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Geopolymer formation and its unique properties

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Abstract The characteristic property of naturally-occurring geopolymers is a high content of humic materials that are recognized by the nitrogen function. Through a simulated geopolymerization, biopolymers with non-nitrogen function, such as xanthan gum, were found to have the characteristics of humic acid by means of UV–Vis spectrometry. This fact ascertains that any kind of biopolymer may naturally transform to a geopolymer. A geopolymer is a type of crosslinked long-chain compound, built in three-dimensional structures whose property is immune to microbial degradation. A crosslinked biopolymer was shown to have the same characterization as a geopolymer that has a long life due to its crosslinking capacity and antimicrobial properties. In this study, the formation of petroleum-based geopolymers (e.g., kerogen) was introduced. This study may elucidate the structure of geomacromolecules and the mechanism of their formation, closely related with crosslink reaction between inorganic and organic molecules. This will further change the conventional definition of geopolymer that involves only the inorganic geopolymer.

Keywords Biopolymer ·
Crosslink · Geopolymer ·
Humic acid · Kerogen

Introduction

The term "polymer" is frequently used to refer to a large organic molecule with repeated units or sequences. Geopolymers have been used by geochemical communities to indicate the transformation of geomolecules through geochemical processes during diagenesis (Kim et al. 2004, 2005). Yen proceeded with the concept of "geopolymer" (Young et al. 1974; Kim et al. 2004) and has drawn attention to it, in association with kerogen and petroleum. Geopolymer is the most stable material and the final alternating product in the Earth. Some geopolymeric materials can last for a long time due to their unique geopolymeric structure, so-called three-dimensional crosslink. Geopolymers can be classified into two major groups: pure inorganic geopolymers and organic containing geopolymers, synthetic analogue of naturally-occurring macromolecules (Kim et al. 2003, 2004). The definition of geopolymer proposed by Davidovits (1993) refers only to the pure inorganic geopolymers without organic content, which is a narrow concept that may not cover the true meaning of geopolymer. Its comprehensive applications thus should have been more accurately called "inorganic geopolymers." Some historical examples may explain this biased definition of geopolymers. Egyptian builders used plants (e.g., straw) and riverine mud to manufacture construction materials. The riverine mud they used must have contained considerable amounts of organics (e.g., humic materials). As a result, these materials can provide more strength for ancient concretes and mortars. Roman concretes (*opus*

caementicium) also contain mud as a binding material. The Romans already recognized the role of organics to improve the properties of their building materials. Even dried blood was used as an air-entraining agent, whereas biopolymers such as proteins served as the set retarders for gypsum (Plank 2004). They mixed inorganic materials with organics that required a small amount compared to the bulky requirements of inorganics. Therefore, Roman and Egyptian building structures are still standing, as materials were made under the theory of geopolymers, where organic involvement is structurally required for the formation of geopolymers. Herein, the crosslink between inorganic and organic materials can be achieved. Small content of organics is a key parameter governing the strength and durability of material in a large volume of inorganics. In the previous study (Kim et al. 2003, 2005), it was found that the organic containing concretes (small amounts of biopolymer solution) induced very high strength and immobilization of heavy metal, Pb.

With regard to sediments, a substantial fraction of the organic matter deposited with the sediments is hardly remineralized during early diagenesis (Larsen and Chilingar 1967). This preservation of organic matter in sediments is still puzzling. However, the inorganic–organic combinational structure can be a key point to explain this. Organic compounds can be incorporated into the refractory macromolecules such as lignin and melanodin or humic materials (Henrichs 1992). Humic materials represent an inorganic–organic structure. In this study, the synthesis of geopolymer based on petroleum was introduced by showing the formation of kerogen from biomass, which will give clues to the geopolymer formation, its fundamental structure, and unique properties.

For the experimental segments, the geopolymer formation was characterized through a liaison between a humic material (a precursor of geopolymer) and a biopolymer that converts to a material possessing characteristics of humic acid (HA) under heat and pressure. UV–Vis spectrometry showed the similarity between a HA and a biopolymer that underwent the simulated geopolymerization. The experiments also verify how stable and durable the biopolymers stay in the microbial environment, especially when they become crosslinked in an intramolecular and intermolecular network. The objective of the biological experiment is to create a non-biodegradable biopolymer, which can resist the biodegradability of biopolymers caused by microorganisms. This crosslinked structure of biopolymers was obtained by blending two different biopolymers or adding a crosslinker (crosslinking agent) to a biopolymer, allowing the reactive sites of biopolymers to interact with crosslinkers.

Theoretical background

Kerogen and bitumen (or asphaltene) are carbonaceous organic macromolecules, which can be recognized as geopolymers, because they have been formed in the lithosphere over a long geological time period. Kerogen is one type of geopolymer, containing massive amounts of organics and a small quantity of inorganics. Kerogen does not dissolve in most organic solvents because of its crosslinked structure. Kerogen can transform into asphaltene that upon pyrolysis becomes oil, gas, and residual carbons that are the precursors of petroleum (Yen 1972). Kerogen is one of the most abundant carbon-based materials in the world. It is also known that carbenes are present in meteorites and other celestial bodies (Yen 1972).

A modern analogy of geopolymers at a primitive stage of geopolymer formation includes the humic material form that is resistant to biodegradation due to their crosslinking characteristics (Kim et al. 2004). In other words, geopolymers contain large amounts of humic materials and show the crosslinking capability. Humic materials are widely distributed in all terrestrial and aquatic ecosystems, though particularly rich in marine sediment or peat that may be considered as a precursor to petroleum (Young et al. 1974). Herein, the correlation between humic materials and petroleum can be explained. A sample geopolymer formation can be visualized through the transformation scheme as shown in Fig. 1. In natural systems, the carbohydrate characterized by carbon–hydrogen chain reacts with the protein by nitrogen functional groups and would give rise to the humic substance, which features the distinct presence of polysaccharide and amide groups (Barancikova et al. 1997). Thus, the structure of geopolymers stems from that of humic material. In addition, the humic material combines with the lipid that is characterized by saturated triglycerides, finally allowing interpenetrating polymer network (IPN) to occur. The role of the lipid is like a wrapping material that will help encase the carbohydrate and the protein. A large number of IPNs would build in a three-dimensional structure, which may lead to the formation of kerogen or bitumen in a long geological time scale. The Green River kerogen has a straight-chain aliphatic structure (Young and Yen 1977; Yen 1976). This IPN structure consists of a polymethylene bridge, both unbranched and branched aliphatic structures, and also the entrapped species. The centers of cross-linked terminals can be cyclic skeletal structures such as naphthenics. There is evidence (Young and Yen 1977) that the long-chain aliphatics are attached via only one terminus to the core, the center where crosslinking takes place. The centers are saturated condensed ring structures from terpenoids or from partially aromatized terpenoids. Kerogen is a geopolymer that contains a

Fig. 1 The schematic diagram of geopolymer (kerogen) formation from biomass
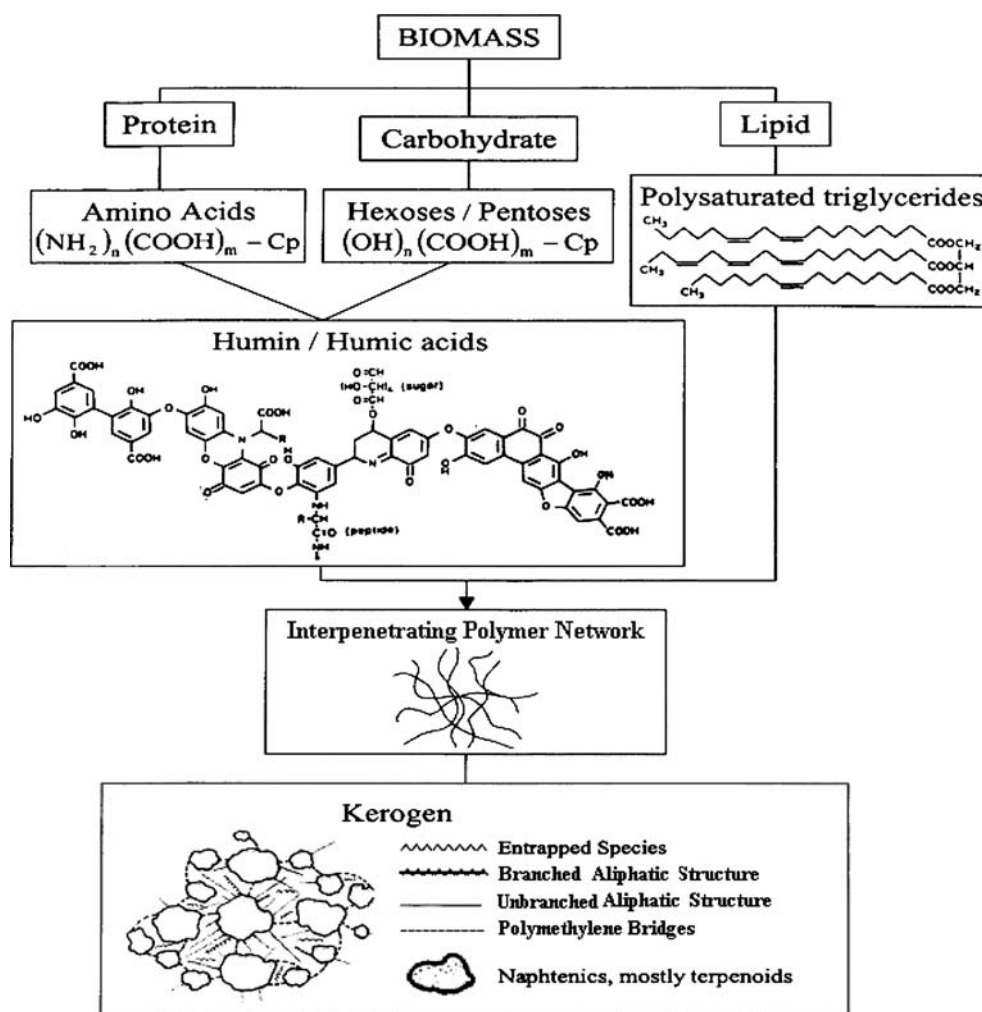
high content of organics. Geopolymers generally occur in numerous forms: some have more organics and less inorganics, while others have the opposite. It is, however, evident that both inorganics and organics are required in a mix at a certain ratio, which will result in a geopolymeric structure. This geopolymeric structure exhibits the similar structure of human bone and teeth, typical inorganic–organic composites that show extreme durability and mechanical strength.

Materials and methods

Xanthan gum, guar gum, and alginate were used as biopolymers. Xanthan gum was of food-grade quality. Table 1 summarizes the information on biopolymers used in this study. For the experiment (UV–Vis) of geopolymer formation from biopolymer, xanthan gum powder was dissolved in deionized water at a concentration of 0.1% and heated at 105°C, 15 psi in a 6-quart pressure cooker manufactured by Presto. The conver-

sion time of geopolymer formation can be manipulated by appropriate temperature treatment in a geo-chamber, as a trade-off can be made between time (geological age) and temperature. For example, whereas the degradation (decarboxylation) of alanine in aqueous solution to an extent of 50% (half-life time) needs over 1 billion years at 50°C (122°F), only 30 years are required at 150°C (302°F) (Yen 1972). It was also known that serine decomposes at 300°C (572°F) within seconds, but it would take over 1 million years at 0°C (32°F) (Yen 1972). For this reason, artificial aging can be achieved in a pressure cooker used as an aging chamber. Reaction times were 16 and 20 h. Twenty milliliters of xanthan gum solution were poured into 30-mL vials and placed in the aging chamber, with glass wool clogged on top of vials to prevent an evaporation of sample solutions. Reacted samples were withdrawn for UV–Vis Spectrometry. UV–Vis spectrophotometric absorbance within a wavelength of 200–800 nm was recorded by UV/Visible Spectrometer, Vectra 286/12 of Hewlett Packard.

Table 1 Source, structure, and property of xanthan gum, guar gum, and alginate

	Source	Structure and Property	Note
Xanthan gum (extracellular biopolymer)	Produced by *Xanthomonas campestris* that is a genus of the Pseudomonaceae family	Five sugar residues: two glucose, two mannose, and one glucuronic acid, in the molar ratio 2.8:2.0:2.0[a] Molecular weight: from 2 to 20×10^6 Da (2,000 up to 20,000 repeating units) Functional groups: CH_2OH, OH, O, COOH, H	High viscosity at even low concentration, high viscosity at low shear rates, high degree of pseudoplasticity, high elastic modulus[b] Compatibility with ionic strength variation, heat, pH, shear, enzymes, chemicals
Guar gum (plant biopolymer)	Extracted from the seed of Guar Gum Plant, the leguminous shrub *Cyamopsis tetragonoloba*	$1 \rightarrow 4$-linked β-D-mannopyranose backbone with branchpoints from their 6-positions linked to α-D-galactose (i.e., $1 \rightarrow 6$-linked-α-D-galactopyranose), every galactose residue between 1.5 and 2 mannose residues[c] Molecular weight: 2×10^6 Da (up to 10,000 repeating units) Functional groups: CH_2OH, OH, O, H	Economical thickener and stabilizer Viscous pseudoplastic, high low-shear viscosity, shear thinning, less affected by ionic strength or pH, synergic effect with xanthan gum
Alginate (marine plant biopolymer)	Extracted from brown seaweed, so-called marine polysaccharide	Linear unbranched polyanionic polymer or block copolymer of β-(1–4)-linked D-mannuronic acid (M) and α-(1–4)-linked L-guluronic acid (G), and chain sequences of the type $(M)_n$, $(G)_n$, and $(M-G)_n$[d] Molecular weight: 230×10^3 Da Functional groups: CH_2OH, COOH, O, OH, H	M/G ratios in alternating residues decide on different conformational preferences and behavior. M:G ratio: 0.5–0.6. Flexible rod structural shape. High G content produces strong gels with good heat stability but prone to syneresis on freeze-thaw, whereas high M content produces weaker, more-elastic gels with good freeze-thaw behavior. M alginate crosslinked with Ca^{2+} has become the stronger gels. Solubility and water holding capacity depend on M:G ratio, molecular weight, temperature, pH, ionic strength, and the nature of ions present. Intrinsic viscosity, $[\eta]$: 700–1,200°C mL/g^{-1} Sequential residues can bind Ca^{2+}, Ba^{2+}, Sr^{2+} and Mg^{2+} intra- and inter-molecularly[e] The crosslinked alginate by calcium ions is widely used in molecular biotechnology, removal of radioactive nuclides, pharmaceutical application (pH-sensitive uniform gel beads for DNA adsorption and temperature modulated drug release)[f, g]

[a] Garcia et al. (2000)
[b] Kelco Technical Brochure (1999)
[c] Kesavan and Prud'homme (1992)
[d] Walton and Blackwell (1973)
[e] Mimura et al. (2002)
[f] Tuncel et al. (2000)
[g] Park and Choi (1998)

Biodegradability was determined to evaluate the effectiveness of crosslinking capacity of biopolymers. The biometer flask method designed by Bartha and Pramer (1965) was adopted. The principle is based on monitoring the generation of CO_2 produced by the microbial degradation of compounds. Biometer flasks were used in measuring the biodegradability of cross-linked or non-crosslinked biopolymers in soil. Activated sludge inoculum was utilized as a bio-seed, obtained from Terminal Island Wastewater Treatment Plant in San Pedro, California. It was added to the garden soil in a ratio of 1 mL to 10 g of soil, composed of 87.2% sand, 12.8% silt and clay, and with a pH adjustment of around 5.68. An appropriate amount of biopolymer sample was added to the soil (0.2% w/w). In the case of XACa (xanthan + alginate + calcium), 50 g of garden soil

were placed in a biometer flask, and 5 mL of activated sludge inoculum were then added to the soil. The biopolymer solution of xanthan and alginate was prepared as follows: 0.8 g of alginate and 0.2 g of xanthan gum were dissolved in 50 mL of distilled water. Five milliliters of biopolymer solution were added evenly to the soil followed by 1 mL of 0.4 M $CaCl_2$. Therefore, all ingredients such as biopolymer solution, crosslinker ($CaCl_2$), and seed microorganisms were well mixed with the soil sample. The crosslinking agents for biopolymers are calcium, barium, and borax. Samples of XABa (xanthan + alginate + barium) and XGB (xanthan + guar + borax) were prepared using the same method as XACa. For the experiment of XGBg, glutaraldehyde was added to the XGB biopolymer mix as a bactericide.

A 200-mL sample was mixed with 200 mL of nutrient composed of 1.0 g/L KH_2PO_4, 1.0 g/L K_2HPO_4, 1.0 g/L KNO_3, 1.0 g/L NaCl, 0.2 g/L $MgSO_4$, 0.02 g/L $CaCl_2$, and 1 mL of trace elements of solution. The mixture was then stirred, aerated with ambient air, and placed on the bench for 80 days. Twenty-five milliliters of mixture were removed and replaced by 5 mL of 20% (w/v) glucose solution and 20 mL of nutrient solution. Blank (without biopolymers) and glucose samples were also used as a reference.

10 mL of 0.1 N NaOH was added to the cell of each flask to absorb CO_2 generated by microbial activity. The amount of CO_2 produced can be determined by titrating alkali solution with 0.01 N HCl. Using the following equation (Momeni 2001), the quantity of CO_2 can be calculated for each period of time.

$$\frac{(V_{HCl,blank} - V_{HCl,sample})(0.01 \text{ N HCl})(44 \text{ mg CO}_2/\text{mmol})}{2 \text{ meq/mmol for CO}_2}$$

$$= 0.22(V_{HCl,blank} - V_{HCl,sample}), \quad [\text{unit}: \text{mg CO}_2],$$

where:

$V_{HCl,blank}$ = Volume (ml) of HCl used to titrate blank to pH 7,

$V_{HCl,sample}$ = Volume (ml) of HCl used to titrate sample to pH 7.

Results and discussion

Similarities of HA and geopolymerized biopolymer

Humic acid is believed to have a random coil structure. Even though the biogeochemical and environmental conditions remain the same, different source materials can lead to the formation of chemically, structurally, and molecularly different HAs. When it comes to identifying this random polymer of HA, a great deal of effort has been made to reveal their amorphous structure, and at best their type structure may be established. The actual model of HA therefore remains controversial, subject to constant revision, and to be further elucidated, although recent research to unveil this material seems to be appealing, such as building a computer-assisted model in a 3D graphic simulation. As shown in Fig. 1, the rings in HA bear a variety of functional groups, the more prominent of which are carboxyl, phenolic hydroxyl, and carbonyl groups. Attached to this core are amino acids, peptides, sugars, and phenols, which will form further cross linkages and build a three-dimensional sponge-like structure (Atlas and Bartha 1998).

UV–Vis spectra of HA may be varied depending on their source of nature, but the characteristic peak of HA can be identified. Geopolymer formation includes the HA structure. Thus, the structural property of geopolymer can be characterized by the structure of HA. Simply put in the experiment, the results of UV–Vis spectra showed the similarity of HA and geopolymerized biopolymer. In the study, HA represents the humic materials. In Fig. 2, the UV–Vis absorbance of HA decreased as the wavelength increased, as is typical for HA. Its absorption spectra are broad, which is in accordance with other studies (Andelkovic et al. 2001; Duarte et al. 2003). The characteristic peak of HA was around 275–280 nm of wavelength with certain range of intensity (Andelkovic et al. 2001; Duarte et al. 2003). Absorbance in this region is attributed to π–π^* electron transitions in phenolic arenas, aniline derivatives, polyenes, and polycyclic aromatic hydrocarbons with two or more rings (Duarte et al. 2003). Aromatic or π system is necessary for typical geopolymer structure.

For 16 or 20 h, xanthan gum in the form of dilute solution was under pressure and heated in the aging chamber. The resultant xanthan gum exhibited the same peak HA showed after the reaction of the simulated geopolymerization, whereas the original peak of xanthan gum before the reaction had no peaks around 275–280 nm that was confirmed in the previous study (Kim et al. 2004). Biopolymer was seen to become a larger molecular polymer resembling HA after the simulated aging process.

In the previous work (Kim et al. 2004), biopolymers containing nitrogenous functional groups showed the HA characterization of UV–Vis spectra in the form of melanoidin, a precursor of HA. Xanthan gum did not show the melanoidin characteristic peak, given that xanthan gum contains no nitrogen function in its structure. However, after the simulated reaction with artificial addition of nitrogen organic molecules such as green tea or urine, xanthan showed exactly the same pattern of peaks as melanoidin. In this study, the

Fig. 2 Comparison of UV–Vis spectra for HA and xanthan gum after the simulated geopolymerization (HA adopted from Duarte et al. 2003)
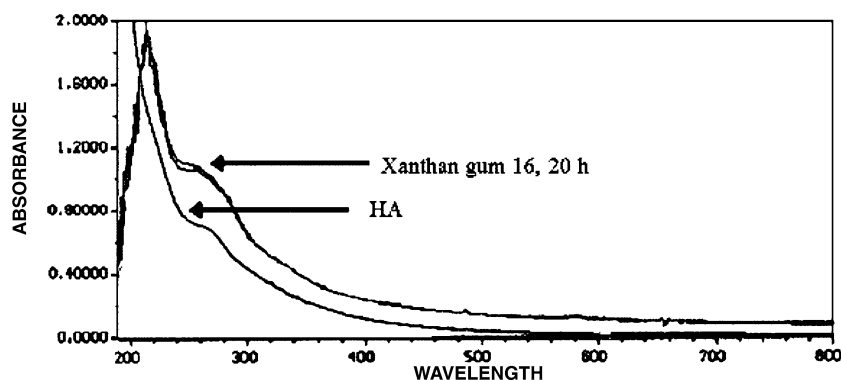
nitrogen source was not supplied. However, xanthan gum showed very identical UV–Vis spectra of HA after the simulated reaction. It is speculated that xanthan gum reacts with atmospheric nitrogen and will resemble HA. Nitrogen sources in nature can be available from either soil or atmosphere. The functional role of nitrogen in the crosslinked structure may have to be discussed because nitrogen is certainly attributable to the strong peak of the UV–Vis spectra, around 275–280 nm. Not a few crosslinked systems in nature, inevitably, involve the nitrogen functions as the core of structure or the bridge of crosslinking reaction. Examples are nitrogen in peptide bond and nitrogen in petroleum as described in denitrogenation (Kim and Yen 2006). Therefore, biopolymers like xanthan gum are likely to have the nitrogen function and characteristics of HA throughout the geopolymerization. Clarifying the difference between

the melanoidin peak and the HA peak in the UV–Vis may explain why materials tend to show the UV–Vis characteristic peak of melanodin when reacting with a large amount of nitrogen, while they show the characteristic peak of HA when reacting with a small amount of nitrogen. For the previous work, the stronger melanoidin peak of around 280 nm seemed to be overlapping the HA peak. The melanoidin could presumably be the precursor of humic material. In terms of chemical structure, both have similar systems featuring the involvement of carbon–hydrogen and nitrogen functions. Basically, melanoidin and HA are types of pigments showing the characteristic peaks in the UV–Vis spectra. Still, there is much to study the relations between melanoidin and HA. However, both melanoidin and HA conclusively have equal implications of representing the precursors of geopolymeric materials.

Fig. 3 Cumulative carbon dioxide generation for each sample
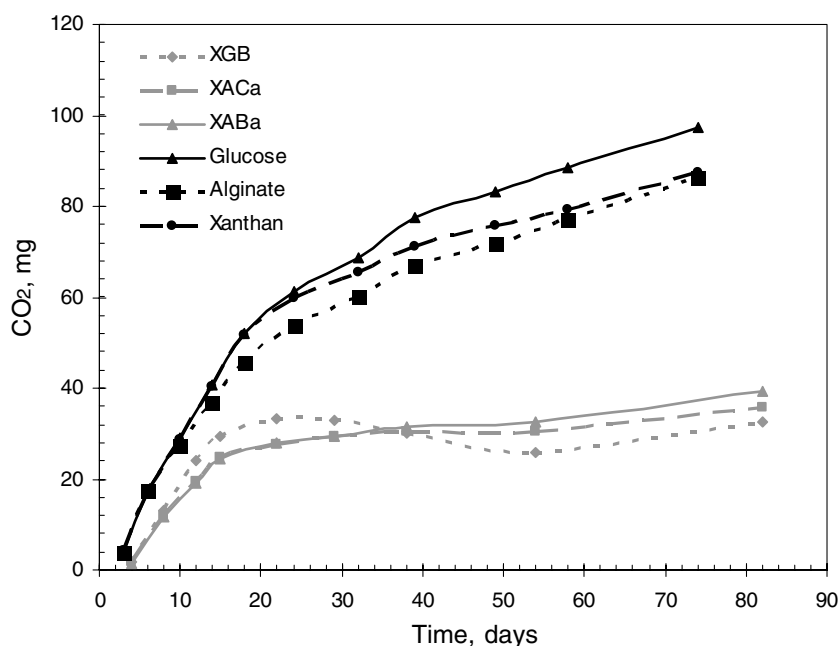
Table 2 Biodegradation rates of crosslinked biopolymers and pure biopolymers

Biodegradation rates (mg CO_2/day)						
XGB[a]	XACa[b]	XABa[c]	Glucose	Alginate	Xanthan	XGBg[d]
0.395	0.437	0.477	1.316	1.168	1.182	0.068

[a]XGB: xanthan + guar + borax
[b]XACa: xanthan + alginate + calcium
[c]XABa: xanthan + alginate + barium
[d]XGBg: xanthan + guar + borax + glutaraldehyde

## Microbial endurance of crosslinked biopolymer

As shown in Fig. 3, the carbon dioxide evolution of crosslinked biopolymers (XGB, XACa, and XABa) is significantly reduced as compared with glucose and non-crosslinked biopolymers such as alginate and xanthan gum. Typically, the cumulative CO_2 generated from easily biodegradable materials (glucose, non-crosslinked biopolymers) was approximately 80–100 mg during the 80 day test period, which is equal to the amount of 100 mg that was added at the beginning of the experiment. The CO_2 generation starts leveling off around day 20 for both crosslinked and non-crosslinked groups of biopolymers. Biodegradation reached an equilibrium point for the crosslinked biopolymer samples, while the degradation still continued for the non-crosslinked groups in the biopolymers. For 20 days, the small molecules in crosslinked biopolymers might be consumed by microorganisms to approximately 30% of total molecules of biopolymers. This mineralized fraction of crosslinked biopolymers may result from

incomplete crosslinked products or the side parts of biopolymer remnants. The mineralization of glucose, alginate, and xanthan was seen to be complete after 80 days.

These results are consistent with the results obtained by Yabannavar and Bartha (1994), noting that the formation of IPN is recalcitrant to microbial activity. Complex structures and stronger chemical bondings are involved in the formation of IPN, thus reducing the mineralization of compounds (Andrady 1994). In addition, the insolubility of crosslinked macromolecules may be caused by the reduction in the permeability across the biopolymer entanglement and microbial cell membrane, which is required for microbial biodegradation. As shown in Table 2, the biodegradation rates around 80 days were 0.395 mg CO_2/day, 0.437 mg CO_2/day, and 0.477 mg CO_2/day for XGB, XACa, and XABa, respectively. These results represent about one-third to one-fourth of the CO_2 production rates of non-crosslinked biopolymers. The present study did not consider the most efficient crosslink agent in different biopolymer combinations for the crosslink reaction.

Figure 4 shows the comparison of accumulative carbon dioxide generation from simple molecules (glucose), non-crosslinked biopolymer (xanthan gum), crosslinked biopolymer (XGB), and crosslinked biopolymer mixed with bactericide (XGBg). There was almost no mineralization in the case of XGBg, to which gluatraldehyde was added as a bactericide. In Table 2, XGBg had a biodegradation rate of 0.068 mg CO_2/day, indicating that microbial activity scarcely occurred.

The experiments were carried out to approach the geopolymerization concept in order to better understand

Fig. 4 Comparison of cumulative carbon dioxide generation from glucose, xanthan gum, XGB, and XGBg
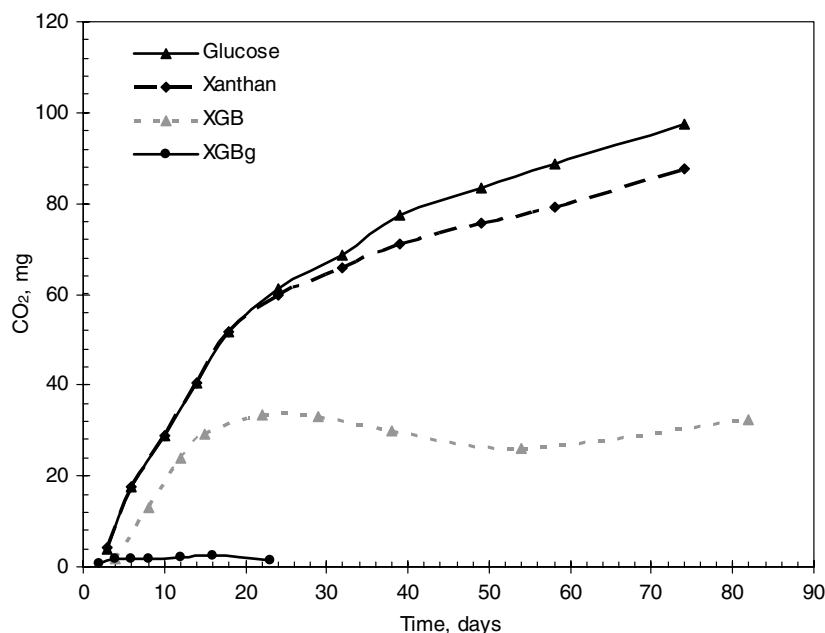
the formation of geopolymer and its authentic definition and properties. Two major properties of geopolymers were identified through the simulated geopolymerization by observing the characteristic UV–Vis peaks of crosslinked biopolymers and CO_2 production experiments. Crosslinked biopolymers were found to have the characteristics similar to those of geopolymer so that they will last long due to their crosslinking capacity and antimicrobial structure. Crosslinked biopolymers, a preform of geopolymers, contain a high content of humic materials. Unique characteristics of geopolymers can be summarized as follows:

- Metals cannot be leached out in aqueous solution at various pH levels.
- Metals are coordinated through gaps or holes of the carbonized and peri-condensed aromatic rings or in the π-system.
- Radiation stable: Asphaltene is a free-radical inhibitor and has extremely low G-yield, even under a Van de Graff accelerator (2 MeV).
- Chemically stable: Kerogen can be stable in concentrated acids, e.g., HF, HCl, H_2SO_4, and CF_3COOH.
- Thermally and mechanically stable: not pyrolyzed below 400°C.

- Novel combinational structure in inorganic and organic composites.
- Three-dimensional IPN.
- High content of humic materials.
- Microbial resistance.

In the formation of kerogen-derived geopolymers, the analysis and determination of products involve multi-tasks because the geopolymers come in various forms, similar to those of HA, whose standard model should also have to be elucidated. Considering the complexity of amorphous HA, indeed, HA has a random cross-linked structure resembling that of a geopolymer. This study may be one step toward a better understanding of the liaison between the humic substance and re-defined geopolymers that can comprise the conventional inorganic geopolymer. This can also provide a concrete evidence for the mechanism of geomacromolecule formation that should involve the crosslink reaction between the inorganic and organic materials.

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