

Biopolymers to improve physical properties and leaching characteristics of mortar and concrete: A review

M Olivia, H Jingga, N Toni and G Wibisono

Department of Civil Engineering, Faculty of Engineering, Universitas Riau,
Pekanbaru 28293 Indonesia

E-mail: monita.olivia@lecturer.unri.ac.id

Abstract. The invention of environmentally friendly, high performance, and green material such as biopolymers marked an emerging trend for sustainable construction over the past decades. Biopolymer comprises of natural monomers and synthesized by plants or other organisms. The sustainable, biodegradable, and renewable biopolymers were used in concrete mixes to improve their physical and mechanical properties and durability. The aim of this paper is to provide a brief an overview of the impact of biopolymer addition into concrete and mortar mixes. Many studies on the influence of biopolymer on the properties of concrete and mortar by adding biopolymers at a certain proportion (usually less than one wt.%) to the concrete or mortar mixes, and the heavy metal leaching, rheological, and mechanical properties of the mixes were conducted. Biopolymers included in this review are chitosan (CH), xanthan gum (XG), guar gum (GG), lignosulphonate (LS), and cellulose ethers (CE). Data from previous studies showed that the addition of certain types of biopolymer into concrete and mortar mixes improve workability, water retention, and compressive strength by up to 30 percent. Chitosan strengthens heavy metal encapsulation in the mortar and neutralizes the negative impact of heavy metal on the mortar properties and environment. To sum up, the use of biopolymers improve physical properties and leaching characteristics of mortar and concrete.

1. Introduction

The construction industry is one of the most significant pillars that support the development of every country. According to Plank [1], the world spent approximately 3 trillion USD to construct home buildings, industrial buildings, and other infrastructures such as bridges, highroads, and railroads in 2000. Some countries with a massive population such as India has invested 1 trillion dollars in infrastructures between 2012-2017, and in the USA, rehabilitation of public infrastructures such as bridges will cost 1.6 trillion dollars in the next 5 years [2, 3]. Concrete is an essential infrastructure material. The primary binder of concrete, cement, is the second most used material with production reach 6000 million tons annually [4]. On the other hand, the processes involved in the cement production have a detrimental impact on the environment. The production of cement worldwide contributes to approximately 5% of global CO₂ emission [5]. CO₂ is one of the greenhouse gasses that accelerates global warming. Due to these facts, researchers continuously study and create inventions in the construction field. New construction methods and materials are intensively investigated to open the window for better sustainability and efficiency with less detrimental impact on the environment.



Bio-based materials such as vegetable fat, animal oil, egg white, fish oil, olive oil, linseed oil, and blood have been used as historical construction materials for many centuries [6]. It was used mostly as an admixture of mortar and plaster to improve viscosity or retarder agent for gypsum. Builders in Brazil used whale oil for concrete workability and durability (waterproofing). The Romans used blood as an air-entraining agent and the Portuguese added vegetable oil in the mortar [7, 8]. In modern building construction, approximately 500 different bio-based admixture products such as lignosulphonate to modify concrete fresh and hardened state have been utilized [7].

The bio-based admixtures can be classified as biopolymers since it is consisted (partly) of bio-based raw materials and biodegradable. The biopolymers are mostly produced by a sustainable process using renewable agricultural and biotechnological biomass residues. It has non-toxic, easy extraction, biocompatibility, and biodegradability characteristics. Biodegradability is an important characteristic that allows decomposition of polymeric chains into smaller molecules [9]. These characteristics indicate a tight relationship between biopolymer and sustainable construction concepts. Since it comes from raw materials such as plants and animals, the material has less cost in producing it, and very popular due to demand for sustainable materials in the construction industry.

The usage of more environmentally friendly material such as biopolymers in concrete and mortar mixtures has been studied intensively. Biopolymers such as polysaccharides, cellulose, starch, chitin, chitosan, alginates from nature are entirely sustainable and biodegradable. In this review paper, the influences of the biopolymer to the rheological, mechanical, and leaching properties of concrete and mortar are discussed. This paper also presents the impact of the biopolymer in mortars which encapsulate heavy metal. The biopolymers in this review paper are limited to chitosan, xanthan gum, guar gum, lignosulphonate, and cellulose ethers.

2. Biopolymers as additive to concrete and mortars

Biopolymers are polymers were synthesized by plant or organism with more complex chemical structure than human-made polymer [10]. Recently the definition of biopolymer has been expanded to any polymer synthesized using natural monomers such as polylactic acid which comprises of lactic acids.

Biopolymers are used in cement mortar and concrete as admixtures to improve properties, as matrices in biocomposites with high mechanical strength, and insulator or high-temperature retardant properties [11, 12]. Two sources of biopolymers for mortar and concrete are from agro-resources extraction and biotechnology through microorganism fermentation and conventional synthesis. Extraction of natural materials or agro-resources materials produce biopolymers such as polysaccharides, cellulose, starch, chitin, chitosan, and alginates. Alginates are extraction polysaccharide from brown algae and act as a self-healing agent for crack repair in concrete without reducing the strength [13]. Biotechnology through microorganism fermentation produces polyhydroxyalkanoates. Biotechnology using conventional synthesis could produce polylactides, and biopolyethylene (PE). Both sources give different dosage levels, product quality, price and environmental safety. Microbial biopolymers such as welan gum are more expensive hence just could be added at 0.002-0.1 wt% from the total formulation of the building material [7]. Lignosulphonate from lignin could be included more in the mixture at 0.1-0.4 wt% since lignin is available abundantly and cost of processing is relatively cheaper than biopolymer from microbial fermentation. Raw materials, process, and equipment cost of biopolymers determine the price and significant contribution of biopolymers to the material properties.

Three basic forms of biopolymers can be included in concrete, i.e., powder, liquid, and fiber [6]. Powder biopolymer, such as chitin, chitosan, and starch is added to cement and water in concrete manufacturing preparation. Chitosan increased viscosity, reduced porosity and improved the final strength of cement pastes, however when added to the concrete mixture it gave adverse impact to the properties [14]. Chitosan is more beneficial to absorb heavy metals although it was included in the mix in small amount (0.4wt.%) [15]. Rubber, xanthan, rubber, guar, gelatin, and gutta-percha are the liquid biopolymer. While natural fiber biopolymer without any biopolymerization process and added

to the cement mix such as coconut, sisal, jute, hemp, kenaf, and pineapple was used to increase stiffness and tensile strength of concrete. Natural fiber must have several criteria such as high thermal stability, excellent adhesion of fibers and matrix, good long time behavior, high elongation at failure, dynamic behavior and low price and processing cost. Fibres as a part of biopolymer composite matrix are necessarily required to have good fiber-matrix adhesion to allow optimum impregnation in the system [16].

3. Chitosan, Xanthan Gum, and Guar Gum as admixtures to heavy metal encapsulating mortar mixes

Biopolymers such as chitosan, xanthan gum, and guar gum are good viscosizers. Chitosan is derived from chitin by a process known as deacetylation [17]. Chitin is from crustacean shells (crabs and lobsters). Figure 1 shows chemical structure of chitosan and chitin. Xanthan gum and guar gum are usually used to thicken paint materials, soups, and drilling muds. Xanthan gum is produced by the bacterial: *Xanthomonas campestris*, whereas guar gum is acquired from legume seed: *Cyamopsis tetragonolobus* which is abundant in India and Pakistan.

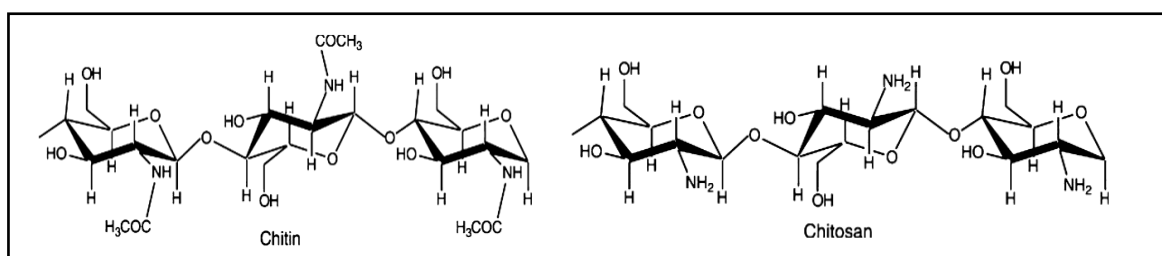


Figure 1. Chemical structure of chitin (left) dan chitosan (right) [18].

Heavy metal is high-density metal which is toxic to the environment. Heavy metal includes lead (Pb), chromium (Cr), zinc (Zn), and mercury (Hg). Heavy metal is not degradable and might contaminate human body at high concentration. Heavy metal enters the human body through food, water, and air. The use of lead-based pipe in clean water distribution pipeline might dissolve lead substance into the water by the process of corrosion [19]. Industrial activity produces heavy metal that adversely impacts nearby air quality. Despite these facts, heavy metal such as zinc is still required in a specific concentration to support metabolism in human body.

Heavy metal is hazardous due to a process called bioaccumulation. Bioaccumulation is defined as the steadily increasing concentration of the chemical substance in an organism over a long time [20]. If the accumulation speed of particular chemical substance is faster than the ability of the organism to degrade or dispose of it, then bioaccumulation occurs. Related to lead exposure, people that work in demolition, welding, or lead-based paint material combustion are at risk of lead poisoning. In 1989, eight workers suffered from lead poisoning while working on nuclear reactor's protective structure in Monroe, Louisiana. Another issue related to lead contamination is the accumulation of cathode ray tube (CRT) wastes which contained a high concentration of lead.

A study conducted by Lasheras-Zubieta et al. [15] showed that chitosan added to mortar contains heavy metals Pb, Cr, and Zn to reduce their detrimental impact on the environment. This process is known as heavy metal encapsulation or immobilization in a mortar. The experiment results showed that the addition of chitosan improves the rheological, mechanical, and leaching characteristics of mortar. Slump test results indicate that chitosan reduces the deleterious impact of heavy metal encapsulation (Pb and Cr) to the workability characteristic of fresh-state mortar. The addition of chitosan neutralizes the influence of heavy metal encapsulation to the setting time of mortar but does not significantly affect water retention characteristic of mortar. The XRD analysis results also showed that the heavy metals were not merely encapsulated inside the mortar matrix system; instead, they formed new silicate and aluminosilicate structures which are not quickly released from the mortars.

Heavy metals encapsulated in mortar might be released to specific liquid medium. This process is called leaching. The leaching test results showed that mortar system efficiently encapsulates heavy metals. The cumulative leaching of Pb and Zn at 64th day are 58 mg/m² and 15 mg/m², which are less than the maximum allowable value of 400 mg/m² and 800 mg/m², respectively for Pb and Zn. For Cr, the retention value is lower at 70-75% due to the formation of weaker chromatic compounds compared to the silicate compounds formed by Pb and Zn. On the other hand, the addition of other types of chitosan produces a lower retention value compared to chitosan-free mortar samples.

Kim et al. [21] also performed a study related to heavy metal encapsulation in a mortar by biopolymer. The heavy metal Pb was acquired from cathode ray tube (CRT) wastes. CRT is the component of television which is considered toxic due to its high lead content. The lead content in CRT is 0-3 wt.% for the panel, 22-25 wt.% for the funnel, 30-40 wt.% for the neck and 60-85 wt.% for the solder. In the study, CRT was mixed with mortar that contains biopolymer, which is further called CRT-Biopolymer-Concrete (CBC) composite. The CRT was shattered into pieces of glassy aggregates and used as a replacement for silicate sand. The CRT aggregates were then submerged in biopolymer solution. The biopolymer solution was made by mixing xanthan gum and guar gum into the pure water at 0.1% concentration. For specific variations, 0.1% boric acid was also added as a crosslinking agent. The CBC sample casting process was conducted by mixing Paste I and Paste II. Paste I is the mixture of water, cement, and sand, whereas Paste II is the mixture of water, cement, sand, CRT aggregates, and biopolymer solution. The resulting CBC samples were 10.16 x 20.32 cm² cylinders which were cured for 7 days. The CBC samples were then put into compressive strength tests and toxicity characteristic leaching procedure (TCLP) tests. The mortar sample variations and laboratory test results are tabulated in Table 1.

Table 1. Mortar sample variation dan laboratory test results [21]

Variation	Ordinary Mortar (Control)		Mortar + CRT		Mortar + XG 0.1%		CBC 1 GG + BA 0.1% (70 gram)		CBC 2 GG + BA 0.1% (417 gram)		CBC 3 XG + GG 0.1% (70 gram)		CBC 4 XG + GG 0.1% (417 gram)	
Composition	Weight		Weight		Weight		Weight		Weight		Weight		Weight	
	gram	%	gram	%	gram	%	gram	%	gram	%	gram	%	gram	%
Water	417	11.2	417	11.2	347	9.34	347	9.34	- ^a		347	9.34	- ^a	
Cement	1050	28.3	1050	28.3	1050	28.3	1050	28.3	1050	28.3	1050	28.3	1050	28.3
Sand	2250	60.5	1900	51.1	2250	60.5	1900	51.1	1900	51.1	1900	51.1	1900	51.1
CRT Aggregate	N/A		350	9.42	N/A		350	9.42	350	9.42	350	9.42	350	9.42
Boric Acid Solution	N/A		N/A		70	1.88	70	1.88	417	11.2	70	1.88	417	11.2
Biopolymer	N/A		N/A		0.07	1.93x10 ⁻⁵	0.07	1.93x10 ⁻⁵	4.17	1.12x10 ⁻⁴	0.07	1.93x10 ⁻⁵	4.17	1.12x10 ⁻⁴
Laboratory Test Results														
TCLP (mg/L)	N/A		4.6		N/A		N/D		0.148		N/D		0.2529	
Compressive Strength (MPa)	28.5		28.3		35.4		34.8		34.6		37.6		21.2	

N/A: Not available

XG: Xanthan gum

GG: Guar gum

BA: Boric Acid

N/D: Not detected (< 0,001 mg/L)

-^a: no extra water for cement hydration other than that from biopolymer solution

The laboratory test results is shown in Table 1 indicate that the addition of xanthan gum and guar gum improves the compressive strength of CBC samples by approximately 30%. For the case of CBC 4, compressive strength reduction of 26% relative to control samples was noticed. This is due to the large water usage by xanthan gum and guar gum in the biopolymer solution; thus the remaining water was less for cement hydration (lower w/c). On the other hand for CBC 3, water was added after the biopolymer was mixed with cement and aggregate mixture. Therefore, more water was available for cement hydration. Judging from CBC 1 and CBC 2 test results, it is clear that the addition of boric acid as the crosslinking agent was more successfully produced specimens with high compressive strength. The crosslinking between guar gum and boric acid is shown in Figure 2.

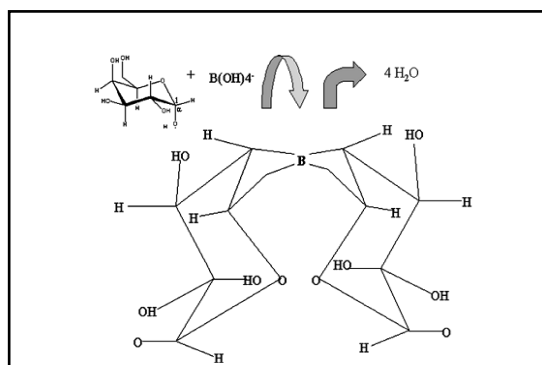


Figure 2. Crosslinking between guar gum and boric acid [21].

TCLP test results show that mortars are good Pb encapsulating agents. For mortar + CRT without biopolymer samples, the leachable lead measured was only 4.6 mg/L, which is far less than the leachable lead of CRT aggregates that reach hundreds of mg/L. This value is also less than the allowable leachable lead of 5 mg/L [22]. For CBC samples, the results were much more remarkable with the leachable lead of 0.2529 mg/L. Specifically for CBC 1 and CBC 3, the leachable lead was not detected (< 0.001 mg/L). According to Olmo et al. [22], cement matrix alone is not capable of retaining Pb permanently due to its porous microstructure. However as stated earlier, the crosslinking of biopolymer molecules: xanthan gum and guar gum in the mortar matrix system creates nano-sized barriers which retain Pb particles effectively and provide long-term Pb encapsulation. Thus, it can be concluded that the addition of chitosan, xanthan gum, and guar gum is capable of modifying and improving the rheological, mechanical, and leaching characteristics of mortars which encapsulate heavy metals.

4. Lignosulphonate to increase compressive strength

Lignosulphonate is one of macromolecule organic and polyelectrolyte [23]. Lignosulphonate produced from lignin chemical process, that is a natural biopolymer from wood and grass. Wood cell wall layers are a complex mixture of polymers which are 70-80% holocellulose (contained in cellulose and hemicellulose), and the rest is lignin [1]. Lignin and hemicellulose are then dissolved in a hot acid liquid (usually calcium bisulfite $\text{Ca}(\text{HSO}_3)_2$) to produce sulfite liquor that containing lignosulphonate [24]. Sulfite liquor composition is shown in Table 2.

Table 2. Sulfite liquor composition obtained from soft wood [1]

Component	[% (wt/wt)]
Lignosulphonate	55
Sugar Hexose	14
Sugar Pentose	8
Hemicellulose, sugar acids	12
Acetic-, formic acid	4
Resin, tall oil	2
Ashes	5

One of the most popular characteristics of lignosulphonate is its ability as dispersant or plasticizer. Lignosulphonate does not contain toxic at a severe level and not causing any health problem to human, animals, and plants. In concrete, lignosulphonate is used as plasticizer mixture to separate cement particle and another fine particle, thus increasing the workability of fresh concrete. Results from Petersen and Gundersen [23] research about the effect of lignosulphonate on mortar mixture

workability indicated that fresh mortar workability increases exponentially with the number of lignosulphonate added.

Plank [1] researched lignosulphonate effect to slump, water reduction effect, and concrete compressive strength. Table 3 and 4 shows the experimental results. In general, concrete with low wcf has higher strength due to smaller porosity but reducing concrete workability. With the lignosulphonate addition, can be applied low wcf value in the mixture (water reduction effect), with higher compressive strength while keeping maintaining fresh concrete workability (plasticizer effect) at a certain rate. From Table 4, can be seen that water mixture reduction by 7% can be reached by adding 0.14% lignosulphonate, meanwhile adding 0.28%, lignosulphonate can reduce water usage by 10%.

Table 3. Sodium lignosulphonate effect to concrete slump [1]

Characteristics	Without additive material	0,1% Sodium Lignosulphonate*
Water cement factor (wcf)	0,68	0,68
Slump (mm)	95	135
Slump increase (mm)	-	40

* Percentage of cement weight (= 300 kg/m³)

Tabel 4. Lignosulphonate water reduction effect in concrete mixture [1]

Lignosulphonate dose (% weight)	wcf	Air content (% volume)	Compressive strength (% from concrete compressive strength control without additive material)	
			3 days	28 days
-	0,58	1,3	100	100
0,14	0,54	2,4	125	112
0,28	0,52	2,9	130	115

Compared to lignosulphonate, several types of plasticizer synthetics such as β -naphthalene sulfonate (BNS), melamine formaldehyde sulfonate (MFS), polycarboxylate, and amphoteric polycarboxylate have better water reduction effect. For example, amphoteric polycarboxylate has water reduction effect up to 60% (maximum). The plasticizer such as polycarboxylate selected by the construction industry to produce high-quality concrete, although it has a higher price than lignosulphonate. The usage of lignosulphonate reduces due to lower performance compared to new type plasticizer, in addition to the price that relatively increases due to wood reduction for lignosulphonate production process related to environmental issues [24]. However, lignosulphonate have a higher sustainability because it is made from the wood material that can sufficiently renewable, compared to polycarboxylate that based on crude oil (resources that are not renewable).

5. Cellulose ethers to increase mortar water retention

Cellulose ethers (CE) is a biopolymer of cellulose, the most abundant biopolymer in nature. For more than 60 years, CE plays an essential role in several products from construction products, ceramics, paints, to food, cosmetics, and pharmacy [25, 26]. CE that commonly used in construction can be seen in Table 5.

Usually, CE product applied to building product to increase water retention and viscosity. Water retention is fresh mortar mixture ability to maintain its water content when in contact with a substrate (rocks that can absorb water). For example, an installation of a red brick wall, the water content in

mortar can be absorbed by red brick (substrate) thus affecting mortar workability and mechanical properties. This condition can be prevented by improving mortar water retention capability.

Table 5. Cellulose ethers that used in construction [1]

Ether	Abbreviation
Methyl cellulose	MC
Methyl hydroxyethyl cellulose	MHEC
Methyl hydroxypropyl cellulose	MHPC
Hydroxyethyl cellulose	HEC
Hydroxypropyl cellulose	HPC
Na-carboxymethyl cellulose	CMC, PAC
Na-carboxymethyl hydroxyethyl cellulose	CMHEC
Ethyl cellulose	EC
Ethyl hydroxyethyl cellulose	EHEC

Patural et al. [27] researched CE effect to mortar water retention and workability. In that research, three types of cellulose ether were examined, i.e., MHEC, MHPC, and HEC (Table 5). Mortar water retention level was investigated using the standard procedure from ASTM C1506-09 and Standard DIN 18555-7 which mimics a process of fresh mortar water absorption by the substrate. Results showed that mortar with CE (0.27% weight) have water retention rate up to 98.8%, that means water lost from that test only reach 1.2%. Besides, the most important fact is the greater molecular mass of CE is added, the higher consistency and mortar water retention level.

6. Conclusions

Rapid development in the construction industry has recently signaled engineers for the needs of sustainability and the use environmentally friendly materials. The renewable, sustainable, and biodegradable biopolymers have great potential to be used as admixtures in the mortar and concrete mixtures. Previous studies showed that the use of chitosan, xanthan gum, and guar gum as admixture improves the properties of heavy-metal-encapsulating mortars. The addition of chitosan neutralizes the adverse impact of heavy metal encapsulation to the mortar's properties, such as workability, setting time, and compressive strength. The crosslinking features between xanthan gum and guar gum (+ boric acid) in mortar matrix system escalate the compressive strength of mortar by up to 30% and reduce heavy metal cumulative leaching characteristic to less than 0.001 mg/L. Lignosulphonate as plasticizer improves the workability of fresh-state mortar. The addition of cellulose ethers in mortar mixture improves water retention capability of fresh-state mortar by up to 98.8%. Based on the facts stated above, it could be summarized that the use of biopolymers certainly improve physical and leaching characteristic of mortar and concrete.

References

- [1] Plank J 2005 *Biopolymers Online* 10
- [2] Chakraborty S, Iyer N, Khrisna P and Thakkar S 2011 *Assessment of Civil Engineering Inputs for Infrastructure Development* (New Delhi: Indian National Academy of Engineering)
- [3] Davalos J F 2012 *Advanced Materials for Civil Infrastructure Rehabilitation and Protection Seminar* at the City College of New York (New York)
- [4] Flatt R, Roussel R and Cheeseman C R 2012 *J. Euro. Ceram. Soc.* **32** 2787
- [5] Hosseini M M, Shao Y and Whalen J K 2011 *Biosys. Eng.* **110** 351
- [6] Bezerra U T 2016 Biopolymers with superplasticizer properties of concrete *Biopolymers and Biotech Admixtures for Eco-Efficient Construction Materials* ed Pacheco-Torgal F, Ivanov V, Karak N, and Jonkers H (Amsterdam: Woodhead Publishing Series in Civil and Structural Engineering)

- [7] Plank J 2004 *Appl. Micr. Biotech.* **66** 1
- [8] Pacheco-Torgal F and Jalali S 2011 *Eco-efficient Construction and Building Materials* (London: Springer Verlag)
- [9] Nakajima-Kambe T, Shigeno-Akutsu Y, Nomura N and Nakahara T 1999 *Appl. Micr. and Biotech.* **51** 134
- [10] Ebnesajjad S 2013 *Handbook of Biopolymers and Biodegradable Plastics* (Oxford: William Andrew)
- [11] Kim J-H, Shim B, Kim H, Lee Y-J, Min S-K, Jang D, Abas B and Kim J 2015 *Int. J. Precis. Eng. Manufac. Green Tech.* **2** 197
- [12] Nguyen T, Feng J, Ng S, Wong J, Tan V and Duong H 2014 *Coll. Surf. A* **445** 128
- [13] Mignon A, Snoeck D, D'Halluin K, Balcaen L, Vanhaecke F, Dubruel P, van Vlierberghe S and De Belie N 2016 *Con. Build. Mat.* **110** 169
- [14] Bezerra U T, Ferreira R M, and Castro-Gomes J P 2011 *Key. Eng. Mat.* **466** 37
- [15] Lasheras-Zubiate M, Navarro-Blasco I, Fernandez J M and Alvarez J I 2012 *J. Haz. Mat.* **233-234** 7
- [16] Riedel U and Nickel J 1999 *Die Angewandte Makromolekulare Chemie* **272** 34
- [17] Kim D 2004 *Study of Biopolymer-Modified Concrete System: Geopolymerization of Biopolymers* (Los Angeles: University of Southern California)
- [18] Mohanasrinivasan V, Mishra M, Paliwal J S, Singh S Kr, Selvarajan E, Suganthi E and Devi C S 2013. *3 Biotech* **4** 167
- [19] Environmental Protection Agency (EPA) United States. 2014. Basic Information about Lead in Drinking Water. http://water.epa.gov/drink/contaminants/basic_information/lead.cfm Accessed 2 August 2014
- [20] Dimitrakakis E, and Gidakos E 2014 *Closed-loop CRT Glass Recycling Alternatives* (Crete: University of Crete)
- [21] Kim D, Quinlan M and Yen T F 2009 *Waste. Man.* **29** 321
- [22] Olmo I F, Chacon E and Irabien A 2003 *J. Env. Eng.* **129**
- [23] Petersen B G, and Gundersen N L 2004 *Ann. Trans. Nordic Rheology. Soc.* **12** 39
- [24] Adams J W 1988 *Environmental Effect of Applying Lignosulfonate to Roads* (Chicago: Daishowa Chemicals)
- [25] Gargulak J D and Lebo S E 2000 Commercial use of lignin-based materials *Lignin: Historical, Biological and Materials Perspectives* ed Glasser W G, Northey R A and Schultz T P (Washington DC: American Chemical Society)
- [26] Cellulose Ethers Technical Overview and Product Guide. 2012. <http://www.dowconstructionchemicals.com/na/en/pdfs/832-00226.pdf>. Accessed 5 August 2014
- [27] Patural L, Marchal P, Govin A, Grosseau P, Ruot B and Deves O 2011 *Cem. Con. Res.* **41** 46