Carbohydrate Polymers **14** (1991) 221-240

Review Paper

The Conversion of Polysaccharides into Polyurethanes: A Review

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(Received 17 November 1989; accepted 1 December 1989)

ABSTRACT

The conversion of polysaccharides into polyurethanes, which has commanded considerable academic and industrial interest over the past 30 years, is reviewed from chemical, structure-property and economic viewpoints.

The basic chemistry of polyurethanes and the morphological structure of segmented copolyurethane materials are described. The processes used to fabricate such materials are outlined and the properties required in polysaccharides used as feedstocks for polyurethanes are defined.

Several methods of incorporating polysaccharides in polyurethanes are available including their use (i) in unmodified form, (ii) after derivatisation, (iii) after depolymerisation and derivatisation, and (iv) by conversion to non-carbohydrate polyols. (Routes (ii)-(iv) yield a very wide range of glycosidic and non-glycosidic polyol structures.) Specific examples of each route and the advantages of the polyol products for use in polyurethane formation are detailed. Advantages include low cost and structural versatility of the polyols which provide increased cross-linking, and solvent and fire resistance in derived polyurethanes.

Some developments in the understanding of the formation of glycosides and their industrial-scale production are presented, together with an indication of the increasing variety of polysaccharide structures used.

Methodologies for the production of solid polyurethanes with high carbohydrate contents, compared to foams of relatively low carbohydrate

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contents, are described together with the structure–property relationships in both types of materials.

Finally, the future potential of biotechnology in providing novel carbohydrate structures is briefly considered.

INTRODUCTION

Polyurethanes (PU) are a diverse and versatile group of commercially important synthetic polymers which comprise rigid or semi-rigid solids, foams, films, elastomers and adhesives (Bruins, 1969; Hepburn, 1982; Frisch, 1983; Woods, 1987). The principal reaction involved in their preparation is the formation of urethane linkages by the stepwise addition of a diol (or a polyol) to a diisocyanate (or a polyisocyanate):

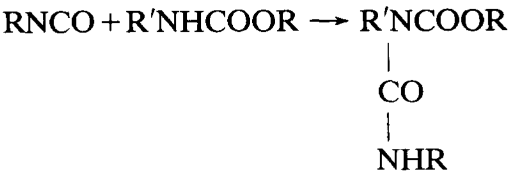
$$n\,\mathrm{OCN{-}R{-}NCO} + n\,\mathrm{HO{-}R'{-}OH}$$
$$\downarrow$$
$$\mathrm{OCN{-}R{-}NHCO}\left[\mathrm{O{-}R'OOCNH{-}R{-}NHCO}\right]_{n-1}\mathrm{O{-}R{-}OH}$$

Considerable controlled variation in the properties of the resultant polymer is possible by the judicious choice of the structure of the reactant containing the hydroxyl functions and that containing the isocyanate functions. In addition, the degree of branching or cross-linking and the chemical nature of the cross-linking groups may be modified by adjustment of the reactants' stoichiometry, the curing conditions, by addition, for example, of controlled levels of acid or water to the reaction (producing foams), or by replacement of a proportion of a diol with, for example, a triol. Some of the dominant reactions of isocyanate chemistry are summarised as follows:

(a) $\mathrm{RNCO} + \mathrm{H_2O} \rightarrow \mathrm{RNH_2} + \mathrm{CO_2} \xrightarrow{\mathrm{RNCO}} \mathrm{RNHCONHR}$
substituted urea

(b) $\mathrm{RNCO} + \mathrm{R'COOH} \rightarrow \mathrm{RNHCOR'} + \mathrm{CO_2}$
amide

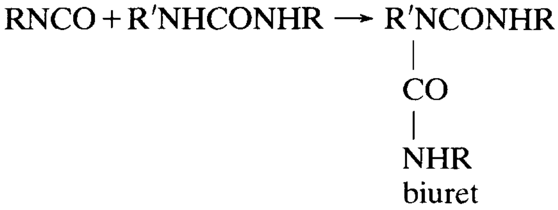
(c)



$$\mathrm{RNCO} + \mathrm{R'NHCOOR} \rightarrow \begin{array}{c}\mathrm{R'NCOOR}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{NHR}\end{array}$$

allophonate

(d)



$$\mathrm{RNCO + R'NHCONHR \longrightarrow \underset{\substack{|\\ \mathrm{CO}\\ |\\ \mathrm{NHR}}}{R'NCONHR}}$$

biuret

The majority of polyurethanes and related materials, however, are segmented block copolymers (Lee, 1980) whose thermal and mechanical properties are significantly superior to those of the polyurethanes just described. The two-phase structure of a block copolyurethane is built up by the reaction of an oligomeric polyol with a diisocyanate to form the chemical moiety defined as the soft segment, and by the reaction of a simple diol (chain extender) with the diisocyanate to form the chemical moiety defined as the hard segment. The formation of a block copolyurethane is shown schematically in Fig. 1. Typically, the chain extender is a low-molar-mass diol such as ethylene glycol or 1,4-butanediol, the diisocyanate is toluene diisocyanate (TDI) or 4,4′-methylenediphenylene diisocyanate (MDI), and the oligomeric polyol is a polyether with molar mass (Mn) and nominal functionality (*fn*) in the ranges 500–8000 g $\mathrm{mol^{-1}}$ and 2–6, respectively. The overall chemical stoichiometry used, defined as the ratio of isocyanate group concentration [—NCO], to total hydroxyl group concentration [—OH] is usually between 1·00 and 1·05. The poly(ether-urethane) moiety is called the soft segment because it has a glass transition temperature, Tg^{S}, below room temperature and is a soft, extensible rubber at ambient. In contrast, the polyurethane moiety containing the chain extender is called the hard segment because at ambient it is significantly below its melting point, Tm, and/or its glass transition temperature, Tg^{H}, and is crystalline, glassy and therefore very stiff.

In the limit of complete reaction (conversion of all functional groups), the structure of the copolyurethane approaches that of the idealised $\text{-}\!\!(AB)\!\!\text{-}_n$-type, block copolymers depicted in Fig. 1. In practice, and depending on the processing route used, the polymeric product is a mixture comprising homopolymers, various —*AB*— type copolymers and small amounts of free monomer. Processing routes for copolyurethanes fall into two general classes: one-stage and two-stage. In the former, chain extender diol and oligomeric polyol are blended and reacted simultaneously with all of the diisocyanate: reaction injection moulding (RIM) (Barksby *et al.*, 1985) is a rapidly expanding example of a one-stage process and is described later. The two-stage process involves pre-polymer formation between the oligomeric polyol only and

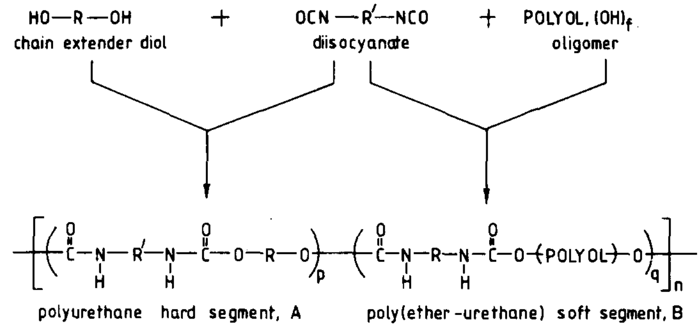


Fig. 1. Schematic representation of the formation of a segmented block copolyurethane.

all of the diisocyanate (which is therefore in stoichiometric excess), followed by copolymer formation with the stoichiometric equivalent amount of the chain extender.

In the more extensively used one-stage process, copolymerisation occurs by competitive-consecutive reactions in which the much higher rate of reaction between chain extender and diisocyanate, compared with that between polyol and diisocyanate, leads to the preferential development of the hard segments. Under these conditions, there exists initially an effective but transient stoichiometric imbalance so that hard segments of relatively short sequence lengths are formed with a distribution such that the number average degree of polymerisation, p, is typically in the range 1–10. Nevertheless, the high aromatic (and therefore urethane) content in the hard segments makes them intrinsically rigid and extensively hydrogen bonded, and confers sufficiently high solubility parameter difference (Ryan *et al.*, 1988) relative to the poly(ether-urethane) soft segment, that phase separation invariably occurs. Furthermore, even though p is small, the hard segment molar mass is sufficiently high that Tm and Tg^{H} far exceed the copolymerisation reaction temperature (despite any exotherm) and vitrification/crystallisation occurs adding further to the driving force for phase separation. The slower reactions involving the oligomeric polyol serve to join up the NCO-tipped hard segments, as well as developing soft segment molar mass (increasing q in Fig. 1) by reaction with free diisocyanate, forming ultimately a coherent copolyurethane with good connectivity between hard and soft phases. In the case of polyether diols ($fn = 2$), the copolyurethanes formed are linear and therefore soluble and thermoplastic: the use of polyether polyols ($fn \geq 3$) result in the formation of heterogeneous, copolyurethane macro-networks (Barksby *et al.*, 1985). In the latter, chemical gelation also occurs to further enhance phase separation during copolyurethane formation. As a general rule, copolyurethanes formed by a one-stage process, compared to a two-stage process, possess hard segments of longer sequence lengths, although their distribution is broader. In both cases, the phase-separated hard segments aggregate to form domains of various sizes, with those of the one-stage copolyurethanes being less well-defined and more readily deformed.

Segmented copolyurethanes therefore have complex microstructures and morphologies, as determined by the nature and extent of phase separation which occurs during copolymerisation (and any subsequent thermal annealing process). The essential microstructural features, which define the detailed morphology of copolyurethanes, are shown schematically in Fig. 2 in which the thin lines represent the amorphous poly(ether-urethane) soft segment chains and the sequences of circles and squares represent the chain-extender-based, polyurethane hard segment chains. As stated previously, phase separation results in aggregation of the hard segments into extensively hydrogen-bonded, rigid domains which, as Fig. 2 depicts, vary in size and orientation and which comprise a distribution of chain lengths. Note also that there are some isolated hard segments dispersed (or phase-mixed) within soft segment chains. The nature of the microstructure, in terms of hard segment domain size, cohesive strength of domains and their ability to orient during copolyurethane deformation, clearly affects the materials properties at given hard segment content (defined as the mass of chain extender plus the corresponding stoichiometric mass of diisocyanate, divided by the total mass of the copolyurethane system). However, it is the relative proportions of hard and soft segments which is the main factor determining the morphology and hence materials properties. At low hard-segment contents, the rubbery soft segments form the continuous phase in which dispersed hard segment domains act essentially as a reinforcing filler and macroscopic, multifunctional cross-links. At high hard-segment contents, typically above 60% by weight, phase inversion can occur and the copolyurethane can be regarded as a rubber-toughened plastic in which the hard segments form the continuous phase and the soft segments are dispersed rubber particles. Seldom is phase separation complete, particularly in copolyurethanes in which appreciable hydrogen bonding between hard segment and polyether soft segments occurs. Consequently, the transition from one morphology to the other is not sharp and at intermediate hard segment contents, the copolyurethane may comprise a bi-continuous and interpenetrating, two-phase structure.

The versatile chemistry of polyurethanes and the control and variety of copolyurethane morphology, therefore, clearly demonstrate the wide

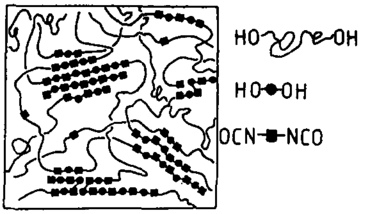


Fig. 2. Schematic representation of the major microstructural features in a phase-separated, segmented block copolyurethane.

range of materials behaviour, from soft elastomeric to rigid plastic, which can be achieved. It is for these reasons that the polyurethane industry is so extensive and continues to expand with the wide range of urethane-based commercial products referred to earlier. The market size for polyurethanes and copolyurethanes is therefore extremely large, and recent estimates (Anon., 1988*a*) reported world-wide production to be at 4·25 million metric tonnes per annum, of which flexible (50%) and rigid (25%) foams were the major products.

Polysaccharides are also a diverse group of polymers available in quantities commensurate with an envisaged use in the preparation of PU (Vlitos, 1981; Yalpani & Sandford, 1987). At first sight these hydroxyl-containing polymers would seem to be eminently suitable. However, their crystalline nature, high polarity, lability to heat (Houminer & Patai, 1967), acidity or alkalinity (Gelpi & Cadenas, 1975), their tendency to contain high proportions of water and the ability of reducing end-groups to react with isocyanates (Yeh & Gilbert, 1973) tends to limit the use of native polysaccharides to reactive fillers (Boggs, 1959; Bennett *et al.*, 1968; Hostettler, 1979). Nevertheless, unmodified polysaccharides do display some advantages in PU foams such as increased high-temperature stability (Haggis, 1976), or increased hardness (Haggis & Kerrigen, 1975); for applications such as artificial planting beds, biodegradability may be attained by the incorporation of starch (Kishimoto & Fuju, 1976).

Some saccharides have been shown to react with TDI in solvents such as pyridine to yield rigid cross-linked polymers on removal of solvent (Long, 1959). However, complete removal of solvent is difficult and costly and as a route to PU foams or solids is impractical from an economic viewpoint, although this procedure can be useful for structure–property studies.

For a wider range of polymer end-uses, modifications of the polysaccharide is therefore required to obtain polyols suitable for incorporation into the PU. Preferentially, for the fabrication of PU by efficient techniques such as RIM, fast-reacting liquids of relatively low viscosity are required (Schick, 1979; Reinforced Reaction Injection Moulding Conference, 1981).

The RIM process is a one-stage, in-situ moulding technique (Barksby *et al.*, 1985) which essentially consists of high-speed impingement mixing of two liquid reactant streams, one a polyisocyanate and the other a polyol blend with or without a filler (Stanford, 1988), in a mixing chamber. The mixture then flows into a mould and reacts at relatively low temperatures and pressures to yield a finished article. The RIM process, based on copolyurethane chemistry, is therefore capable of producing large and complex mouldings such as car bumpers in a one-shot process. Mould cycle times are very short — typically less than 30 s.

MODIFICATION OF POLYSACCHARIDES

For the modification of polysaccharides several approaches are possible so that a reduction in polarity of the molecules occurs, hence decreasing their melting point and viscosity, and increasing miscibility and reactivity with relatively non-polar isocyanates. Reaction at the anomeric positions of the polysaccharide can also lead to an increase in heat and alkali stability arising from the removal of aldehydic or potential aldehydic groups via the formation of various glycosides.

Some generalised routes can be described as follows:

(a) depolymerisation of the polysaccharide to monomers or oligomers followed by modification of the anomeric site. A further optional stage of modification of the remaining hydroxyl groups may take place;
(b) simultaneous depolymerisation and anomeric site modification. Further reactions at the other hydroxyls may be required;
(c) derivatisation of the polysaccharide followed by depolymerisation; and
(d) conversion of the polysaccharide (with loss of the carbohydrate structure) into molecules such as diols which remain suitable for incorporation into PU.

Some methods of depolymerising polysaccharides are well known and form the basis of established industries. For instance, starch may be enzymatically degraded to yield saccharide mixtures (containing about 24% dextrin, 32% maltose, 8% maltotriose and 36% glucose), or high maltose syrups (~70% maltose), or to high glucose syrups (~94% glucose) via the use of α-amylase, pullulanase and amyloglucosidase enzymes (Gacesa & Hubble, 1987; Hull, 1987). The high glucose syrup may then be converted to high fructose syrup (~42% fructose, ~50% glucose) employing glucose isomerase (Gacesa & Hubble, 1987), or into a 'very high' fructose syrup (~95% fructose) by semi-continuous chromatography (Barker & Ganetsos, 1985). The recent appearance of isoamylase in commercial quantities, when combined with the action of β-amylase, can now offer a route for the conversion of starch to a maltose-rich syrup containing up to ~90% maltose and ~10% glucose (Tu *et al.*, 1987).

Cellulosic material derived from trees, wood wastes, agricultural residues and straw offers another high tonnage source of carbohydrates. These materials contain cellulose, hemicellulose and lignin; recent technology, however, has opened up the possibility of using these relatively intractable materials.

Thus cellulose yields glucose and hemicellulose yields pentoses, especially xylose, when subjected to controlled acid hydrolysis in either a batch or continuous process (Porteus, 1967; Converse, 1971; Straw Utilization Conference, 1977). A promising development is the specific, mild-acid hydrolysis of hemicellulose which leaves cellulose fibre in a condition suitable for paper making. Thus even wood required for paper making can be exploited.

Alternatively, after being chemically modified (e.g. methylated) and reacted with a polyhydric alcohol and hydrochloric acid, wood yields a viscous solution which upon reaction with a polyisocyanate formed a PU of very low density but high strength (Shiraishi *et al.*, 1985).

Significant advances have also been made in the enzymatic breakdown of cellulose. In particular, high yields of glucose have been produced from α-cellulose (derived from agricultural residues such as corn stalks, bagasse, alfalfa, etc.) by carrying out a solvent pre-treatment followed by a hydrolysis employing a highly selective cellulose enzyme (Ladisch *et al.*, 1978). This approach has the advantage that no undesirable side-products are formed which is not the case if hydrolysis is carried out using acid, and the solvent pre-treatment prevents the crystalline structure of cellulose protecting the macromolecules from attack by the enzyme.

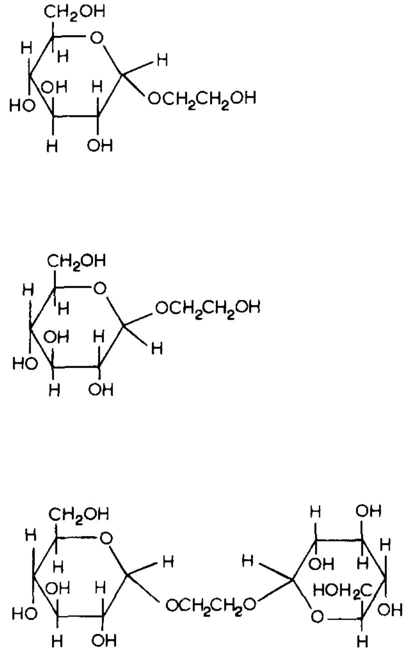
In addition, the isolation of different strains of thermophilic actinomycetes possessing different proportions of the enzymes of the cellulose complex allows the conversion of cellulose to predominantly cellobiose or, for those strains containing a high proportion of β-glucosidase, to either predominantly glucose or a mixture of glucose and cellubiose; in the latter case the celluloses were derived from a wide range of sources of different crystallinities (Eveleigh *et al.*, 1986; Klyosov, 1986).

Specific examples of each of the generalised routes (a) to (d) given above will now be described. Much of the pioneering work in this area has been carried out by Otey and his groups at the Northern Regional Research Centre, Peoria, Ill. Their efforts have centred on the exploitation of plant-derived materials as chemical feedstocks for the past quarter of a century.

POLYOLS FROM STARCH AND RELATED COMPOUNDS

In 1963 Otey and co-workers produced starch-based surfactants by the transglycosylation of starch with a diol such as ethylene glycol using sulphuric acid as catalyst. The polyol glucosides produced are then sufficiently heat- and alkali-stable to permit polyetherification with ethylene oxide. The glucoside polyethers were then reacted with fatty acids to produce non-ionic surfactants (Otey *et al.*, 1963*a*). Shortly afterwards Otey incorporated the same glucoside polyethers into PU foams and evaluated properties such as compression strength, density and stability to ageing (Otey *et al.*, 1963*b*). The glucosides were subsequently shown to be a mixture of predominantly α- and β-monoglucosides together with smaller amounts of bis-glucosides and also some glycol oligosaccharides (Otey *et al.*, 1965*a*). Some of these structures are represented in Fig. 3.

Glycosides and diglycosides have also been prepared directly from sugars such as glucose, xylose or arabinose, and from glycerol, ethylene



1

2

3

Fig. 3. Structures of some of the products formed from the transglycosidation of starch: 1, ethylene glycol-α-glucoside; 2, ethylene glycol-β-glucoside; 3, ethylene glycol bis-glucoside.

glycol or reduced sugars like xylitol, via acid catalysis both with and without the application of vacuum (Takeshita, 1955; Sharkov, 1961).

At the end of 1963 a Belgian patent was granted to Olin Mathieson employing starch, alcohols such as sorbitol, glycerol, ethylene glycol, propylene glycol, and epoxides such as propylene oxide (PO) or epichlorohydrin, to form polyol glucoside ether products suitable for incorporation into PU foams (Fuzesi, 1963). Other glucosides suitable for foams by the above route are formed by the reaction of reducing sugars such as glucose and maltose with polyethylene glycols (Mn 200–400), ethoxylated glycerol, ethoxylated 1,4-butane diol, or 2-hydroxy-3-chloropropanol. They have, however, only been considered as surfactants (Langdon, 1976; Henkel, 1980). Similar comments apply to alkyl glucosides (Farris, 1983; Davis & Letton, 1985), alkyl oligosaccharides (Mao, 1983), and to phenol glucosides (Onodera *et al.*, 1983).

A great deal of attention has been given to the incorporation of carbohydrate materials into PU foams since Otey's original work and very many variations of this methodology continue to be patented. This is due to the continued growth of the foam industry and its potential for future development.

In the early development of polyethers for foams sorbitol, an alditol obtained by hydrogenation of glucose, was used as a raw material (Wilson & Fowler, 1958). In the mid-1960s alkoxylated methyl glucoside was also used (Upjohn, 1967); methyl glucoside may be prepared directly from starch (Langlois, 1942; Cantor, 1943) or from glucose. The above polyethers are prepared by alkoxylation of the carbohydrate to a degree necessary to give a liquid of the desired viscosity and hydroxyl number. Both of these polyethers however suffered in a price comparison with petroleum oil-derived polyols such as pentaerythritol and this restricted their ability to take a large share of the market. Although today this statement cannot be justified, with the variable and often escalating price of petroleum oil, in the mid-1960s price comparisons lead to the investigation of the use of starch-based polyols. Starch has shown a relative price stability over other raw materials (Otey, 1976) and resulted in Otey's 1963 work on polyol glucosides. They were found to be economically viable in performance in foam evaluations and also in pilot-plant trials (Leitheiser *et al.*, 1966). However, non-acceptance by the PU foam industry at that time seemed to stem from concern over profit-margins and uncertainty over the flame resistance of PU in general, together with a reluctance of industry to change their technology base. However, recently there has been a swing away from this viewpoint by the PU foam and other industries who are actively employing starch-based derivatives (Otey, 1985). Butyl, and in particular methyl, glucosides appear to have returned to favour (Short, 1984; Daicel Chemical Company, 1985; Defaye *et al.*, 1986).

Much research has also been carried out over the past two decades on enhancing the fire resistance of PU by the incorporation of phosphorus, halogens or nitrogen-containing compounds, or by the use of rigidly structural molecules either as polyol or as isocyanate. The provision of a double bond for the introduction of halogen via the preparation of allyl glucosides is one route of achieving fire resistance (Wilham *et al.*, 1975; Otey *et al.*, 1978). Another approach is to treat propoxylated starch with polyphosphoric acid which, after reaction with isocyanate, yields non-burning or self-extinguishing foams (Molotsky & Granera, 1976). This area and other variations of Otey's original work have been reviewed by Frisch and Kresta (Hickson, 1977) and by Otey (Otey, 1976). More recently, polyols with very high nitrogen contents (~ 20%) have been prepared by reaction of diethylene glycol glucoside (derived from starch) with propylene oxide and diethanolamine (Fuzesi & Bayusik, 1982).

Over the last few years a more detailed examination of the chemistry of glycoside formation has taken place. For example, the reaction conditions have been improved to provide the consistent polyol properties (colour, viscosity, hydroxyl number) required for use in foams (Otey *et al.*, 1965*b*). The use of potassium bromide to remove residual reducing end-groups present in diethylene glycol glucoside formed from starch, led to foams with better physical properties than those obtained without a bromide treatment (Manabe, 1977). Similarly, Stoenescu has studied the effect of the aldehyde groups from unreacted glucose on the properties of polyether glucosides (Stoenescu, 1979). Starch derived polyether polyols prepared from 2-methoxymethanol and PO, are claimed to have much lower viscosity than those prepared from ethylene glycol glucoside and PO, or methyl glucoside and PO (Moss & Cuscurida, 1972).

A number of patents have been granted for the large-scale productions of polyol glucosides from starch — for example, by continuous extrusion of the reaction mixture through a barrel heated to high temperatures and pressures (Roth, 1967; C.P.C., 1969).

POLYOLS FROM OTHER TYPES OF CARBOHYDRATES

There has also been much work carried out into deriving polyols from a wider range of types of carbohydrates. The following are examples of such sources: alkoxylated acetone glucose (Gibbons, 1972); and hydroxypropylated levoglucosans derived from pyrolysis of starch or cellulose (Lakshmanan *et al.*, 1969; Stirma, 1974). Reaction of these polyols with hexamethylene diisocyanate (HDI) gave elastic, transparent films (Lazdina *et al.*, 1984). Crude sources of polyols derived from canary corn dextrin and corn syrup solids have been proposed (Case, 1970), as have alkoxylated ethylene glycol fructoside (Yotsuzuka & Fujima, 1972). Foams from alkoxylated fructose itself have been shown to give good adhesion to steel and good fire resistance (Toyodo *et al.*, 1987).

An important indirect method of incorporating carbohydrate derivatives into PU is the commercial production of polytetrahydrofurandiol from corn cobs or oat hulls via furfural (Hay, 1981). Furfural is obtained from xylose which is, in turn, obtained from the plant polysaccharide pentosan. In addition, xyloses can be derived in high yield (95%) from cellulosics by treatment with hydrogen chloride gas in a fluidised bed reactor (Antonoplis, 1982). The PU elastomers produced from these polytetrahydrofuran diols show interesting properties due to their regular polymer chain structures (Pechhold & Prucknayr, 1982). A recent patent, combining acid and enzymatic routes, produces glucose, D-xylose and L-arabinose from corn kernal hulls (Arena & Allenza, 1988). Furfural has been converted to dihalogenated glycols, useful as a reactive flame-retardant in rigid PU foams (Marzec & Lesiak, 1983).

Although many of the above carbohydrate-based polyols currently employed in PU foams and as surfactants have potential use for the manufacture of solid PU, relatively little work has been reported on the bulk reaction of these polyols and isocyanates. An early German patent (Dijkhuizen, 1970) claims that the additions of MDI to a glucose–PO adduct, when catalysed by an organo-metal catalyst such as $Zr(OPr)_4$, gave a bubble-free resin sheet of superior properties than when other types of catalysts were used.

TABLE 1
Representative Physical Properties of PU Derived from Castor Oil and Ethylene Glycol Glucoside

Compositions (%)			*Tensile strength (psi)*	*Elongation (%)*
Starch	*Isocyanate*	*Polyol*		
0	42·6	57·4	5517	12
30	34·0	36·0	7296	4
60	16·8	23·2	6837	2

Otey and co-workers have prepared solid PU suitable for floor tiles by the reaction of polymeric diisocyanates and a series of mixed polyols derived from castor oil or the products from alcoholysis of castor oil with glycol glucosides (Otey *et al.*, 1969). Polyols of different hydroxyl number were produced by altering the ratio of castor oil and ethylene glycol glucoside. Each polyol was reacted with an excess of polyisocyanate so that starch could be incorporated as a reactive filler in the range 0–60% (w/w). A wide range of physical properties of these filled solids were then evaluated. Table 1 gives some representative examples.

CARBOHYDRATE-BASED POLYURETHANES: STRUCTURE–PROPERTY RELATIONSHIPS

Structure–property relationships of some carbohydrate-based PU have been investigated. Thus Darr and co-workers have examined both solids and foams derived from the reaction of sorbitol or methyl glucoside polyethers with TDI, MDI or HDI (Darr *et al.*, 1963). Impact strength, hardness, stiffness and softening point of carbohydrate-based and oil-based polyols (such as pentaerythritol and trimethylol propane) were compared. Softening point was gauged to be the most sensitive indicator of the effect of structural changes of the polyols. Increases in polyol functionality caused a shift in softening point to higher temperatures. The influence of isocyanate structure on the PU properties is also described.

Similar carbohydrate and oil-based polyethers have been investigated by other workers, but were reacted with polyphenyl polymethylene polyisocyanate, TDI or xylylene diisocyanate (Reegan & Frisch, 1967). These polymerisations were carried out in solution and the cast films after removal of solvent were tested for thermal, hydrolytic and solvent resistance. Whilst some of these properties were influenced by isocyanate structure, they were improved generally by the high cross-link density imparted by the high functionality of the carbohydrate-based polyols.

SOLID POLYURETHANES FROM RENEWABLE RESOURCES

In our studies at the Wolfson Polymer Unit we have investigated the synthesis of polyols and also diisocyanates from renewable resources. The PU were prepared from these precursors, largely by bulk phase reaction (although some useful data such as indications of functionality were also gleaned from solution polymerisations), and structure–property studies were carried out. One aspect of this work was to prepare polyols with high carbohydrate contents. In this regard, the use of glycosides with low molar mass aglycons such as ethylene glycol glucoside, would be desirable. However, despite reacting rapidly with diisocyanates in solution, the polyol was found to be immiscible with MDI even at 100°C where the polyol viscosity is markedly reduced. Alkoxylation of the glucoside to a high degree, as frequently used in the work previously described for PU foam production, leads to a polyol which does react with isocyanates but reduces the carbohydrate content of the polyol. In addition, alkoxylation reagents like propylene oxide are not available from renewable resources. It was found that controlled alkoxylation of ethylene glycol glucoside in solutions to a low degree (approximately 3 moles of PO per anhydroglucose unit) still produced a polyol reactive with MDI in the bulk phase (Cawse *et al.*, 1985*a*). Blending of this polyol (OPEGG, idealised structure given in Fig. 4) with carbohydrate-derived polytetrahydrofuran diol of Mn 750 (PTHF 750) in various proportions and reaction with crude liquid MDI allowed synthesis of polymers with a range of properties (Donnelly, 1984; Cawse *et al.*, 1985*b*). Table 2 gives some tensile properties of these polymers.

The formation of glucosides by the acid-catalysed reaction of glucose and polytetrahydrofuran diols of selected molar masses in the range 90–2000 (PTHF 90–2000) proved to be another useful route to carbohydrate-based polyols. Conversion of glucose was 80–90% and a 1:1 molar ratio of glucose to diol produced largely mono-glucoside whilst a 2:1 ratio produced largely bis-glucosides. Idealised structures for the glucosides are given in Fig. 5 (Donnelly, 1984). This route was also used to prepare polypropylene glycol glucosides.

Reaction with MDI gave glassy polymers for glucosides containing the lower molar mass aglycons through to elastomers from those glucosides containing the higher molar mass aglycons. Generally, increasing glucose contents — for example, in comparing the series of polymers from the higher molar mass polytetrahydrofuran diols/MDI, polytetrahydrofuran monoglucosides/MDI and polytetrahydrofuran bis-glucosides/MDI — caused a softening of the rubbers and a lowering of *Tg*. This trend is

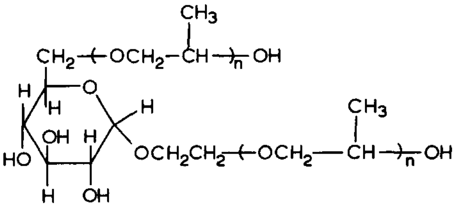


Fig. 4. Idealised structure of propoxylated ethylene glycol glucoside (OPEGG).

TABLE 2
Tensile Properties of Polyurethanes Derived from the Polyols Oxypropylated Ethylene Glycol Glucoside (OPEGG) and Polytetrahydrofuran Diols[a]

Polyol composition (%)		*Polyurethane properties*		
OPEGG	*PTHF 750*	*Modulus (MPa)*	*Tensile strength (MPa)*	*Elongation (%)*
100	0	2728	46·3	2·6
75	25	252	16·5	220
50	50	2·97	4·08	430
25	75	0·337	0·391	1300
0	100	0·448	0·0088	1040

[a] Molar mass 750; PTHF, 750).

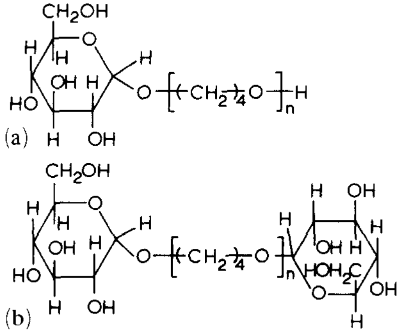


Fig. 5. Polytetrahydrofuran diol derivatives: (a) mono-glucoside (b) bis-glucoside.

reversed when comparing the series of polymers derived from polyols prepared from the lower molar mass polytetrahydrofuran diols and their respective glucoside derivatives. The latter trend of increasing *Tg* was also observed when comparing the properties of copolyurethanes formed from the same series of polyols as above but also using ethylene glycol as chain extender. Increasing glucose content of the polyols is reflected in an increased stiffness of the copolyurethane which is retained even at elevated temperatures (Donnelly, 1984).

A further approach to obtaining polyols of sufficiently low viscosity and polarity to be reactive in the bulk phase with MDI is the acid hydrolysis of ethyl cellulose in the presence of ethylene glycol to yield glucosides of different hydroxyl numbers, (Cawse *et al.*, 1985*a*).

Research in the area of the production of polymer precursors from renewable resources in the Manchester Materials Science Centre has recently been reviewed and this includes a more detailed description of polyol and polymer properties (Stanford *et al.*, 1987).

Other research workers have also examined components and derivatives of cellulose as polyols. Kurita and co-workers have reacted cellobiose with diisocyanates to produce films with very high water absorption capability. The latter ability was radically decreased when the pendant hydroxyl groups were acetylated even at a low degree of substitution (Kurita *et al.*, 1979, 1980; Iwakura *et al.*, 1980). Other Japanese workers have used cellulose acetate to produce flexible films (Miyamoto & Shibatu, 1985), whilst Russian workers have investigated the action of methyl cellulose on the structurisation of segmented polyurethanes (Kercha *et al.*, 1987), and the influence of carboxymethyl cellulose sodium salt as filler on the properties of PU. In the latter case, the selection of the correct particle size range of filler led to an improvement in mechanical properties (Sobko *et al.*, 1986).

FUTURE DEVELOPMENTS

For the future, the recent dramatic increase in knowledge of biotechnology could offer opportunities relevant to the polyurethane industry. For example, the structure of microbial heteropolysaccharides such as xanthan may be tailored by the application of recombinant DNA technology so that the content of specific substituents or monosaccharides may be increased or eliminated altogether (Barrere *et al.*, 1986; Betlach *et al.*, 1987; Cleary & Rosen, 1987; Doherty *et al.*, 1987). These and other microbial polymers could be degraded via chemical or enzymatic means to produce polyol structures quite different from those obtainable from starch or cellulose. However, it is probable that a reduction in production costs would be required to make this route commercially attractive.

Alternatively, the synthesis of oligosaccharide structures via the use of enzymes is feasible. Although chemical methods are also possible, they require a large number of protection–deprotection steps when starting from monosaccharides or yield a wide spectrum of structures when degradation of polysaccharides is employed. In contrast, the reversal of the hydrolytic activity of glycosidase enzymes or the use of glycosyl transferase enzymes can allow the synthesis of complex oligosaccharides with control of the monosaccharide component structure, type of sugar linkage and number of sugar units in the chain (Nilsson, 1988). Disaccharides may also be prepared via this condensation reaction (Fujimoto *et al.*, 1988; Nilsson, 1988): one example is the conversion of glucose to nigerose and Kojibiose. The rapidly increasing number of enzymes becoming available in industrial quantities could yield large amounts of disaccharides not previously readily available by chemical means. Thus a Japanese consortium of companies has developed a continuous bioreactor to convert cotton seed xylan to xylobiose (Anon., 1988*b*). Another Japanese company uses *Penicillium* β-mannase to produce mannobiose from mannan (Towa, 1988), whilst a β-mannosidase from an alkalophilic *Bacillus* species, converts mannans to mannose and oligomannose (Akino *et al.*, 1988). A further example is an amylase from *Pseudomonas stutzeri* capable of maltotetraose formation (Kubota *et al.*, 1988).

All of these routes could offer interesting, and some potentially useful, structure–property studies if these saccharides were incorporated into PU.

ACKNOWLEDGEMENTS

The authors wish to thank the Wolfson Foundation for a grant which supported some of the research work reported in this review.

REFERENCES

Akino, T., Nakamura, N. & Horikoshi, K. (1988). *Agric. Biol. Chem.*, **52** (6), 1459.

Anon (1988*a*). *European Plastics News*, October 15 (10), 35.

Anon (1988*b*). *Bioprocessing Technol.*, October 4.

Antonoplis, R. A. (1982). *Energy Res. Abst.*, 7 (20), Abstract no. 53321.

Arena, B. J. & Allenza, P. (1988). US Patent, 4, 752, 579.

Barker, P. E. & Ganetsos, G. (1985). *J. Chem. Tech. Biotechnol.*, **35B**, 217.

Barksby, N., Dunn, D., Kaye, A., Stanford, J. L. & Stepto, R. F. T. (1985). In *Reaction Injection Moulding* (ACS Symp. Ser. 270), ed. J. E. Kresta. American Chemical Society, Washington DC, USA, Chap. 6, p. 83.

Barrere, G. C., Barber, C. E. & Daniels, M. J. (1986). *Int. J. Biol. Macromol.*, **8**, 372.

Bennett, F. L., Otey, F. H. & Mehltretter, C. L. (1968). US Patent, 3, 405, 080.

Betlach, M. R., Doherty, D. H. & Vanderslice, R. W. (1987). PCT 8705 938.

Boggs, F. W. (1959). US Patent, 2, 908, 657.

Bruins, P. F. (1969). *Polyurethane Technology*. Interscience Publishers, NY.

Cantor, S. M. (1943). US Patent, 2, 390, 507.

Case, L. (1970). US Patent, 3, 510, 471.

Cawse, J. L., Stanford, J. L. & Still, R. H. (1985*a*). British Patent, 00500.

Cawse, J. L., Donnelly, M. J., Stanford, J. L. & Still, R. H. (1985*b*). British Patent, 00388.

Cleary, J. M. & Rosen, I. G. (1987). European Patent, 0, 233, 019.
Converse, A. O. (1971). *Final Report to P.H.S. (U.S.) Grant No. UI 00597-02*, Dartmouth College, Mass., July.
C.P.C. Int. (1969). Corn Products Corporation International. British Patent, 1, 139, 110.
Daicel Chemical Company (1985). Japanese Patent, 85, 01, 196.
Darr, W. C., Gemeinhardt, P. G. & Saunders, J. H. (1963). *Ind. Eng. Chem. Prod. Res. Develop.*, **2** (3), 194.
Davis, J. E. & Letton, J. C. (1985). European Patent, 132, 043.
Defaye, J., Wong, E. & Pedersen, C. (1986). French Patent, 2, 567, 891.
Dijkhuizen, W. (1970). German Patent, 1, 923, 934.
Doherty, D. H., Ferber, D. M., Marelli, J. D. & Vanderslice, R. W. (1987). PCT. 8705 939.
Donnelly, M. J. (1984). PhD thesis, Victoria University of Manchester.
Eveleigh, D. E., Waldron, C. R. & Bartley, T. (1986). US Patent, 4, 628, 029.
Farris, D. D. (1983). European Patent, 96, 917.
Frisch, K. C. (1983). *Plastics and Rubber International*, **8**, 1.
Fujimoto, H., Nishida, H. & Ajisaka, K. (1988). *Agric. Biol. Chem.*, **52** (6), 1345.
Fuzesi, S. (1963). Belgian Patent 634, 198.
Fuzesi, J. & Bayusik, J. G. (1982). US Patent 4, 342, 564.
Gacesa, P. & Hubble, J. (1987). *Enzyme Technology.* Open University Press, Milton Keynes.
Gelpi, M. A. & Cadenas, R. A. (1975). *Adv. Carb. Chem. Biochem.*, **31**, 81.
Gibbons, J. P. (1972). US Patent, 3, 706, 726.
Haggis, G. A. (1976). British Patent, 1, 440, 831.8.
Haggis, G. A. & Kerrigen, V. (1975). German Patent, 2, 448, 216.
Hay, T. K. (1981). *J. Coatings Technol.*, **53**, 682.
Henkel, K. G. (1980). German Patent, 2, 724, 350.
Hepburn, C. (1982). *Polyurethane Elastomers.* Applied Science Publishers, London.
Hickson, J. L. (ed.) (1977). In *Sucrochemistry* (A.C.S. Symposium Series 41) Washington, DC, pp. 238–56.
Hostettler, F. (1979). US Patent, 4, 156, 759.
Houminer, Y. & Patai, S. (1967). *Tetrahedron Lett.*, 1297.
Hull, P. D. (1987). *Tunnel Refineries Ltd Brochure*, London.
Iwakura, Y., Kurita, K. & Ngugen, C. (1980). *Int. Prog. Urethanes*, **2**, 99.
Kercha, Y. Y., Shekkovnikova, L. A. & Khailenko, C. V. (1987). *Vysohomol Soedin*, Ser A., **29** (9), 1865.
Kishimoto, T. & Fuju, O. (1976). Japanese Patent, 76, 11, 895.
Klyosov, A. A. (1986). *Appl. Biochem. Biotechnol.*, **12** (3), 249.
Kubota, M., Nokuda, T. & Sakai, S. (1988). European Patent, 0289, 138.
Kurita, K., Hirakawa, N. & Iwakura, Y. (1979). *Macromol. Chem.*, **180** (3), 855.
Kurita, K., Hirakawa, N. & Iwakura, Y. (1980). *Macromol. Chem.*, **181** (9), 1861.
Ladisch, M. R., Ladisch, C. M. & Tsoa, G. T. (1978). *Science*, **201**, 743.
Lakshmanan, C. M., Gal-or, B. & Hoelscher, H. E. (1969). *Ind. Eng. Chem. Prod. Res. Develop.*, **8** (3), 261.
Langdon, W. K. (1976). US Patent, 3, 931, 148.

Langlois, D. P. (1942). US Patent, 2, 276, 621.

Lazdina, B., Pernikis, R. & Barkane, R. (1984). *Latv. PSR Zinat. Akad. Vestis. Kim. Ser.*, **4**, 456.

Lee, L. J. (1980). *Rubb. Chem. Tech.*, **53**, 542.

Leitheiser, R. H., Impola, C. N., Reid, R. J. & Otey, F. H. (1966). *Ind. Eng. Chem. Prod. Res. Develop.*, **5** (3), 276.

Long, L., Jr. (1959). *Final Report of Project 141.* US Army, Natick, Mass., July 31.

Manabe, T. (1977). Japanese Patent, 77, 126, 499.

Mao, M. H. K. (1983). European Patent, 92, 875.

Marzec, K. & Lesiak, T. (1983). *Top. Furan. Chem.*, Proc. 4th Symp. Furan Chem., ed. J. Kovac. Slovak Tech. Univ., Bratislava, Czechoslovakia, p. 177–9.

Miyamoto, T. & Shibatu, T. (1985). Japanese Patent, 85, 135, 423.

Molotsky, H. M. & Granera, R. C. (1976). US Patent, 3, 957, 702.

Moss, P. H. & Cuscurida, M. (1972). US Patent, 3, 655, 590.

Nilsson, K. G. I. (1988). *Tibtech*, **6**, 256.

Onodera, J., Mitsuru, T., Kishi, Y., Yokoyama, N. & Ishida, R. (1983). *Chem. Lett.*, **10**, 1487.

Otey, F. H. (1976). *Polym.-Plast. Technol. Eng.*, **7** (2), 221.

Otey, F. H. (1985). In *New Approaches to Research on Cereal Carbohydrates*, ed. R. D. Hill & L. Munck. Elsevier Science Publishers, Amsterdam, pp. 191–200.

Otey, F. H., Mehltretter, C. L. & Rist, C. E. (1963*a*). *J. Am. Oil Chem. Soc.*, **40**, 76.

Otey, F. H., Zagoren, B. L. & Mehltretter, C. L. (1963*b*). *Ind. Eng. Chem. Prod. Res. Develop.*, **2** (4), 256.

Otey, F. H., Bennett, F. L., Zagoren, B. L. & Mehltretter, C. L. (1965*a*). *Ind. Eng. Chem. Prod. Res. Develop.*, **4** (4), 228.

Otey, F. H., Zagoren, B. L., Bennett, F. L. & Mehltretter, C. L. (1965*b*). *Ind. Eng. Chem. Prod. Res. Develop.*, **4** (4), 224.

Otey, F. H., Westhoff, R. P., Kwolek, W. F., Mehltretter, C. L. & Rist, C. E. (1969). *Ind. Eng. Chem. Prod. Res. Develop.*, **8** (3), 267.

Otey, F. H., Wilham, C. A. & Russell, C. R. (1978). *Ind. Eng. Chem. Prod. Res. Develop.*, **17** (2), 162.

Pechhold, E. & Prucknayr, G. (1982). *Rubber Chem. Technol.*, **55** (1), 76.

Porteus, A. (1967). A.S.M.E., Paper No. 67-WA/PID-2, *Energy Systems Exposition*, Pittsburg, Pa, 12–17 November.

Reegan, S. L. & Frisch, K. D. (1967). *J. Polym. Sci., C*, **16**, 2733.

Reinforced Reaction Injection Moulding Conference (1981). Solihull, 25–26 Feb. 1981. Plastics and Rubber Institute, London.

Roth, C. D. (1967). US Patent, 3, 346, 558.

Ryan, A.J., Stanford, J. L. & Still, R. H. (1988). *Polym. Comm.*, **29**, 196.

Schick, H. P. (1979). *Materials Engineering*, October, p. 43.

Sharkov, V. I. (1961). *Sb. Tr. Gos. Naucha — Issled. Gidorliza i Sul' fitno-spirit Prom.*, **9**, 138.

Shiraishi, N., Onodera, S., Ohtani, M. & Masumoto, T. (1985). *Mokuzai. Gakkaishi.*, **31** (5), 418.

Short, R. W. P. (1984). European Patent, 99, 183.

Sobko, T. E., Polukhina, L. M. & Anuchenkova, M. A. (1986). *Nov. Primen Polim. Mater. Legk. Prom-sti.*, p. 87.

Stanford, J. L. (1988). *AIChE Symp. Ser.*, **260** (84), 74.

Stanford, J. L., Still. R. H., Cawse, J. L. & Donnelly, M. J. (1987). *Adhesives From Renewable Resources Symposium*, ed. R. W. Hemmingway, A. H. Conner & S. J. Branham. ACS Div. of Cellulose, Paper and Textile Chemistry, September, New Orleans, La, Chap. 30, pp. 424–42.

Stirma, U. (1974). *Plast. Massy*, **1**, 7.

Stoenescu, F. (1979). *Mater. Plast. (Bucharest)*, **16** (1), 4.

Straw Utilization Conference (1977). Papers and discussion for 3rd Conference, February 1977, Oxford. MAFF/ADAS, London.

Takeshita, T. (1955). *J. Jap. Chem. Soc.*, **4**, 245.

Towa Kasei Kogyo (1988). Japanese Patent, 3, 209, 595.

Toyodo, T., Sekiguchi, M. & Iwani, E. (1987). Japanese Patent, 62, 243, 613.

Tu, T., Zhenghuei, Z. X. & Chen, L. (1987). Chinese Patent, 86, 102, 356.

Upjohn, C. (1967). British Patent, 1, 083, 394.

Vlitos, A. (1981). *Chemistry and Industry*, 2 May, p. 303.

Wilham, C. A., Otey, F. H., Mehltretter, C. L. & Russell, C. R. (1975). *Ind. Eng. Chem. Prod. Res. Develop.*, **14** (3), 189.

Wilson, J. E.& Fowler, R. H. (1958). *Science*, **128**, 1343.

Woods, G. (1987). *The ICI Polyurethanes Book*, J. Wiley & Sons, Chichester.

Yalpani, M. & Sandford, P. A. (1987). *Progr. Biotechnol.*, **3**, 311.

Yeh, Y. H. & Gilbert, R. D. (1973). *Carbohydr. Res.*, **30** (1), 155.

Yotsuzuka, M. & Fujima, S. (1972). Japanese Patent, 72, 41, 437.