Surface modification of cellulose membranes

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Abstract. *This review is intended to give a concise overview of methods used in the modification of polymeric cellobiose fibres, with a focus on the surface functionalisation of commercially available cellulose membranes in particular. Reliable and readily available methods will be highlighted, as well as a green approach to grafting-from cellulose membrane composites.*

1. INTRODUCTION

Cellulose based membranes have played a major role in membrane dependant processes since Loeb and Sourirajan established a method for the casting of asymmetric cellulose acetate membranes (CAMs) in 1962 (Kang and Cao, 2012). Currently membrane processes are used widely in water treatment, biotechnology, food industry, oil industry, medicine and other fields (Kochkodan et al., 2014). Each field imposes different requirements on membrane functionality and characteristics and therefore novel membranes are of great interest. Some features of investigation are antifouling properties of membranes in water purification (Kang and Cao, 2012), heavy metal adsorbents for treating industrial waste streams (O'Connell et al., 2008) or improved biocompatibility in medical applications (Wang et al., 2015; Yuan et al., 2003; Zhang et al., 2003).

As a starting material cellulose is of particular interest, since it is the most abundant natural polymer on earth, renewable, biodegradable and non toxic (Kang et al., 2015). It is a polydisperse homopolymeric substance of varying chain length with monomers consisting of the $\beta(1 \rightarrow 4)$ -linked β -D-glucose disaccharid cellobiose. The β -D-glucose unit gives access to three reactive hydroxyl groups at the C2, C3 and C6 carbon atoms, however, the polymeric cellulose is not dissolvable in many conventional solvents (Heinze and Liebert, 2001).

2. GENERAL METHODS IN MEMBRANE FUNCTIONALISATION

One general method in obtaining new membrane characteristics is the functionalisation of dissolved cellulose before casting of the membrane occurs. T. Heinze and T. Liebert composed a review of many not commercial pursued techniques to achieve this (Heinze and Liebert, 2001). A second method is the creation of blend membranes, where cellulose is mixed with another polymer of interest, e.g. polyurethane (Ferjani et al., 2002), however, both this processes require the casting of the actual membrane.

A more convenient approach in the development of new cellulose based membranes is the surface

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functionalisation of commercial available cellulose acetate (CA), regenerated cellulose (RC) or bacterial cellulose (BC) membranes. For this approach many chemical and physical methods have been established over the years; those are not only applicable for cellulose functionalisation, but also for surface modification of many available polymeric membranes in general (Kang and Cao, 2012; Kochkodan et al., 2014). When handling polymers in general and cellulose membranes in particular one has to keep in mind that under certain conditions swelling of the polymer can occur; this will lead to intrusion of solvent molecules into the polymer framework and in addition might facilitate the accidental functionalisation of the inner membrane. This is crucial, because inner functionalisation could potentially alter the characteristics of the cellulose backbone in an unfavorable way. The swelling of cellulose in different protic and aprotic solvents was investigated in two studies by Seoud and Fidale et al. (El Seoud et al., 2008; Fidale et al., 2008), where it was established that solvent molecular volume, basicity and dipolar character play a crucial role in the swelling process. Dibutyl ether, ethyl acetate, 1-octanol and 2-methyl-2-propanol showed the least amount of swelling, thus solvents with similar characteristics are to be preferred in surface modification attempts.

The interfacial polymerisation or grafting process is one of the most widely used processes in surface functionalisation. Usually there is a distinction between grafting-to and grafting-from approaches, where the former one utilises preformed functionalized polymer chains and the latter one requires either an initiator on the (cellulose) backbone or the creation of free radicals on the backbone (Kang and Cao, 2012; Kochkodan et al., 2014). Special cases include redox-initiated and enzymatic grafting, which is of special interest and will be addressed in 3.4 (Gullinkala and Escobar, 2010).

Other established methods include initiated chemical vapor deposition (iCVD) and different approaches employing plasma treatment of the membranes (Kochkodan et al., 2014), which will both not be addressed further in this review.

Another convenient approach is the physical coating of the membrane surface, through adsorption, filtration or by embedding nanoparticles in the membrane (Kang and Cao, 2012; Kochkodan et al., 2014), however, this approach is prone to leaching of the membrane modification.

Lastly there is the possibility to utilise classical chemical reactions with the C2, C3 and/or C6 hydroxyl groups, depending on the membrane and reaction type.

It is apparent that there are several methods which can be used to modify the surface of polymeric membranes, however, only a minor fraction of the literature seems to be focussed on the surface modification of commercial cellulosic membranes. In addition, only simple and easy to use methods for cellulose membrane modification, which require no specialised equipment and no recasting of membranes, will be highlighted further on.

3. SELECTED METHODS IN SURFACE FUNCTIONALISATION AND DISCUSSION

3.1 MODIFICATIONS UTILISING CLASSICAL CHEMICAL APPROACHES

Surface modifications utilising classical chemical approaches require stoichiometric use of reactants and therefore have a higher E Factor (ratio of mass waste to synthesised product (Sheldon, 2007)) than, for example, interfacial polymerisation techniques. However, since classical chemical approaches are usually convenient to carry out and require no specialised machinery they can provide a quick and reproducible route.

Madaeni and Heidary (Madaeni and Heidary, 2011) used periodate oxidation of RC membranes to introduce dialdehyde groups on the membrane surface. In a further step they created the corresponding Schiff-base in a condensation reaction with diethylenetriamine. The treatment with the strong oxidising agent posed a challenge in their approach, because the RC membrane showed a significantly reduced mechanical strength after 9 h of reaction time. An optimisation of the reaction time to 7 h yielded a mechanically sound membrane. Since the experiment employed water as a solvent swelling might have added to the destabilisation of the inner membrane structure (water/MC: 4.82 nSw; (El Seoud et al., 2008)). A milder oxidation approach was investigated by DiFlavio et al. (DiFlavio et al., 2007). They conditioned RC membranes with TEMPO/NaBr and afterwards subjected them to oxidation by sodium hypochlorite, which yielded presumably a mixture of the corresponding carboxylic, aldehyde and hemiacetal groups. The opportunity was not investigated, but their functionalisation would also open the possibility to apply Schiff-base chemistry for surface modification.

3.2 MODIFICATIONS UTILISING COUPLING AGENTS

Coupling agents usually provide an easy access to bond formation and have become widely available commercially and discussed in literature. Therefore the use of coupling agents for surface modification provides an interesting approach, however, commercially available CAMs have partially or fully acetyl (Ac) protected hydroxyl groups and thus usually have to be deprotected before they can undergo coupling reactions. In a study conducted by Yu et al. (Yu et al., 2013) CA hollow fibre membranes were deprotected using 0.1 M NaOH / 1.0 w/v% MeOH as deprotecting agent. Afterwards they utilised monochloroacetic acid and yielded the corresponding carboxymethylation product, which increased the membrane hydrophilicity and surface charge.

The usage of RC membranes instead of CAMs will omit the deprotection, which was utilised by Meng et al. (Meng et al., 2015). Their study explored the use of alkoxysilane polycondensation using the three silane coupling agents trimethoxysilylpropyltrimethyl ammonium chloride, trimethoxysilylpropyltrimethyl octadecyldimethyl and 3-aminopropyltrimethoxysilane directly on the surface of RC

membranes. A more recent study by Wang et al. (Wang et al., 2015) used another set of silane coupling agents, (3-carboxypropylbetaine-propyl)-trimethoxysilane (CPPT), (3-sulfopropylbetaine-propyl)-trimethoxysilane (SPPT) and (3-sulfobutylbetaine-propyl)-trimethoxysilane (SBPT), on cellulose membranes. The functionalized membranes showed superior fouling resistance and biocompatibility. Stöllner et al. (Stöllner et al., 2002) used the coupling agents 1,1'-carbonyldiimidazole (CDI) and *N*-Cyano-4-dimethylaminopyridinium tetrafluoroborate (CDAP), which are readily available and used in peptide chemistry, on neat cellulose membranes. The activated membranes could be coupled with GOx and 1,8-diamino-2,6-dioxaoctane. Even though these functionalisations do not seem useful for an application in water technology it shows that cellulose membranes can be activated with classical peptide coupling agents and subsequently reacted with secondary amines.

Microbial or bacterial cellulose possesses the same monomer characteristics as plant cellulose, however, a lower degree of polymerisation and a microcrystalline structure, as well as a higher degree of purity set it apart from conventional cellulose (Jonas and Farah, 1998). BC membranes also do not need a deprotection step and are nevertheless quite similar to RC membranes in their reactivity, which was exploited by Kurniawan et al. (Kurniawan et al., 2013). They synthesised mPEG-IPDI from monofunctional methyl ether PEG and IPDI, which was then subsequently coupled with the BC membrane surface. However, IPDI has to be distilled and is prone to hydrolysis which might be unfavorable due to its toxicity. Nevertheless the fouling resistance could be improved by 70% compared to virgin BC membranes.

3.3 MODIFICATIONS UTILISING DIFFERENT TECHNIQUES OF GRAFTING

There are several ways to graft cellulose with another substrate (Kang et al., 2015), however, some methods are favorable over others. Especially controlled and living radical polymerisation, such as atom transfer radical polymerisation (ATRP) and reversible addition fragmentation chain transfer (RAFT), offer a reliable method with lower environmental impact regarding stoichiometric waste stream, than coupling reactions.

In a study conducted by Liu et al. (Liu et al., 2010) an ATRP grafting-from approach was carried out utilising poly(*N,N*-dimethyl-*N*-(*p*-vinylbenzyl)-*N*-(3-sulfopropyl)ammonium) (PDMVSA), poly(2-(methacryloyloxyethyl) ethyl-dimethyl-(3-sulfopropyl)ammonium) (PDMMSA) and poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) to modify the surface of an α -bromoisobutyryl bromide (BIBB) modified cellulose membrane. The resulting membrane showed even higher hydrophilicity than the virgin cellulose membrane, which is attributed to the zwitterionic groups that support a stronger hydration layer by electrostatic interaction. Also CAMs can be grafted-from using

the same initiator, BIBB, and the monomer 2-hydroxyethyl methacrylate (Worthley et al., 2011). Both methods employed esterification of free hydroxyl groups on the cellulose surface with BIBB as an initial step. Esterification in general is an established method to modify hydroxyl functional groups and is widely used as an approach in grafting-from cellulose chemistry. In regards to cellulose modification BIBB seems to be a commonly used esterification agent and initiator for consequential grafting reactions. Even though it possesses strong oxidising properties it is far less toxic than other esterification agents like 4-dimethylaminopyridine (4-DMAP), *N,N'*-diisopropylcarbodiimide (DIC) and *N,N'*-dicyclohexylcarbodiimide (DCC), which are commonly used in Steglich esterification. However, Singh et al. (Singh et al., 2008a, 2008b) suggested that immobilisation of BIBB not only occurs on the membrane surface, but that the grafting initiator is also covalently bound to inner hydroxyl groups of the cellulose membrane matrix, which has to be taken into account when calculating the loading for the membrane. They grafted both poly[poly(ethylene glycol)methacrylate] (PPEGMA) layers (Singh et al., 2008a) and poly(acrylic acid) (PAA) (Singh et al., 2008b) utilising BIBB as a linker. In the case of PPEGMA a Cu(I)/Cu(II)/2,2'-bipyridyl (bipy) complex was used for ATRP and in the case of PAA a Cu(I)/Cu(II)/Me₄Cyclam complex. After successful modification of the RC membrane with PAA they employed confocal laser scanning microscopy (CLSM) in wet state to verify that the membrane's pore structure was intact after ATRP grafting-from, which is essential to the performance and mechanical stability of the membrane.

As stated above the 4-DMAP/DCC system is more toxic than BIBB, but it is worth noting that it can also be employed in cellulose surface modification. Kishida et al. (Kishida et al., 1992) used this approach to graft PEG mono- and diacid to RC cellulose membranes. The esterification reaction with 4-DMAP/DCC yields a graft with no linker in between the cellulose surface and the PEG acid, which is a major difference from the BIBB grafting-from approach.

3.4 A GREEN APPROACH IN SURFACE FUNCTIONALISATION UTILISING ENZYMATIC GRAFTING

A special case of grafting was described by Escobar and Gullinkala (Gullinkala and Escobar, 2010) in 2010. They modified the surface of a commercial available CA ultrafiltration membrane via enzymatic grafting of polyethylene glycol. The porcine pancreatic crude type II lipase (PPL) enzyme is readily available and was dissolved directly in PEG, which made this approach solvent free. The reaction time was 50 h and synthesised membranes showed superior fouling resistance. This approach is especially interesting since it is solvent free and uses only environmental benign reactants, however, the reaction time is high in comparison with standard coupling or graft reactions.

4. CONCLUSION AND FURTHER PROPOSITIONS

While cellulose is a renewable and versatile material only membranes of a few of its modifications are commercially available. Fortunately the chemistry of RC and CA membranes give the opportunity to modify these existing membranes to obtain a specifically tailored or improved functionality. For modification attempts commercially available RC membranes are usually more attractive than CA membranes, due to a higher ratio of available hydroxyl groups per membrane surface area. However, the acetyl esters of CA membranes can be cleaved and thus allow for further modification of the CA membrane surface.

Although there are classical chemical and physical approaches to membrane surface modification more convenient ways utilise coupling agents or rely on ATRP. Grafting reactions with a focus on living and controlled polymerisation, namely ATRP, seem to be most popular in recent literature, because pore size, layer thickness, chemical properties and degree of modification or graft density can be tuned according to reaction conditions as well as length and type of grafted side-chains. Furthermore one can obtain many studies on grafting in general, which can give more insight into possible reaction conditions, reactants and available monomers (Bhattacharya, 2004). However, to carry out a controlled modification using a radical polymerisation approach the polymer growth kinetics for the specific system should be taken into account to ensure uniform and linear layer buildup as well as a nicely modulated pore size (Singh et al., 2008b). A promising approach in green grafting was carried out by Escobar and Gullinkala in 2010, as discussed in 3.4, which highlights the possibility of a more sustainable approach to cellulose membrane surface modification.

Since the cellulose backbone offers reactive hydroxyl groups it provides the opportunity to employ esterification reactions in modification attempts. Esterification in general is a highly available route from classical organic chemistry, however, as seen in presented cases often toxic or hazardous reactants are used in cellulose esterification. The coupling and esterification agents 4-DMAP and DCC are two examples which allow for Steglich esterification of cellulose membrane surfaces under mild conditions. These kind of coupling agents are readily available from peptide chemistry, but have to be evaluated for their toxicity. Another commercially available coupling agent for esterification is *n*-propylphosphonic anhydride (T3P®), which is highly versatile, possesses comparably less toxicity and offers mild reaction conditions and workup (Waghmare et al., 2014). While ATRP grafting approaches seem more reasonable for large scale modification of RC membranes the direct esterification approach utilising benign esterification agents appears to offer an easy, least-toxic and reproducible route to small scale and prototyping reactions.

5. ABBREVIATIONS

Ac	acetyl	Me	methyl
ARTP	atom radical transfer polymerisation	nSw	swelling expressed as number of moles of solvent
BC	bacterial cellulose		
BIBB	a-bromoisobutyryl bromide	PAA	poly(acrylic acid)
bipy	2,2'-bipyridyl	PDMMSA	poly(2-(methacryloyloxyethyl) ethyl-dimethyl-(3-sulfopropyl)-ammonium)
CA	cellulose acetate		
CAM	cellulose acetate membrane	PDMVSA	poly(<i>N,N</i> -dimethyl- <i>N</i> -(p-vinylbenyl)- <i>N</i> -(3-sulfopropyl) ammonium)
CDAP	<i>N</i> -Cyano-4-dimethylaminopyridinium tetrafluoroborate	PMPC	poly(2-methacryloyloxyethyl phosphorylcholine)
CDI	1,1'-carbonyldiimidazole	PPEGMA	poly[poly(ethylene glycol)methacrylate]
CPPT	(3-carboxypropylbetaine-propyl)-tri-methoxysilane	PEG	poly ethylene glycol
CTA	cellulose triacetate	PPL	porcine pancreatic crude type II lipase
DCC	<i>N,N'</i> -dicyclohexylcarbodiimid	RAFT	reversible addition-fragmentation chain transfer reaction
DIC	<i>N,N'</i> -diisopropylcarbodiimide		
DMAP	dimethylaminopyridine	RC	regenerated cellulose
GOx	glucose oxidase	SBPT	(3-sulfobutylbetaine-propyl)-trimethoxy-silane
h	hours		
iCVD	initiated chemical vapor deposition	SPPT	(3-sulfopropylbetaine-propyl)-trimethoxy-silane
IPDI	isophorone diisocyanate		
MC	microcrystalline cellulose		

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