ENZYMATIC MODIFICATION OF GUAR SOLUTIONS

Viscosity–Molecular Weight Relationships

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1. ABSTRACT

Structurally modified guar galactomannans find application in food and petroleum industries as rheology modifiers. Enzymes provide a powerful and convenient method to modify guar structure. In this study, the kinetics of enzymatic degradation of guar solutions were investigated using SEC and rheology. Molecular information from SEC reveals the degradation reaction to be zeroth order in guar concentration. Further, the rate constant was proportional to enzyme concentration, demonstrating that the enzyme acts as a true catalyst. The zero shear viscosity was very sensitive to degradation, with several orders of magnitude change being observed over the course of polymer chain scission. A unique correlation was developed between degradation time, guar molecular weight and viscosity. This enables superposition of the viscosity-time profiles for different enzyme concentrations to a master curve; providing for a priori prediction of guar solution viscosity as a function of degradation time and enzyme concentration.

2. INTRODUCTION

Water-soluble polymers, such as guar, tara or locust bean, are used extensively in many applications because of their ready availability, low cost compared to other synthetic polymers, and ability to produce high viscosity solutions and gels at low polymer concentrations. In particular, these industrial gums have found a variety of uses in industries ranging from printing and paper to mining, textiles, foods, and, oil/gas production. Guar gum and its derivatives are used in the paper industry in the production of different grades.
of paper and paperboard to improve dry strength, formation, drainage and retention properties. In the mining industry, they are used as processing aids in the separation of minerals, such as aluminum and uranium, from their ores with the gums performing two independent functions, flocculation of particles in aqueous suspension and depression of slimes in froth flotation. The textile industry uses guar gum and its derivatives as thickeners for dye liquors to impart desired mobility since they exhibit good electrolyte tolerance, high thickening efficiency and good compatibility with other dye liquors. Gums are also used in flatgoods printing where their greater solubility, easier wash out and lower level of insolubles results in better runnability and improved prints.

By far, the two major applications for guar are in oil and gas production and as food additives. In the oil and gas industry, viscous formulations of guar are used to enhance oil or gas production. In this process, known as hydraulic fracturing, metal-crosslinked guar, together with particulate suspensions (sand), are injected at high rates under high pressures through well-bores. This induces fractures in the rock that propagate hundreds of meters radially outward from the well bore. The fracturing polymer is then degraded (typically using chemicals) and flushed out leaving behind a highly permeable channel of sand for outflow of gas or oil. Enzymes offer an efficient and environmentally benign way of degrading the guar gels. More importantly, the use of thermostable enzymes that are active only at high temperatures would allow to tap deeper reservoirs and enhance oil/gas production significantly.

Enzymatically modified guar also has tremendous potential in food applications. Galactomannans such as guar and locust bean gum are widely used in foods such as cheeses, dressings, dairy and bakery products to improve mouthfeel and chewiness, elongate shelf-life through moisture retention and prevent syneresis. Many of these functions are achieved by mixing galactomannans with other polysaccharides, such as xanthan and carrageenans. Galactomannans have the ability to effect gelation in polysaccharide systems that are otherwise non-gelling, rendering stability, texture and controlled rheological characteristics to food. Locust bean gum forms smooth, firm, elastic synergistic gels with xanthan, κ-carrageenan and agarose, for example. Such synergistic combinations are employed in canned meat products, confectionery products, dips and spreads, acidified milk gels, etc. The supply of locust may dwindle in the future owing to the long maturation period, labor-intensive harvesting and competition from other cash crops. In comparison, guar is cheaper and readily available which makes it a suitable replacement for locust bean. Hence, it is of commercial interest to see if the structure of guar can be modified to convert it to a material having the desired functional properties of locust bean. Guar and locust bean both have an irregular distribution of galactose side chains along the mannann backbone, with the primary difference being that guar has a higher mannose to galactose ratio (3:2) compared to locust bean (4:1). This mannose to galactose ratio is critical as the extent of interaction of galactomannans with other polysaccharides depends on the level of substitution of the (1–4)-linked β-D-mannan chain by the (1–6)-linked α-D-galactose side chain. Enzymes offer a powerful way to selectively clip off the galactose side chains from guar molecules to not only mimic the architecture of locust beans but also provide new materials for making synergistic gels with other polysaccharides.

Guaran, the functional polysaccharide in guar gum is a chain of (1–4)-linked β-D-mannopyranosyl units with single (1–6)-linked α-D-galactopyranosyl units as the side chains. Recent information on the fine structures of guar galactomannan indicate that the galactose distribution is irregular to random. The molecule is susceptible to enzymatic hydrolysis at three types of sites, namely, the endo- and exo- β-1,4 linkages between the D-mannose sugar units on the backbone and the α-1,6 linkage between the mannose unit