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REVIEW

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The future of isosorbide as a fundamental constituent for polycarbonates and polyurethanes

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ABSTRACT

Isosorbide is a biobased compound which could become in the near future an advantageous competitor of petroleum-derived components in the synthesis of polymers of different nature. When the reactivity of isosorbide is not enough, it can be successfully transformed into secondary building blocks, such as isosorbide bis(methyl carbonate), which provides extra functionalities for polymerization reactions with diols or diamines. The present review summarizes the possibilities for isosorbide as a green raw material to be used in the synthesis of polycarbonates and polyurethanes to obtain products of similar or enhanced properties to the commercial equivalents.
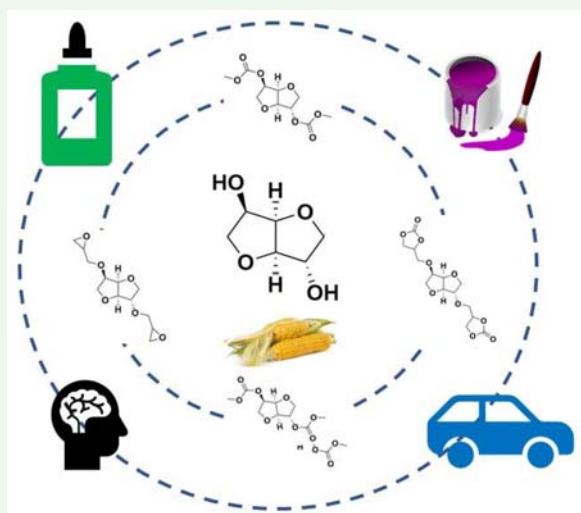
1. Introduction

The Chemical Industry originally only exploited biomass-derived resources. However, the development of new cheaper and more versatile petro-derived materials emerged with overwhelming force at the end of the nineteenth century. Now, is the turning point for reducing the global dependence on fossil-based sources facilitating the transition towards a more sustainable economy approach. In this sense, the research in new biomass-derived resources is attracting significant attention. Renewable monomers and polymers may contain diverse functional combinations that would not be cost-effective if they are produced through petrochemical routes. The lower toxicity and carbon footprint, as well as the inherent biodegradability are advantageous characteristics that differentiate them from their fossil-derived counterpants.

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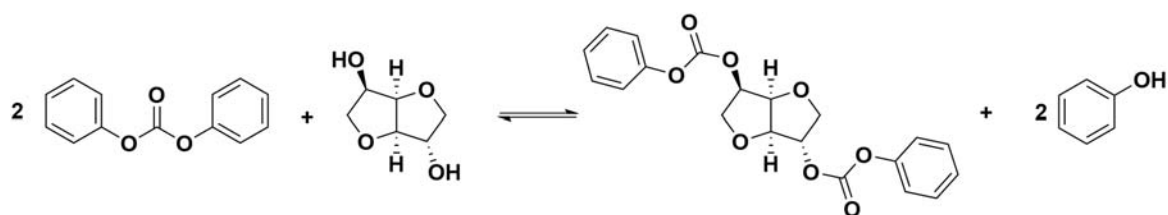
Scheme 1. Synthesis of IBPC from isosorbide and DPC.

Isosorbide (1,4: 3,6-dianhydro-D glucitol or1,4: 3,6-dianhydrosorbitol) is a commercial primary bio-based diol obtained from glucose by dehydration of D-sorbitol (*1*, *2*). It is biodegradable, soluble in water, and classified as a GRAS (generally recognized as safe) substance (*3*). Isosorbide possesses a stereochemistry and geometry suitable for making cost-effective chemicals, and a molecular rigid configuration constituted by two tetrahydrofuran rings that provides mechanical strength to the corresponding derivatives (*1*, *4*). Isosorbide presents two secondary hydroxyl groups of different reactivity that, after suitable derivatization reactions, can lead to a broad spectrum of bifunctional derivatives.

Some of these derivatives (nitrates, esters, ethers.) are already employed in industrial processes for the manufacturing of medical vasodilators (*5*), plasticizers (*6*), or surfactants (*7*). Others are also commercially converted into different polymers, such as poly-(ethylene-isosorbide)terephthalate (PEIT), poly(isosorbide oxalate), or poly(isosorbide carbonate) known as DURABIO® (Mitsubishi) and PLANEXT® (Teijin) (*8*). Moreover, isosorbide is characterized by a high glass transition temperature (Tg), tensile modulus, UV stability, and visible light transmission (*6*, *9*). These are features to make isosorbide a promising renewable candidate to replace non-renewable and toxic bisphenol-A in polycarbonates production. Moreover, isososorbide can also be incorporated in the formulation of a new type of non-isocyanate polyurethanes that can suppose a safer alternative than the traditional ones.

2. Isosorbide monomers

The pronounced hygroscopic character of isosorbide and the poor reactivity of one of its secondary hydroxyl groups are two main drawbacks for polimerization reactions. Therefore, its conversion into more stable and homogeneous secondary bio-based monomers becomes a very interesting alternative (*10*).

Several compounds as phosgene or its derivatives have been incorporated into isosorbide to obtain carbonated monomers (*11*). These syntheses have been described in patent applications, such as US 2004/241553 which use isosorbide and a choloroform ester,

a very toxic compound. JP 6–261774 also discloses a process for preparing isosorbide di-alkylcarbonates, but it also using toxic species, in particular alkyl chloroformate in a molar excess to isosorbide of 2:1. However, this type of chemistry is not aligned with the basic rules of sustainable green economy.

Different authors proposed solutions to compensate the low isosorbide reactivity. Yoon et al. (*12*) studied this property in the synthesis of a biobased copolyester with high thermal resistance. The structure of isosorbide provided rigidity to the polymer, but the low reactivity of hydroxyl functionalities of the biobased diol made necessary the combination with other alcohols (1,4-cyclohexane dimethanol and ethylene glycol) to achieve a polymer with a desirable Tg. The authors concluded that it was necessary to mix both biobased and nonbiobased resources to obtain a product with the properties required for commercial plastics' applications.

Isosorbide bis(phenyl carbonate) (IBPC) is the isosorbide-based monomer currently employed in the synthesis of isosorbide polycarbonates. IBPC can be obtained by reacting isosorbide with toxic molecules as diphenyl carbonate (Scheme 1) or phenyl chloroformate using pyridine as a catalyst (*13*). Zang et al. (*14*) studied the reactivity of the endo and exo hydroxyl groups of isosorbide in the reaction with diphenyl carbonate (DPC) using basic catalysts as alkaline hydroxides, temperatures of 160°C or higher, and high vacuum to promote the elimination of toxic phenol. The transesterification reaction can be speed up by increasing the temperature, but also oligomers of different *Mw* were formed leading to a monomer of poor quality which must be purified by a costly and time-consuming procedure.

Isosorbide bis(methyl carbonate) (IBMC) is presented as a *green* alternative to the synthesis of isosorbide derivatives which avoids the use of toxic substances as phosgene, disphosgene or DPC. IBMC is produced from the methoxycarbonylation reaction between isosorbide and dimethyl carbonate (DMC) (Scheme 2). It consists of a double transesterification assisted by basic catalysts which promote the abstraction of the isosorbide alcoholic protons, resulting in alcoxide groups that attack the DMC carbonyl moiety. Methanol is
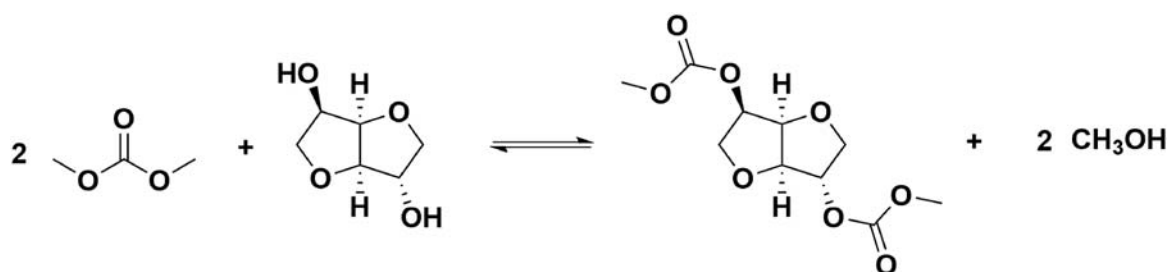
Scheme 2. Synthesis of isosorbide bis(methyl carbonate) from isosorbide and dimethyl carbonate.

obtained as a co-product which is easily evaporated from the reaction media and reused in other chemical processes.

DMC is considered a nontoxic and biodegradable agent obtained by an eco-friendly process that not generates undesirable by-products (special in comparison to phosgene derivatives which are characterized by toxic and non-selective processes) (*15*). It behaves like a versatile reactive, not only in the carbonylation reaction, but also in the methylation to give dimethyl isosorbide (DMI). The preference by one or other pathway depends on factors such as the catalyst basicity strength and nucleophile character and the reaction conditions (time and temperature) (*16, 17*).

According to the green chemistry principles, DMC is a significant contributor to all impact categories of the IBMC production (*18*). The synthesis process focuses special attention on the safer use of chemicals and products in comparison with equivalent petro-derived synthesis routes. DMC is not only an efficient alternative to any harmful phosgene derivatives, but also improves the overall process efficiency optimizing the use of resources. DMC simultaneously acts as a green solvent that can be partially recovered to the next reaction cycle, and as a reactant. In this sense, the IBMC synthesis process presents an atom efficiency of 80.4%, superior to the corresponding one of IBPC production. Moreover, the only coproduct obtained in the first case is methanol, in contrast with phenol, a toxic compound that must be properly managed.

Fuertes et al. (*19*) patented a process to obtain *green* isosorbide monomers useful for polycarbonates production from isosorbide and DMC. They used a large carbonate excess to shift the reaction equilibrium and favour the dilution media preventing undesired oligomers generation. (molar ratio DMC/isosorbide of 40 to limit the oligomeric fraction to approximately 5% of the total product). The coproduct methanol was continuously eliminated to shift the equilibrium reaction towards the IBMC synthesis using a rectification column with enough plates to permit the isolation of DMC from methanol, which forms an azeotrope at a

composition ratio of 70:30 (weight ratio) (*20*). DMC can be substituted by diethyl carbonate (DEC) to produce isosorbide bis(-ethyl carbonate) and ethanol instead of methanol. However, costs for this co-product removal by distillation are higher than for methanol.

Ochoa-Gómez et al. (*10*) optimized the IBMC synthesis using alkaline carbonates and DMC in excess of 30:1 with respect to isosorbide; enough to maintain the oligomer production between 5% and 10%. In both processes, IBMC purities up to 99% can be obtained with the use of different purification techniques as short path distillation (*19*), or organic solvent nanofiltration membranes (*21*).

Indeed, the catalysts play a relevant role in the reaction of IBMC production since they can activate both the endo and exo isosorbide -OH groups in a different way depending on the size of the metallic cation used. Catalysts containing larger ionic radius metal (K^+ or Cs^+) easily promoted the exo-OH attack to carbonyl groups of DMC. On the other hand, the catalysts composed of smaller ionic species (Na^+) preferentially promoted the reaction between the endo-OH of the isosorbide and the DMC (*6, 16, 22*).

Chatti et al. (*11*) showed that low nucleophilic catalysts as potassium tert-butoxide (KOtBu), tin dioctanoate ($SnOct_2$) or titanium tetrabutoxide ($Ti(OBu)_4$) promoted the methylation instead of the carboxylation of isosorbide with DMC, giving mixtures of alkyl ethers (DMI) and a very low proportion of IBMC.

Qian et al. (*23*) designed a new type of ionic liquids with specific basicity and nucleophilic properties. They tuned the properties of the catalysts altering the basicity of the anions in the ionic liquids. Activation of functional groups occurs by electrostic and H-bonds interactions.

Ochoa-Gómez et al. (*24*) offered a very interesting approach to assess the influence of both the basicity and the nucheophilic character of a catalyst into the isosorbide conversion and the IBMC yield. They demonstrated that the IBMC production was very adversely influenced by the presence of residual acidic impurities resulting from the isosorbide synthesis by sorbitol dehydration using mineral acids such as sulfuric acid

as catalysts. These impurities can deactivate typical heterogeneous basic catalysts. However, homogeneous nitrogenated bases and superbases with a suitable dual nucleophilic-basic character were able to form a acyl intermediate able to effectively react with the electrophilic reactant DMC.

Some similarities can be found between the IBMC and bisphenol-A synthetic processes. The petro-derived monomer is obtained from the catalytic condensation between phenol and acetone at 50–90°C in the presence of a strongly acidic catalysts with a ratio acetone:phenol of 1:3–30 (25). IBMC is obtained at similar temperatures but with basic catalysts and a ratio of ISO:DMC 1:30 (24). In both cases, the formation of undesired secondary products is an issue that must be still further optimized to decrease the purification costs.

Another monomer of great interest for the synthesis of polyurethanes/epoxy resins is the isosorbide diglycidyl ether. This compound is intended to constitute a bio-based alternative to the diglycidyl ether of bisphenol-A (DGEBA) which is by far the most common starting monomer used in the epoxy networks (26). The synthesis of isosorbide diglycidyl ether is extensively described in the patents applications WO 2008/0021209A1, WO 2008/0009599A1, and in the US Patent 7,619,056 B2. It is obtained by the direct reaction of isosorbide with an excess of epichlorohydrin under alkaline conditions (50% excess of sodium hydroxide). Isosorbide diglycidyl ether can effectively be cured with hardening agents as aliphatic diamines to generate polymers useful for coatings, adhesives, and composites in biomedical applications (27, 28).

Besse et al. (28) reported a process for the synthesis of isosorbide di-glycidyl ether using isosorbide with m-chloroperbenzoic solubilized in chloroform. Isosorbide diglycidyl ether oligomers were obtained by reacting isosorbide with an excess of epichlorohydrin in a concentrated solution of NaOH (50%) added dropwise. The epoxidized isosorbide was next carbonated with 6 bar of CO_2 using LiBr as a catalyst (Scheme 3). Finally, the

resulting cyclocarbonated monomers were converted into linear and branched poly(hidroxyurethanes) by the addition of different types of diamines. This reaction presents some advantages in comparison to polycondensations of IBMC with diamines, since the addition of these reactants to the cyclocarbonated isosorbide avoids the release of methanol as a co-product.

Finally, Darroman et al. (29) developed blends of isosorbide and cardanol to substitute the DGEBA in epoxy resins. The new mixed resins once formulated, were cured at room temperature and compared to commercial petro-derived equivalents in coating applications. The rigid structure of isosorbide increased the Tg of the resulting materials giving similar hardness to the epoxy networks with the DGEBA addition.
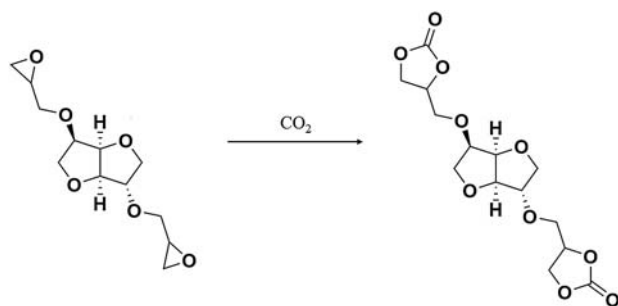
3. Isosorbide polycarbonates

Polycarbonates (PC) constitute a principal family of polymers of daily use in many fields due to their properties as mechanical strength, good transparency, and excellent thermal stability (16). Accordingly, polycarbonate diols are an important PC sub-class, precursors of polyurethanes, which find broad applications in the manufacture of adhesives but also in coatings such as paints, varnishes, and lacquers among others (30).

Interfacial and melt polymerization are the principal ways of obtaining commercial PCs. In the first case, bisphenol-A reacts with phosgene in presence of a chlorinated solvent, water and a catalyst. In melt polymerization, more severe reaction conditions are demanded for the removal of condensates if high-molecular-weight polymers are desired (31). In this case, bisphenol-A reacts with DPC in absence of a solvent. The proper selection of operational conditions and catalysts is fundamental to obtain polymers of high molecular weight and transparency.

The potential of isosorbide and its corresponding monomers (IBMC and IBPC) to substitute bisphenol-A (Scheme 4) is very promising since the current worldwide annual production of petro-derived polycarbonates is over one billion pounds (25), and bisphenol-A has been recently forbidden to be applied to children's products and drink/food packaging due to its possible toxicity (31). A second important limitation of conventional polycarbonates is the poor UV-stability derived by the high aromatic content. Poly(bisphenol-A carbonate)s lead to relative yellowing, especially evidenced in coatings for external applications (13).

But, in any case, isosorbide polycarbonates must compete in quality and price with their petro-derived homologs. Compared to BPA homopolycarbonates, isosorbide-containing polymers still do not constitute an

Scheme 3. Structure of isosorbide diglycidyl ether and the corresponding carbonated isosorbide.
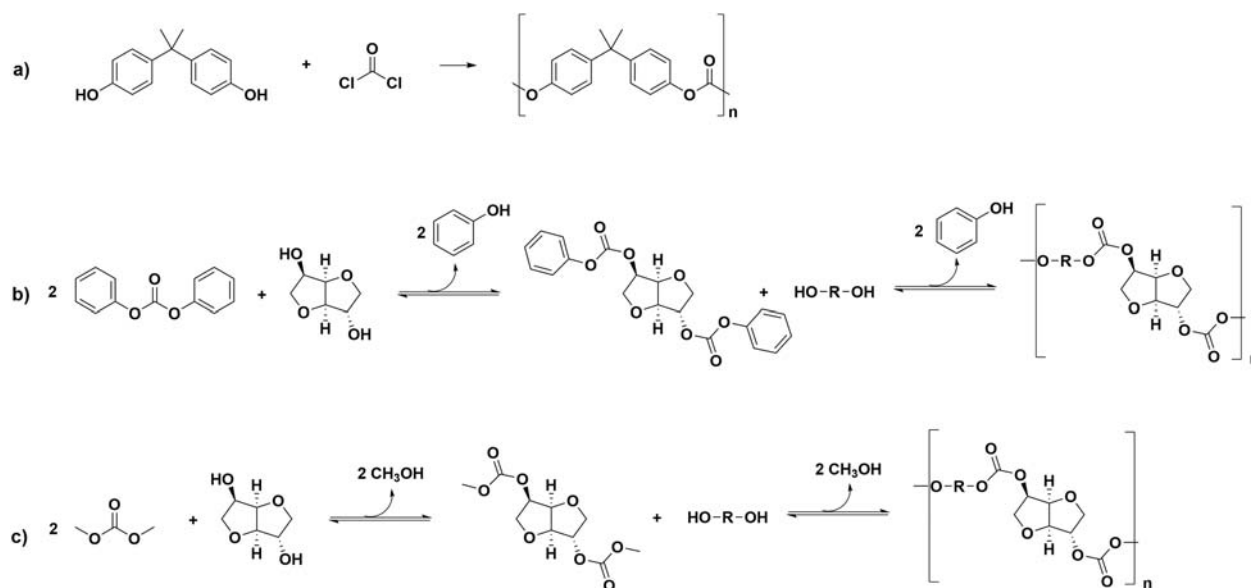
Scheme 4. Polycarbonates synthesis: (a) from bisphenol-A and phosgene; (b) from IBPC and a diol (isosorbide); (c) from IBMC and a diol (isosorbide).

ideal solution since they present some limitations related to fragility, color instability and crosslinking at high temperatures. The principal cause of this is the presence of β-hydrogens which are prone to elimination reactions, evidenced at temperatures even below 280°C (9). Researches are currently oriented to discern which are the more appropriate operational conditions, isosorbide derivatives, and catalysts to obtain polycarbonates of enough molecular weight, as well as equivalent stability and mechanical properties than those of BPA polycarbonates.

Different strategies have been developed for producing new bio-based polycarbonates by the combination of isosorbide and its derivatives with aliphatic diols or glycols and other alcohols with more than two hydroxyl functional groups. Two steps are defined in the synthesis of isosorbide-derived polycarbonates (PIC); the first one consists of a transesterification stage between isosorbide and the alkyl/aryl carbonate to obtain a mixture of the monomer, dimers, and oligomers. Operational conditions are milder in order to maximize the reaction selectivity. If DMC is used as a reactant, temperatures for this first stage are close to the DMC reflux temperature. It is not necessary to use vacuum since the methanol produced is easily eliminated by distillation (19, 24). On the other hand, if DPC is used with isosorbide, temperatures from 160°C to 220°C coupled with high vacuum must be considered to remove the phenol formed (32).

The second stage needs higher temperatures under continuous vacuum to remove the alcohol formed. Temperatures between 100°C and 200°C are employed

and optionally vacuum is used to increase the product molecular weight. The melt polymerization process using DPC requires higher reaction temperatures, from 230°C to 250°C, under vacuum (from 270 till 5 mbar) (32) and leads to almost exclusively hydroxy-functional poly(1,4:3,6-dianhydrohexitol carbonate)s.

Apart from the low molecular weight of the products, the rigid structure of isosorbide causes that homopolycarbonates present fragility, high melt viscosity and, hence, difficulties in moldability.

An effective way to increase the molecular weight is the addition of more active substances apart from the isosorbide and the carbonate molecules. An option is to include aromatic molecules (similar to bisphenol-A), but they present relatively rigid structures that do not decrease the melt viscosity. However, these raw materials suppose a concern related to the toxicity of the secondary products (33).

Another possibility lies in incorporating flexible diols in the polymerization process. The introduction of certain soft blocks as C2-C12 linear diols (34) improves the processability and transparency of the polymer although the glass transition temperature of the product is reduced (11, 34).

Park et al. (35) developed a biomass-derived polycarbonate composite from nanocellulose crystals dispersed in poly(isosorbide-co-CHDM carbonate). The nanocomposites obtained overcome the disadvantages of isosorbide homopolycarbonates showing higher transparency as well as improved mechanical strength under both tensile and impact conditions. This was achieved by an

optimal dispersion of the cellulose nanofiller into the iso-sorbide polymer matrix that improved the tolerance to cracking initiation and the ductility of the polymer.

The advantages of using DPC vs. DMC in the synthesis of polycarbonates of isosorbide are related to the reactivity of the raw materials. The aryl group makes the carbon of the carbonyl group more electrophilic, and the bulky aromatic moieties in DPC difficult the nucleophilic attack to the carbonyl by steric hindrance. Park et al. (36) confirmed the low stability of the alkoxides of isosorbide in comparison to the corresponding phenoxides.

However, DPC possesses several disadvantages because is obtained from poisonous phosgene by a complicated synthetic process (23). Moreover, large amounts of toxic phenol are generated as a byproduct of the polymerization reaction of PICs (30). This is the case of the patent EP2033981 (37) which describes the production of polycarbonates using isosorbide, a diol, and DPC. The polycondensation reaction generates phenol as a principal co-product (phenol boiling point 181.7°C, 1 atm.) Noordover et al. (13) reported the synthesis of biobased polycarbonates using various isosorbide isomers. Three different synthetic routes were screened for obtaining OH-functional poly-carbonates for coating applications. The first one employed triphosgene as a carbonyl source. In this case, molecules with low end-OH groups were obtained. The second strategy considered the use of a large excess of diols. Significant amounts of cyclic chains, which do not participate in the curing reactions were obtained. The third one considered DPC as a co-reactant and optionally different alcohols such as 1,3-propanediol or TMP. This synthetic route resulted in several linear and branched polycarbonates that were crosslinked with a conventional polyisocyanate in order to obtain a glossy coating.

Chatti et al. (11) obtained OH-terminated polycarbonates by the polycondensation of isosorbide with a large excess of diphosgene. High molar weight polymers almost free of cyclocarbonates were obtained. However, all the reactants with the exception of isosorbide were not environmentally friendly. The authors unsuccessfully carried out the polycondensation of isosorbide with dialkyl carbonates as dimethyl or diethyl carbonate at 200°C during 2 h since the catalysts employed (KOtBu, Ti (OBu)$_4$ and SnOct$_2$) were not active in the transesterification/polycondensation reactions between both reactants.

Eo et al. (38) obtained high molecular weight polycarbonates by melt-polycondensation of isosorbide with DPC using alkali metal bases, titanium isopropoxide, and lanthanum acetylacetonate [La(acac)$_3$] as catalysts. The authors selected cesium carbonate since it showed the highest catalytic activity. The dissociated ion Cs$^+$ polarized the carbonyl group of DPC which is attacked by the –OH groups of isosorbide giving polymers of Mn up to 26,700. Products could suffer from discoloration due to the high catalyst concentration.

Shen et al. (39) studied the synthesis of several Ca/SBA-15 solid bases to be employed as catalysts for the production of poly(isosorbide carbonate) from DPC and isosorbide via a transesterification/polycondensation process. The authors established that the strong basic sites of the catalysts were responsible for the trans-esterification step but they could favour the decomposition of the resultant polycarbonate, limiting the final average molecular weight. On the other hand, the weak and medium basic sites of the catalyst favoured polycondensation reactions, in special at temperatures between 200°C and 240°C, followed by a gradual variation between 250°C and 260°C. The decomposition of isosorbide generates secondary reactions that limit the polymer growth chain.

Dhara et al. (40) described the transcarbonation of isosorbide and DPC to produce homo and copolycarbonates when combined with bisphenol-A. In all cases, long reaction times, temperatures up to 260°C and a vacuum pressure of 1.5 millibars were precised. The polymers obtained showed high quality and low yellowness, but moderate molecular weights (M$_n$ from 8700 g/mol when isosorbide and DPC were used, to 21,600 g/mol if a ratio isosorbide:bisphenol-A of 25:75 was employed.)

Similar procedure was applied in the US Patent 8,399,598 B2 where isosorbide was reacted with DPC in the presence of tetramethyl ammonium hydroxide as a base. Temperatures up to 260°C and a pressure of 6.66×10^{-5} MPa were required to obtain a moldable polymer. US 2004/0241553 A1 and JP6-261774 describe the synthesis of isosorbide polycarbonates using chloroformate esters as co-reactants. JP 2014–62202 and JP 2014-80590 show two processes for manufacturing poly-carbonate diols of molecular weight lower than 3000 g/mol from isosorbide, a diol and a phenolic derivative. A polycarbonate diol was obtained in the patent EP 2559718 in the reaction between isosorbide, a diol, and DPC to produce a polycarbonate-diol. The high reactivity of the ester causes the unspecific reaction with any diol and nonuniform products obtaining. In the US Patent 8,399,598 B2 a process for obtaining polycarbonates is claimed. Polycarbonates with high heat resistance, thermal stability, and moldability, are obtained by melt-polycondensation of isosorbide, DPC and an aliphatic diol of boiling point higher than 180°C. A final pressure of 0.7 mbar is necessary to distill off the formed phenol.

In WO11/082144 the production of an oligomeric carbonate polyol having a molecular weight of 900–4000 made from isosorbide, a polysiloxane, an aliphatic component, and optionally bisphenol-A is reported. Temperatures up to 200°C and pressures of 4–5 bar are required without the addition of any catalyst.

All the processes described suffering from the generation of hazardous subproducts that must be completely removed from the reaction media. Apart from that, polycondensations of isosorbide with DPC have some other less favourable characteristics, including long residence times at elevated temperatures that originate different side reactions. Products are colored and less suitable for thermally sensitive applications. Bayer evidenced these results in a patent (41) where temperature levels superior to 200°C caused intensive side reactions, resulting in polymers with brown color and highly crosslinked. In the same way, the low acidity and high solubility of isosorbide in water hampered the interfacial (co)-polycondensation reaction (42).

As an alternative, IBMC derived polycarbonates show some desired characteristics as high-impact strength, transparency, heat resistance, flame retardancy, or dimensional stability (8). Both isosorbide, DMC, and IBMC are green reactants in comparison with DPC and IBPC and open the possibility for the development of new polycarbonates without the generation of toxic residues employing energetically less intensive reaction conditions.

However, synthetic processes with isosorbide, DMC, or IBMC are slightly more complicated than with DPC/IBCP due to the lower reactivity of carbonate and hydroxyl groups related to the higher methoxide anion basicity. Moreover, terminal functionalities from DMC can both act as a methylating agent. These dimethyl ether-ended groups prevent the growth of the polymer chain in the polycondensation step (43).

Kim et al. (44) demonstrated that DPC could easily be transesterified with bisphenol-A without any equilibrium restrains. The same reaction with DMC showed low yields and coproduced a significant amount of methylated bisphenol-A. Different strategies must be developed to overcome these difficulties as the design of specific catalysts that promote carboxymethylation reactions.

Ochoa-Gómez et al. (10) reported the use of alkaline carbonates as effective catalysts for the polycondensation of IBMC with 1,4-butanediol. Isosorbide-based oligocarbonates were obtained at 160°C and 600 mbar with molecular weights ranging between 946 and 1243 g/mol and a polydispersity of about 1.40. On the other hand, new thermostable bromine-based ionic liquids were developed by Qian et al. (17) to produce homopolycarbonates from isosorbide and DMC. The cation structure of these catalysts was conveniently modeled to control the reactivity of endo and exo –OH of isosorbide with carbonate moieties. Polymers obtained had molecular weights up to 52,100 g/mol.

Carbonate catalysts were also efficiently employed by Roquette Frères for the production of isosorbide-derived polycarbonates as it is described in EP2694569B1, wherein a process manufacturing rigid polycarbonates at room temperature having a glass transition temperature equal to or greater than 50°C is described. The polycarbonates were synthesized by a transesterification polycondensation reaction between a dialkyl carbonate of isosorbide (preferably IBMC) and a cyclic diol. A maximum temperature of 235°C was employed. Although the vacuum application is not strictly necessary, this parameter can be adjusted according to the temperature at the end of the reaction, which makes it possible to remove some of the residual components of lower molecular weight (19). In the same line, Corpart et al. (30) have recently filed a patent application where an isosorbide oligocarbonate polyol having a molar mass of less than 5000 g/mol was produced. These oligocarbonates can further react with polyisocyanates to obtain polyurethanes for adhesives or coatings applications.

Li et al. (34) employed lithium acetylacetonate as a catalyst for obtaining high molecular polyisosorbide carbonates from IBMC. The basic nature of the catalyst promoted the synthesis of the monomer during the transesterification step at 98°C. After this, a polyisosorbide carbonate (28,800 g/mol) was obtained during the polycondensation step employing a high vacuum and increasing the temperature to 240°C. The molecular weight was increased up to 46,500 g/mol by the incorporation of flexible diols.

Fang et al. (45) reported a one-pot approach for the synthesis of PIC and PDIC using triazabicyclo[4.4.0]dec-5-ene (TBD). In this case, the activation of both imine and amine moieties of the catalyst played a bifunctional role in the activation of hydroxyl and carboxylate groups in the reaction media. The average molecular weight of the polymer obtained was 53,200 g/mol. The authors demonstrated that TBD can dually activate both secondary hydroxyl groups of isosorbide and primary hydroxyl group of linear and cyclic diols.

Finally, one important concept to consider in the production of biobased polycarbonates is their biodegradability. Hult et al. (46) described a process for polycarbonates production from isosorbide and a glycerol derivative as dihydroxyacetone (DHA). They used different monomer ratios and synthesis procedures. The presence of DHA accelerates the degradation profile, increasing the polycarbonate hydrolysis rate.
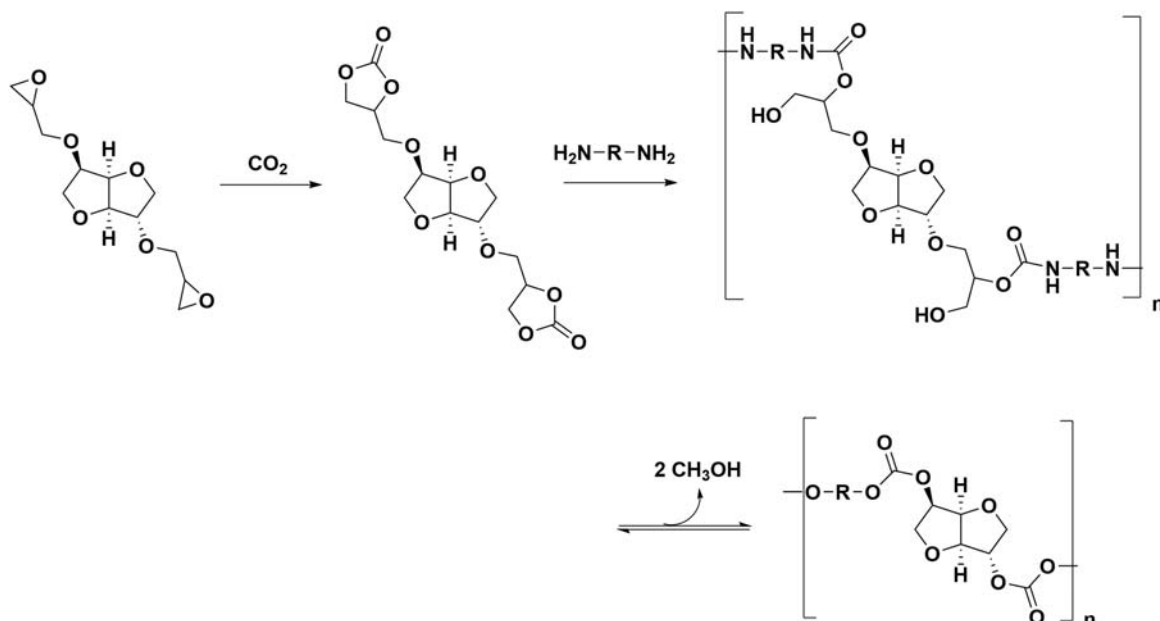
4. Isosorbide-based polyurethanes

Commercial polyurethanes (PUs) are commonly obtained from a polyaddition reaction between a diol (or polyol), a diisocyanate, and a chain extender (usually a short diamine or diol). The polyols, acting as soft segments provide flexibility to the final material whereas the isocyanate and the chain extender provide mechanical strength. Variations of the type and proportion of the diisocyanate, polyol, and chain extender allow achieving widely different properties, which is the main reason for the broad range of applications of PUs.

Diisocyanates are toxic and hazardous for human health, in special the free species present in the ambient during the polyurethane production process (47). The isosorbide rigid structure opens the possibility for a safe substitution of toxic diisocyanates such as toluene diisocyanate (TDI) or methylene diphenyl diisocyanate (MDI).

The replacement of petro-derived components by biobased alternatives in polyurethanes is not new. It is a common tendency to substitute oil-derived polyols with renewable bio-based resources obtained from vegetable oils, sugars, even lignin. Some references mention the synthesis of PUs from isosorbide with the partial use of MDI to achieve enough crosslinking degree and molecular weight. This drawback reduces the interest in isosorbide as a biobased alternative to harmful petrochemical compounds (48, 49).

However, there are not many references about making isosorbide-based polyurethanes that exclude the use of isocyanates, although the synthesis of new polymers that combine isosorbide monomers with carboxyl functionalities and diamines attracts relevant interest (28).

Scheme 5. Synthesis of a non-isocyanate polyurethane from cyclocarbonated isosorbide and a diamine.
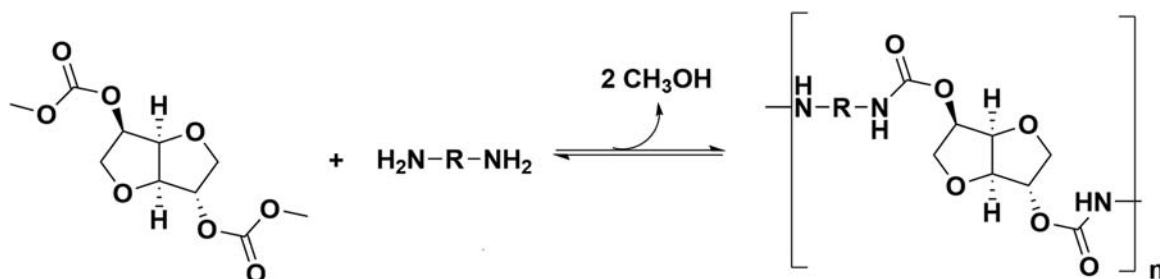
Scheme 6. Structure of a nonisocyanate polyurethane derived from IBMC and a diamine.

The synthesis of nonisocyanate polyurethanes (NIPUs) from isosorbide was reported by Besse et al. (28). The authors first converted the bio-based diol into the corresponding glycidyl ether oligomers, next carbonated them with 6 bars of CO_2 at 80°C for 12 h. Finally, they obtained linear and branched PHUs with Tg from 8 to 59 C, suitable for coatings applications, using 4 types of diamines as Jeffamine D-400, 1,10-diaminodecane, diethylenetriamine, and isophorone diamine. The polyaddition between the cylocarbonated functionalities of isosorbide with diamines (Scheme 5) is the most direct way to obtain a polyurethane structure. With the formation of every urethane linkage, a primary or secondary hydroxyl group is also formed and no methanol is released from the polymer. NIPUs obtained are also known as polyhydroxyurethanes (PHUs) (50).

IBMC can also be used in the synthesis of NIPUs by direct reaction with amines in a dispersed media (Scheme 6). It is shown the capacity for obtaining basic biobased pre-polyurethane structures, however, it is still a challenge to obtain high molecular weight polymers (21).

5. Conclusions

The development of polymer materials obtained from biological resources of a renewable origin has become a necessary environmental and ecological imperative. Isosorbide (in special if it is accompanied with other green reactants such as DMC) presents all the characteristics for replacing oil-derived traditional materials as bisphenol-A or diisocyanates. Although the use of isosorbide in polycarbonates and polyurethanes conforms to a very promising green process that can lead to new products with innovative properties, it is still a great challenge to obtain high-molecular-weight polymers. New developments in the design of new catalysts that will reinforce the isosorbide reactivity are crucial.

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