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Structure–property relationships and biocompatibility of carbohydrate crosslinked polyurethanes

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ABSTRACT

Biocompatible and biodegradable polyurethanes (PUs) based on castor oil and polypropylene glycols (PPGs) were prepared using various carbohydrate crosslinkers: monosaccharide (glucose), disaccharide (sucrose) and polysaccharides (starch and cellulose). The mechanical and thermal properties were investigated and interpreted on the basis of SEM study. The advantage of incorporating various carbohydrates is to have tunable mechanical properties and biodegradability due to variety in their structure. The glass transition temperature and sorption behavior were dominated by the type of polyol than by the type of crosslinker. All the PUs were observed to be biodegradable as well as non-cytotoxic as revealed by MTT assay in normal lung cell line L132. The study supports the suitability of carbohydrates as important components of biocompatible PUs for development of biomedical devices.

1. Introduction

Polyurethanes (PUs) have been used for various biomedical applications due to their considerable physical and mechanical properties and good biocompatibility (Dutta, Karak, Saikia, & Konwar, 2009; Zhou et al., 2012). The preparation of PUs from renewable sources such as vegetable oil-based materials has been receiving increasing attention because of the economic and environmental concerns (Can, Wool, & Kusefoglu, 2006; Lligadas, Ronda, Galia, & Ca'diz, 2007, 2010; Petrovic, 2008; Tanaka, Hirose, & Hatakeyama, 2008). Amongst vegetable oils, castor oil is unique for its application as polyol because it has unique chemical structure as well as physical properties (Oprea, 2010). Castor oil has been used as a polyol for preparation of a wide variety of polyurethanes directly (Ristic et al., 2012; Silva, Kanda, & Nagashima, 2012; Thakur & Karak, 2013; Yeganeh & Talemi, 2007) or after modification (Corcuera et al., 2010). Castor oil based polymers have also been studiedfor its biocompatibility and as drug carrier devices in transdermal drug delivery applications (Shelke, Sairam, Halligudi, & Aminabhavi, 2007).

Compared to polyols, variations in chain extenders and crosslinkers for enhancing biodegradability of polyurethanes have been reported to a less extent (Tatai et al., 2007). Hence we decided to use multi hydroxyl carbohydrates as crosslinkers in PU system which is likely to offer following advantages.

1. Enhance both degradability and mechanical properties of polymer.
2. Provide multifunctional sites to form randomly crosslinked networks.
3. Nontoxic, inexpensive, readily available from renewable resources.

Among carbohydrates, the use of starch and cellulose has been reported in the synthesis of PUs (Chen et al., 2008; Valodkar & Thakore, 2010; Wang, Tian, & Zhang, 2010; Zoua et al., 2011). Incorporation of modified forms of starch and cellulose nanocrystals in PUs also showed enhancement in mechanical strength, biodegradability as well as biocompatibility (Gao et al., 2012; Lee & Kim, 2012). However a systematic investigation and comparison of performance of various carbohydrates as crosslinkers of PUs is not available. Moreover the major concern is the thermal stability of the resulting PUs.

In past, we have compared the sorption properties of a set of biodegradable PUs crosslinked with series of carbohydrate like glucose (monosaccharide), sucrose (disaccharide) and starch (polysaccharide) as crosslinkers (Lalwani & Desai, 2009). As a further development, we synthesized PUs with natural oil and synthetic polyols with variety of carbohydrate crosslinkers. The

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Table 1
The molar composition of PUs synthesized.

Code	Polyol	Crosslinker	*R* value (NCO/OH ratio)	Polyol/crosslinker ratio
A-G	PPG 2000	Glucose	1.2	0.66
A-St	PPG 2000	Starch	1.2	0.66
A-Su	PPG 2000	Sucrose	1.2	0.66
A-Cel	PPG 2000	Cellulose	1.2	0.66
A-St-a	PPG 2000	Starch	0.8	0.66
A-St-b	PPG 2000	Starch	1.0	1.0
A-St-c	PPG 2000	Starch	1.0	0.66
B-G	Castor oil	Glucose	1.2	0.66
B-St	Castor oil	Starch	1.2	0.66
B-Cel	Castor oil	Cellulose	1.2	0.66
C-G	PPG 3000	Glucose	1.2	0.66
C-St	PPG 3000	Starch	1.2	0.66
C-Su	PPG 3000	Sucrose	1.2	0.66
C-Cel	PPG 3000	Cellulose	1.2	0.66

advantage of incorporating various carbohydrates is to have tunable mechanical properties and biodegradability due to variety in their structure. Effect of variation of *R* value and polyol/crosslinker ratio was also studied.

2. Experimental

2.1. Raw materials

Castor oil and polypropylene glycols, molecular weight 2000 and 3000 were purchased from Sigma Aldrich, India. All polyols were dehydrated at 100 °C under 20 mmHg for 3 h prior to use. The crosslinkers – glucose, sucrose, cellulose and starch – were supplied by Qualigens, Bombay, India. DBTDL (Dibutyl tin dilaurate) was supplied by Maharashtra Organometallic Catalysts Pvt. Ltd. (MOMCPL) Mumbai. 2,4-Toluene diisocyanate (2,4-TDI), THF (tetrahydrofuran), methanol, toluene and glacial acetic acid were donated by GNFC Ltd, India.

2.2. Synthesis of PUs

The synthesis of PUs was done by a procedure already reported earlier (Lalwani & Desai, 2009). In short, a mixture of 10 g of polyol and stoichiometric amount of carbohydrate was stirred for 15 min followed by addition of calculated amount of 2,4-TDI. Stirring was continued for 2 h at 25 °C and then catalytic amount of DBTDL was added followed by addition of THF. The mixture was stirred well till it became viscous enough to cast on a glass plate. It was degassed under vacuum and transferred into a glass mould. After slow solvent evaporation at room temperature, it was cured at 80 °C for 4 h. The films were dried at room temperature for 3 days and then used for the measurements.

The molar compositions of PUs synthesized are given in Table 1. The PUs containing glucose, sucrose, cellulose and starch as crosslinkers are designated as G, Su, Cel and St, respectively. The symbols A, B and C denote polyols PPG 2000, castor oil and PPG 3000 respectively. All the three systems were synthesized with constant *R* value (1.2) and constant polyol/crosslinker ratio (0.66). Castor oil based PU with sucrose as a crosslinker leads to film with cracks and low strength hence it was not considered for further studies. In order to study the effect of variation of NCO/OH ratio (*R* value), as well as polyol/crosslinker ratios the PPG 2000 PU containing starch as crosslinker was taken as a representative system.

2.3. Characterization

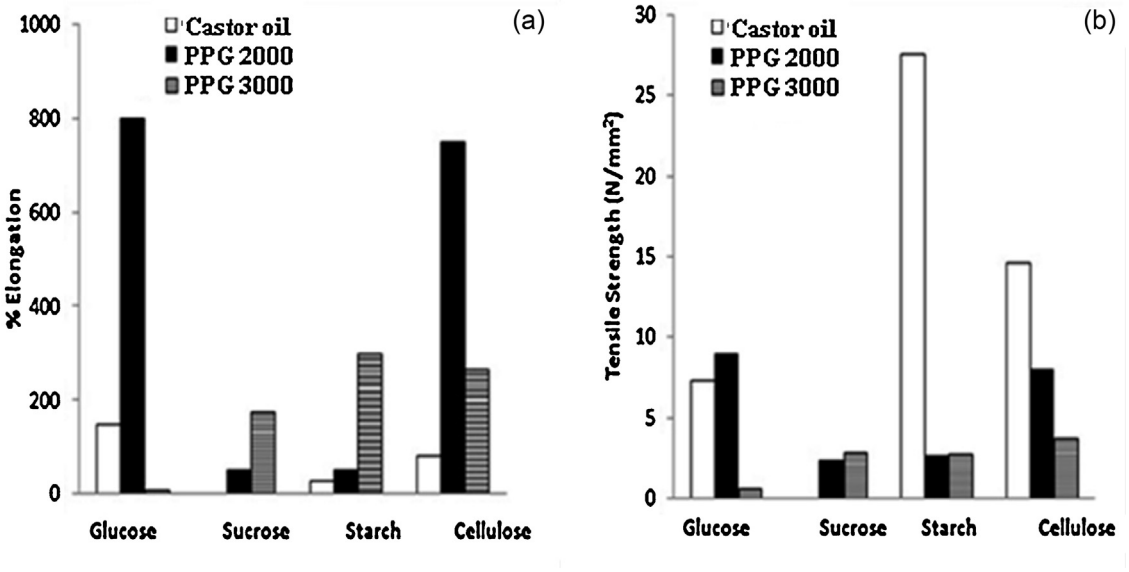
The polymers were characterized for mechanical, thermal and transport properties. Tensile strength and % elongation properties of all of the PU films were measured on a universal testing machine (HOUNSFIELD) using test specimen in the form of dumbbells according to IS 3400(Pt-1)-1987. The gauge length was 50.0 mm. The crosshead speed was 10 mm/min at 25 °C and 50% humidity. The data given are the average of five measurements. Thermo gravimetric analysis (TGA) was recorded on TG–DTA 6300 INCARP EXSTAR 6000 in nitrogen atmosphere in temperature range of 30–450 °C at heating rate of 10 °C/min. The differential scanning calorimetric (DSC) analysis of PUs was performed by using a NETZSCH DSC 200 F3 thermal analyzer with a DSC module, which was purged with nitrogen gas and quenched with liquid nitrogen. This analyzer was pre-calibrated from the melting point of indium at 156.6 °C, tin at 231.9 °C and cyclohexane at −87.06 °C. Then, the sample (approximately 10 mg) was sealed in aluminum pans with lids, and scanned from −100 °C to 300 °C with a rate of 5 °C/min under a 40 ml/min nitrogen atmosphere. The midpoint of the heat capacity change was chosen to represent the glass transition temperature, T_g. The surface morphology of the fractured samples of PUs was examined by means of Jeol Scanning Electron Microscope (model-JSM-5610 LV). An accelerating potential of 15 kV was used for the analysis of the sample. The photographs of representative areas of the samples were taken at different magnifications. The sorption study was carried out by the method as per the procedure described in our earlier work (Lalwani & Desai, 2009). All the samples were subjected to sorption studies in different solvents. The solvents were selected in terms of their polarity beginning with the non-polar toluene to the highly polar solvent such as methanol. Biodegradation of the PUs was studied by the soil burial method as per the procedure described elsewhere (Thakore, Desai, & Sarawade, 2001).

2.4. Cell culture

The normal lung cell line L132 (obtained from National Centre for Cell Sciences, Pune, India) were seeded (1×105 cells/25 mm T Flask) and cultured in DMEM containing 10% FBS and 1% antibiotic-antimycotic solution at 37 °C with 5% CO_2 (Thermo scientific, forma II water jacketed CO2 incubator). Cells were subsequently subcultured every third day by trypsinization with 0.25% Trypsin-EDTA solution. All the reagents were filtered through 0.22 μm filter (Laxbro Bio-Medical Aids Pvt. Ltd) prior to use for the experiment (Valodkar et al., 2011).

2.5. Measurement of cell viability by MTT assay

Cell viability was evaluated by MTT (3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide, Sigma–Aldrich) biochemical assay as per a reported procedure (Zanetta et al., 2009).



(c) **Mechanical properties of St-PUs**

Sr No.	Code	Tensile Strength (Mpa)	Elongation (%)
1	A-St	2.6	50
2	A-St-a	1.14	58
3	A-St-b	1.24	75
4	A-St-c	2.02	63

Fig. 1. Effect of variation of polyols and carbohydrates on (a) % Elongation and (b) tensile strength of polyurethanes.

3. Results and discussion

3.1. Mechanical properties

The properties of a polymer depend upon several factors like molecular weight, chemical nature of the units composing the polymer and the morphology in solid state. Polyurethanes exhibit good mechanical properties due to the existence of alternating hard and soft segments. Due to thermodynamic differences the segments usually segregate to form aggregated pseudo-two-phase structure. At room temperature the macroglycol segments are above their glass transition temperature (T_g) and are denoted as soft segments and the aromatic diisocyanates which are below their T_g act as hard segments. The hard domains act as filler particles and as crosslinks to restrain the motion of soft segment chains. The soft segment provides elastomeric character for the polymer, while hard segment provides dimensional stability (Khinnavar, Aminabhavi, Balundgi, Kutac, & Shukla, 1991).

3.1.1. Effect of type of polyol

Itis well-known that the properties of polyurethanes are remarkablyaffected by the content, type, and molecular weight of the soft segments (Eceiza et al., 2008). As shown in Fig. 1a, when polysaccharides are used as crosslinkers the elongation is higher in PPG based PUs while tensile strength shows reverse trend (Fig. 1b). When the load is applied to the polymer network of PPG based PUs because of its high flexibility it is transferred to the rigid part of the network and creates stress concentration at that region. Ultimately, rupture takes place even at low load resulting in a decrease in tensile strength. Whereas, in the case of castor oil PUs, due to lower molecular weight of polyol, the chain length decreases and crosslink density increases. Further an additional hydroxyl group results into more rigid network with high tensile strength and lower % elongation. The shorter length of flexible chain contributes to bear load along with the rigid hard segment region coordinately.

Higher molecular weight of polyol tends to increase the flexibility due to multiple $-CH_2$ groups and hence a tremendous loss in mechanical strength of PPG 3000 based PUs especially when glucose is used as crosslinker. PPG-2000 system having glucose and cellulose as a crosslinker showed highest elongation property. This might be due to higher reactivity of glucose leading to efficient crosslinking. Cellulose with a polymeric back bone and multiple hydroxyl groups contributes to high mechanical strength. Interestingly both elongation and tensile strength were observed to be high in glucose crosslinked PPG-2000 PU compared to glucose crosslinked castor oil PU. One of the explanations for this may be the hydrophilicity of monosaccharide glucose because of which it offers greater compatibility with PPG compared to hydrophobic castor oil. Castor oil system having starch as a crosslinker showed maximum value for tensile strength.

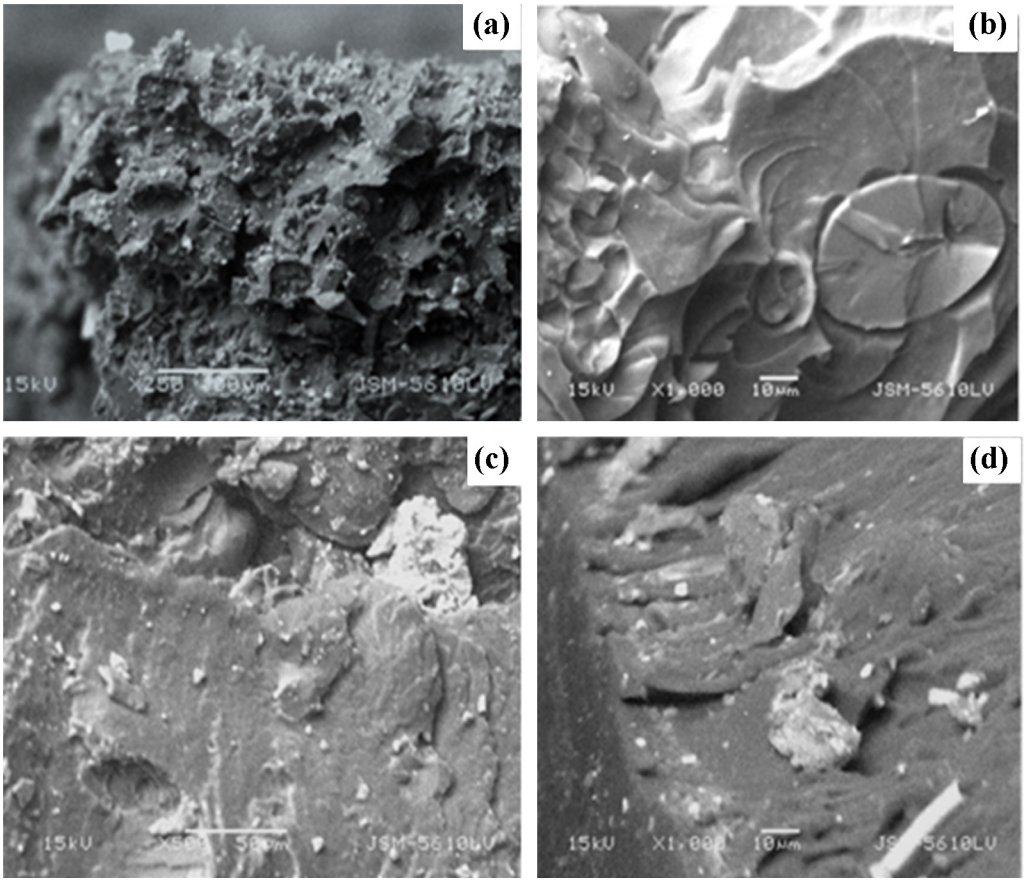


Fig. 2. Scanning electron micrographs of PPG 2000 PUs containing different crosslinkers. (a) B-G at ×250, (b) B-Cel at ×1000, (c) B-Su at ×500, and (d) B-St at ×1000.

3.1.2. Effect of polyol/crosslinker ratio

The effect of variation in *R* value and polyol/crosslinker ratio was investigated for PPG 2000-starchsystem. At a constant NCO/OH ratio (*R* = 1), the PU b with polyol/crosslinker ratio of 1 has higher value for elongation and lower tensile strength as compare to c (polyol/crosslinker ratio = 0.66) (Fig. 1c). An increase in polyol/crosslinker ratio leads to increased relaxation of the polymer chains providing flexibility to the resulting PU. This in turn increases elongation property of polymer. These observations indicate that the crosslinking efficiency of starch is comparable with conventional PU crosslinkers.

3.1.3. Effect of NCO/OH ratio

Two different NCO/OH ratios were selected to obtain two different sets of PUs viz a (NCO/OH = 0.8) and c (NCO/OH = 1.0). Amongst a and c, a has lower tensile strength as shown in Fig. 1(c). This is attributed to the lower *R* value of a. The hard segment structure (isocyanate), in addition to the elastic nature of soft segment, provide enough physical crosslink sites to impart properties ranging from elastomeric to rigid behavior with the increase of hard segment content (Corcuera et al., 2010). The more the *R* value, the higher is the NCO groups. Excess NCO groups may form allophanate crosslinks with urethane or form urea crosslinks with moisture

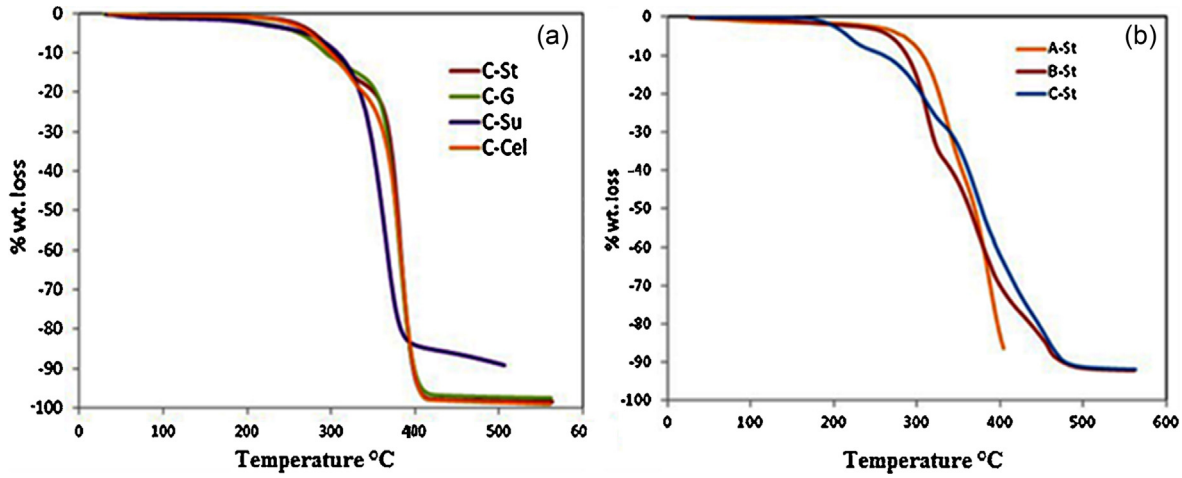


Fig. 3. Thermal degradation plots of (a) PPG 3000 PUs with different crosslinkers (b) Starch crosslinked PUs with different polyols.

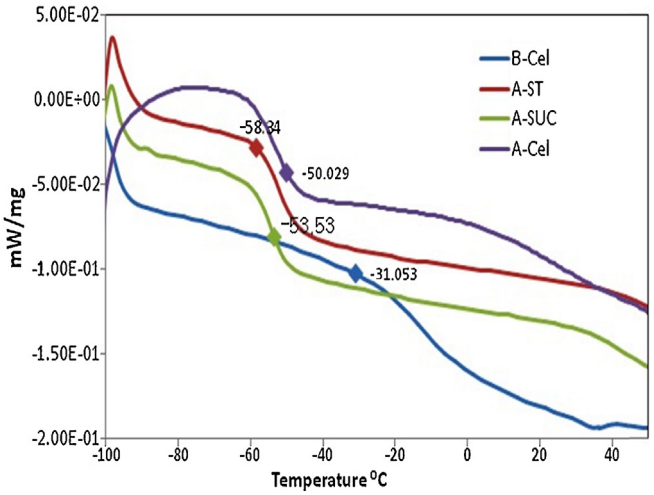


Fig. 4. DSC thermograms of polyurethane polymers.

in the air. These two kinds of crosslinks can enhance the tensile strength of PUs. Amongst a and c, the elongation also increase with increase in *R* value indicating dependence of these properties on NCO content. This is an interesting observation as generally elongation and tensile strength show opposite trend. This can be explained as follows. When the TDI content was less (polymer a) there existed certain domain in the samples due to incomplete crosslinking or possible structural inhomogeneity developed due to the reaction of some of the NCO groups with moisture during curing. Whereas excess of diisocyanate develops a firm network by linking together the dangling chains or reacting with urethane groups through crosslinking, resulting into higher stress-strain properties.

3.1.4. Effect of type of carbohydrates

It is obvious that starch and cellulose, being polysaccharides should have formed more crosslinked structure compared to monosaccharide (glucose) and disaccharide (sucrose) resulting into highest tensile property. Amongst the two, cellulose is derived from D-glucose units, which condense through β (1→4)-glycosidic bonds. This linkage moiety contrasts with that for α (1→4)-glycosidic bonds present in starch, glycogen, and other carbohydrates. Cellulose is a straight chain polymer; unlike starch, no coiling or branching occurs, and the molecule adopts an extended and rather stiff rod-like conformation, aided by the equatorial conformation of the glucose residues (Lehniger, Nelson, & Cox, 1993, chap. 11). Thus, starch having more branched structure, can provide higher crosslinking, resulting into higher tensile strength. This is true in case of castor oil based PUs. But interestingly, in PPG based PUs, cellulose based PUs showed higher tensile strength as compare to starch based PUs. It is possible that due to linearity, PPG based polyols can react better with straight chain architectured cellulose as compare to branched structured starch, resulting into polymer with higher strength.

The mechanical properties of castor oil PUs crosslinked with starch are superior to many other reported PUs with petrochemical based chain extenders (Yeganeh & Talemi, 2007; Corcuera et al., 2010). Similarly PPG 2000 PU crosslinked with glucose was found to be superior to other IPNs based on polyether-castor oil polyols (Xie & Guo, 2002).

3.2. Morphology

The results of mechanical properties can be explained on the basis of SEM morphology of tensile fractured sample. SEM morphology of PPG 2000 PUs reveals that the cellulose and glucose crosslinked PUs exhibited more uniform and single phase surface (Fig. 2) which resulted into good mechanical property. While sucrose and starch crosslinked PUs revealed presence of filler particles probably due to blooming phenomenon or during fracture. This may have resulted into lower mechanical strength

3.3. Thermal analysis

Typical TG curves of the PUs showed an initial mass loss from temperature 101–205 °C attributed to elimination of volatile components such as water. Despite lower thermal stability of carbohydrates, all PUs exhibited good thermal stability upto 200 °C. Fig. 3a indicates TGA plot of %weight loss vs. temperature for PUs (PPG 3000 system) with four crosslinkers. The degradation pattern is similar for all four crosslinkers suggesting that thermal stability of PUs under study is independent of type of crosslinkers. Fig. 3b represents the thermal stability curves for PUs with different polyols and starch as a crosslinker. The PUs exhibited similar TGA pattern and more or less equal thermal stability when starch was used as crosslinker irrespective of the type of polyol.

The differential scanning calorimetric plots of representative samples are given (Fig. 4). A comparison of T_g values of PPG PUs with different crosslinkers revealed that PU with cellulose as a crosslinker showed highest value of T_g. This is in accordance with the results of mechanical properties as PPG-cellulose PU possesses higher mechanical strength as a result of lower mobility of polymer chains. A comparison of cellulose crosslinked PUs having different polyols exhibited a drastic change in T_g. This indicates that the polyols make a greater contribution to the glass transition properties of PUs under study.

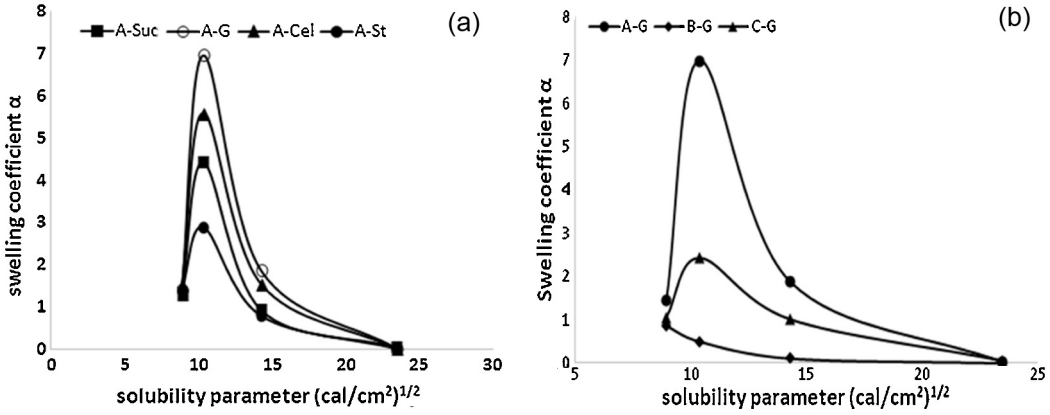


Fig. 5. Swelling coefficient versussolubility parameters of solvents (a) PPG 2000 PUs with different crosslinkers (b) glucose crosslinked PUs with different polyols.

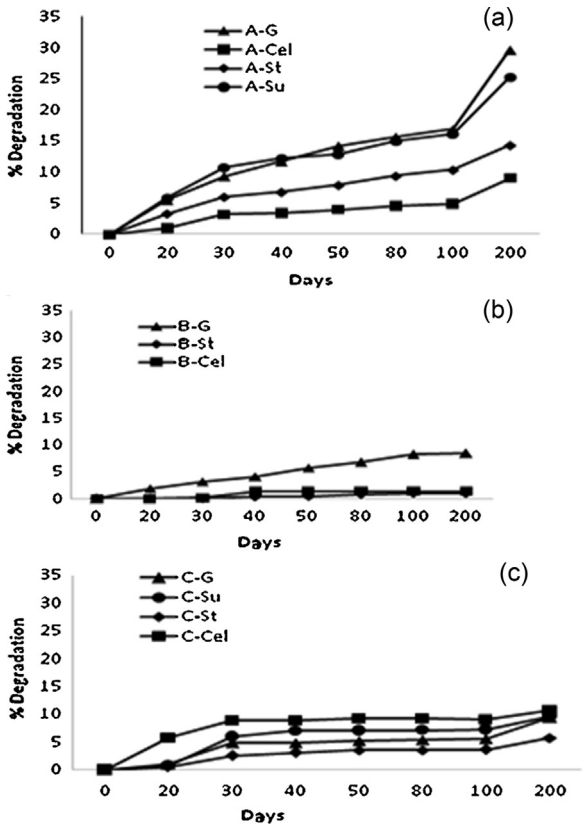


Fig. 6. Plot of percentage degradation with time in soil burial test for PU films (a) PPG 2000 PUs (b) Castor oil PUs (c) PPG 3000 PUs.

PPG based PU (A-Cel) show lower T_g compare to castor oil based PU (B-Cel). This is because the linear structure of PPG provide greater flexibility and mobility to the chain, resulting into lower T_g whereas in case of castor oil, as mentioned earlier, chain length is shorter as compare to PPG, crosslink density increases, which results into more rigid network. Due to this characteristic, movement of chain is restricted leading to higher T_g.

3.4. Sorption studies

From the representative plots of variation of final solvent uptake of PU films in various solvents (Fig. 1S), it is observed that the solvent intake is much higher in case of PPG PUs.

The sorption behavior of PUs indicated that the rigidity of network, molecular weight and nature of polyol dominated extent of solvent uptake. PPG 2000 PUs showed higher solvent uptake followed by PPG 3000 and castor oil PUs. The type of crosslinker used did not have a significant effect on swelling as well as solubility parameters of PUs because all the crosslinkers are chemically very similar.

The representative plot of swelling coefficient α versus solubility parameters of solvents for PPG 2000 PUs containing for different carbohydrates is shown in Fig. 5a. It is observed that maximum swelling takes place in glacial acetic acid. PPG 3000 PUs also showed similar sorption behavior. Hence, the solubility parameter of the PPG PUs under study was considered to be 10.1 $(cal/cm^3)^{1/2}$ irrespective of the type of crosslinker used in the present system. This is because the three crosslinkers are chemically very similar and are expected to have same effect on the solubility parameters. But castor oil PUs showed different fashion of sorption, showing highest swelling in toluene (supporting information) due to hydrophobicity of castor oil. This indicates that although sorption is independent of type of crosslinkers, the type of polyol has a significant effect on sorption pattern of PUs.

3.5. Biodegradation study

The change in weight as a function of time in the biodegradation process is shown in Fig. 6. The PPG based polyurethane samples displayed a continuous weight loss while castor oil PUs showed very low degradation rate (Fig. 6). The poor degradability of castor oil based PUs has been reported in fungal degradation tests (Oprea, 2010). This was attributed to the hydrophobic nature of castor oil which leads to poor wetting of the PUs by the culture medium. Surprisingly similar results were observed in case of soil burial test in the present study.

This probably indicates significant role played by moisture in initiating the degradation of polymers. In addition the flexibility and swellability of network is also an important factor that governs biodegradation (Van den, Samyn, & Kinget, 1994). Higher

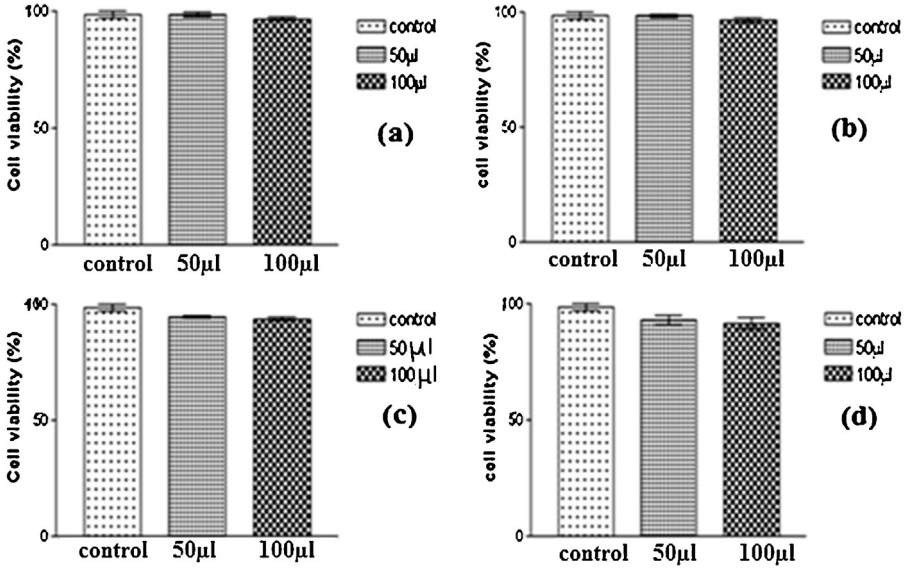


Fig. 7. % cell viability by MTT assay of PUs (a) A-Su, (b) A-St, (c) A-cel and (d) B-st.

degradation rate of PPG 2000 PUs as compare to PPG 3000 PUs is attributed to higher molecular weight of PPG 3000. A comparison of sugars revealed that the observed weight loss was highest in the case of glucose containing PU except in PPG 3000 system. The % degradation decreases as monosaccharide is replaced by disaccharide followed by polysaccharide. In case of PPG 3000, the longer chain of polyol may be susceptible to higher degradation which may not depend on type of carbohydrate crosslinkers.

3.6. MTT assay

Percentage viability of cell lines exposed to some representative PUs is shown in Fig. 7. The MTT absorbance of L132 cells exposed to PUs was almost equal to control and also well below the toxicity limit. This indicated that the PUs under study are noncytotoxic and can be used as drug carriers.

4. Conclusion

The study reveals that carbohydrates can be promising crosslinkers for synthesis of polyurethanes. The performance of the carbohydrate was dependent not only on its structure but also on the type of polyol. With a combination of polyols and carbohydrates a wide spectrum of significant mechanical properties can be achieved which can be further tuned by varying the NCO/OH ratio and polyol/crosslinker ratio. The resulting PUs possessed reasonable thermal stability and interesting sorption properties. Thus this work rendered a strategy for achieving high mechanical performance along with biodegradability and biocompatibility for potential applications as drug delivery systems.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.04.021.

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