation temperature can vary from 40 to 250°C. It was therefore necessary to study this parameter. Reactions were carried out at 100, 120 and 140°C, and, as expected, an increase in temperature affected the reaction time by shortening it progressively. The higher the temperature, the lower the viscosity of the final product, namely from 70 to 15 Pa·s (for the CH\(_2\)Cl\(_2\)-soluble portion) when going from 100 to 140°C. This trend could be readily explained by the fact that the homopolymer formation through chain-transfer reactions was progressively favoured as the temperature was raised.

Again, the choice of the reaction temperature is not related to an actual optimisation, but rather to the end use of the polyol, mostly in terms of its viscosity. However, the shortening of the process duration must also be taken into account and in our system, it was found that, below 120°C, reactions became rather sluggish.

### 4. Conclusion

Having first established that sugar beet pulp can indeed be oxypropylated, the initial purpose of the optimisation of this reaction was to eliminate the fraction insoluble in dichloromethane by changing the experimental parameters in such a way as to avoid the presence of solid particles (insufficiently oxypropylated pulp) in the viscous product isolated at the end of the process.

A second, more specific, study aimed at obtaining a liquid with relatively low viscosity, while using at the same time the largest possible proportion of pulp.

This double approach gave polyols with the most satisfactory properties, relative to the specific use in polyurethane formulations, when using 30% of GP in equilibrium with atmospheric moisture (w/w with respect to the GP + PO mixture) and 10% of KOH (w/w with respect to the GP) as catalyst. These reactions were carried out at 140°C for 3–4 h.

The final product was a homogeneous liquid with an OH number \(\sim 600\) mg of KOH per g of polyol and a viscosity close to 7 Pa·s at 20°C. This product was a mixture of oxypropylated polysaccharides and a low-DP polypropylene oxide glycol.

Pursuit of this work towards the synthesis and characterisation of novel polymeric materials based on an abundant renewable agricultural by-product is in progress (Pavier and Gandini, 1999b).

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### References


