U.S. DEPARTMENT OF AGRICULTURE

Binders for Small-Caliber Gun Primers

Understanding Gum Arabic and Exploring Possible Synthetic Replacements

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Forest Service
Forest Products Laboratory
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Abstract

Misfiring and hang-firing have been long-term, sporadic problems with 7.62-mm ammunition. These types of problems can cause injury to the shooter or others in the vicinity. This issue is believed to be related to inconsistency of the primer binder gum arabic (GA). A multi-organization project involving USDA Forest Service, Forest Products Laboratory, was put together to work on solving this issue. The project was divided into two phases. Phase I was to understand the properties of GA in its application of holding together the explosives in small-caliber gun primers. Understanding the properties helped to provide improved specifications for this use. Phase II was to use this information to select promising synthetic binders to replace GA for more consistent quality and to avoid dependence on a product that comes from sub-Saharan Africa. After several pellet integrity tests (tumbling, vibrating table, and radial crush), several synthetic binders were recommended as possible replacements for GA for use in primer pellets. However, the recommended binders were never tested in live ammunition. The funding and management for the program was provided by the U.S. Army Joint Munitions Command (JMC), but the champion of this program at JMC was reassigned. The project was deprioritized before the live ammunition testing could be carried out.

Keywords: Gum arabic, binder, ammunition, pellet integrity, quality

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Preface

Misfiring and hang-firing have been long-term, sporadic problems with 7.62-mm ammunition. These types of problems can cause injury to the shooter or others in the vicinity. It is believed that inconsistent cohesion of the primer, FA-956, is the major cause of this issue because there have been observations of primer dusting after storage that coincided with increased incidence of misfiring. This problem is believed to be related to inconsistency of the primer binder gum arabic (GA). However, the current specifications do not differentiate among GA from different suppliers in relation to its expected performance.

GA is a natural product from the *Acacia senegal* tree and related tree species and has been used for a long time as a binder in the manufacture of small- and medium-caliber primer pellets. Because GA comes from a natural source, variation in physical, chemical, and mechanical properties may lead to misfiring of the bullets.

The U.S. Army Joint Munitions Command (JMC) of the U.S. Department of Defense (DOD) used the expertise of the USDA Forest Service, Forest Products Laboratory (FPL) in carbohydrate chemistry, adhesives, and analysis to assist in solving the ammunition manufacturing problem. A project was put together with JMC, FPL, and several other organizations. There were two main phases in the project. The goals of Phase One were to understand the structure of GA, measure chemical and physical properties of samples from three suppliers of GA, and determine which properties were related to performance characteristics of bullets made from these gums. The first goal of Phase Two was to identify commercial synthetic polymers that could replace GA as the binder in FA-956 primer formulation. The second goal of Phase Two was to develop a primer formulation using a synthetic polymer binder along with specifications for this binder. This report elaborates on FPL's contributions to the two phases of the project.

To accomplish the goals of this project, an industry–government integrated project team was organized consisting of members of Project Manager-Maneuver Ammunition Systems (PM-MAS); Armament Research, Development and Engineering Center (ARDEC) at Picatinny Arsenal; JMC; FPL; Alliant Techsystems Inc. (ATK); and Lake City Army Ammunition Plant (LCAAP). Key team members are shown with shading in the following list:

Marc D'Auria	ARDEC
Gary Chen	ARDEC
Robert McDuffie	ARDEC
Kevin Im	ARDEC
Susan Polinski	ARDEC
Jim McGrath	PM-MAS
Jennifer Paul	Contracting, JMC
Craig Patterson	JMC
Chuck Frihart	FPL
Jim Beecher	FPL
Ken Patrick	ATK
Lisa Liu	ATK Launch Systems
Hegel Neira	ARDEC
Julie Casey	ATK
Randy Busky	ATK
Pamela Diego	ATK
Dan Clark	ATK
Brice Bentson	ATK Launch Systems
Dave Dunaway	ATK Launch Systems
Jessica Horning	ARDEC
Dr. Edward Hochberg	ARDEC
Maxine Reisdorph	LCAAP Gov. QA
Bill Minner	LCAAP Gov. QA
Mark Mansfield	ATK
Reed Blau	ATK Launch Systems

Phase One

The following chapters record FPL's contribution to Phase One of the project:

"Chapter One: Gum Arabic Overview" is a chemical and physical description of GA based on a review of the available technical literature.

“Chapter Two: Characterization of Three Samples” describes the measurement of chemical and physical properties of GA used in Phase One from three different suppliers.

“Chapter Three: Structure and Rheology” relates the measured molecular shape of the three GA samples to their behavior in solution. This chapter as well as the information in Chapters One and Two provided guidance for the selection of synthetic polymer replacements.

Phase Two

The following chapters record FPL’s contribution to Phase Two of the project:

“Chapter Four: Selection of Synthetic Replacements” gives the criteria used to develop and then to refine the list of synthetic polymer binder candidates.

“Chapter Five: Integrity of Inert Primer Pellets” describes the development and testing of inert model primer pellets used to select a few binder candidates from the extensive list developed in Chapter Four.

“Chapter Six: Recommendations” gives a list of recommended new GA specifications and synthetic polymer adhesives and rationale for their selection.

Chapter One
Gum Arabic Overview

An ammunition primer needs a dense concentration of explosives, which typically consist of solid inorganic and organic nitrates with the impact-sensitive lead styphnate as the igniter. This mixture must be held together with a binder to obtain a smooth, complete ignition of the propellant. Misfiring has been attributed to failure of the binder to hold the primer together during the storage, drying, and insertion of the primers into the bullet casings during production. Occasional significant primer dust has been observed on the production equipment, which indicates the possibility of the binder failing to keep the primer pellet intact. Gum arabic (GA) has long been used as the binder, but the current purchase specifications do not include any useful analysis methods related to its performance or composition in this application. To improve specifications, we needed to develop a better understanding of what makes GA unique for developing high-solids, low-viscosity solutions.

GA is the gummy exudation originating from the *Acacia* spp. tree. Specifically, gums from *Acacia senegal* (L.) Willdenow or closely related species of family *Leguminosae* are considered sources for GA. The *Acacia* trees grow mainly in semiarid climates such as sub-Saharan Africa and produce gum exudate when the tree is distressed.

Perhaps a good chemical description of GA is the one obtained by sorting its components by molecular size. This involves using gel permeation chromatography to separate the components, with the largest components eluting from the column first because they are not retained by the small spaces in the gel.

The three major components for GA have been determined (Randall and others 1989, Vandevelde and Fenyo 1985) with the largest component by size being arabinogalactan-protein (AGP), which is mainly composed of the carbohydrate arabinogalactan (AG) attached to the protein. AGP constitutes about 10% of GA by weight and has a molecular mass of 1.45×10^6 Daltons. The bulk of GA (88% by weight) consists of the nonprotein-containing AG fraction, which has a molecular mass of 2.8×10^5 Daltons. Only a small amount (20%) of total protein is found in this fraction. The third fraction is glycoprotein (GP), which accounts for a little more than 1% of GA by weight. The GP fraction is high in protein content (~50% by weight) with a different protein composition than the AGP fraction. Because there is disagreement in the literature about the presence of peaks, the fraction can be considered a continuum of different molecular weights with varying protein to carbohydrate ratios (Renard and others 2006).

Chemical Structure

The AGP component has been described as a long-chain protein molecule with five arabinogalactan sidechains attached in total (Connolly and others 1987, 1988). This is called the "wattle blossom" model (Fincher and others 1983) (Fig. 1-1).

AGPs, found in all plants, reside mainly at cell surfaces where they are thought to have important roles in plant growth and development (Showalter 2001). The core protein typically contains hydroxyproline, alanine, serine, threonine, and glycine as major amino acid constituents. The C-terminal region of the protein is usually hydrophobic.

The sugar sidechains, which constitute most of the AG fraction, consist of a β1 → 3 linked galactopyranosyl unit backbone with branches of galactopyranosyl unit linked β1 → 6-member arabinopyranosyl unit, arabinofuranosyl unit, and rhamnopyranosyl unit sugars, which terminate with glucuronic acid or 4-O-methylglucuronic acid. The sugar-sidechain is like a tree made by linking ring-like sugar units (six-member pyranose rings) with branches composed of other linked sugar rings (pyranose or five-member furanose rings) (Tryfona and others 2012). Each branch terminates in a carboxylic acid or acid salt (Anderson and others 1966). The highly branched nature of the AG keeps it in a more globular shape with a low viscosity compared with linear sugar polymers, which form long chains that lead to higher viscosity solutions even at low concentrations (Fig. 1-2).

The AG sidechains are very hydrophilic, having many hydroxyl and carboxylic acid groups. These structures are attached to the hydroxyl group of hydroxyproline (sometimes serine or threonine). This accounts for the high

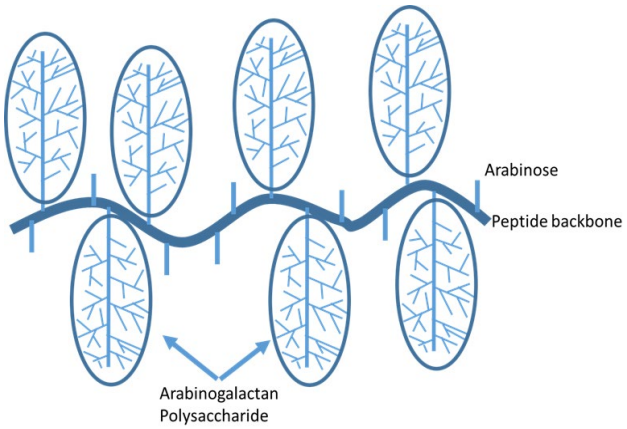

Figure 1-1. Schematic representation of AGP.

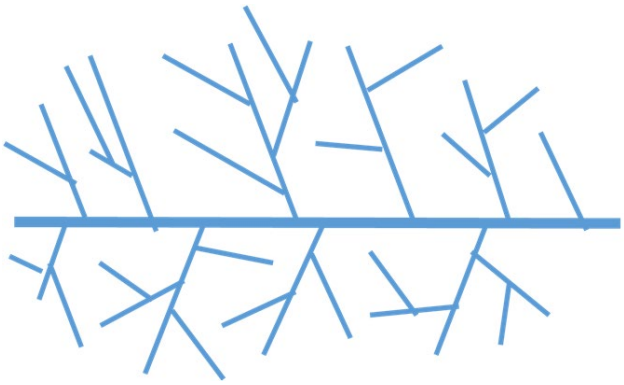

Figure 1-2. Illustration representing the highly branched structure of the AG fraction and carbohydrate side chain structure of AGP and of GA showing its globular shape.

solubility of GA. Short arabinosyl unit chains are also present, which are usually attached at sites with contiguous hydroxyproline residues. The highly hydrophobic protein constitutes the main backbone of the polymer. Because of the side chains having side chains, often the AG sidechains have been described as if they were AG species condensed onto a larger molecular structure. This is no longer regarded as an accurate picture. A better description of GA components has resulted from a thorough characterization of products created by systematic degradation (Mahendran and others 2008).

The AGP component has been described as a block polymer that consists of a large hydrophilic portion and a smaller hydrophobic portion (Fig. 1-3). When the AGP proteins are fully digested, the AG blocks have a molecular weight of about 4.5×10^4 Daltons, which is nearly ten times smaller than the AG species (Mahendran and others 2008). Furthermore, the amino acid compositions of the AGP and AG species are different.

Solution Behavior

The GA molecules have a very compact size in solution with a radius of gyration of about 20 nm or less. This accounts for the low viscosity of GA solutions even at relatively high concentrations. The viscosity only begins to increase when the polymer molecules are packed together closely enough to result in intermolecular interactions.

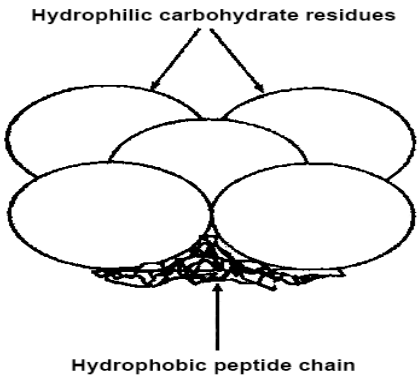

Figure 1-3. Space-filling representation of gum arabic in solution.

Molecules that combine hydrophilic and hydrophobic functions can serve as surfactants or emulsifiers. This is the role of GA in the food and pharmaceutical industries (Snowden and others 1987, Islam and others 1997). It may also be an important characteristic for GA as a binder or adhesive (Fig. 1-3).

Detailed studies have looked at the roles of the components of GA in providing the most effective flavor dispersion in food products. As a laboratory model of beverage emulsification, a suspension of orange oil in water (1:5 by weight) was studied. A stable emulsion was supported by GA at a concentration of 12% (by weight) or higher. However, it was found that only 1% to 2% of the GA, the AGP component, was adsorbed at the oil–water interface. Treatment of the GA with a protease that attacked the protein also destroyed the emulsifying activity. Randall and others (1988) and Yadav and others (2007) revisited this emulsification study to investigate the role of glycosylphosphatidylinositol lipids (GPI) as emulsion stabilizers. GPIs are found as a minor component in GA, and they serve to anchor AGP to the plant plasma membrane (Yadav and others 2007). They performed some chemical treatments that diminished the emulsifying activity of AGP. However, they were not clearly able to distinguish between the importance of GPI and protein.

Another study of GA as an emulsifier used polystyrene latex as a substrate. It was found that the AGP fraction was isolated at the surface of the polystyrene latex particles and enhanced the stability of the suspension. It was also determined that the AG fraction lacked the ability to stabilize the emulsion (Snowden and others 1987).

Early studies of the configuration of GA in aqueous solution concluded that it is a highly compact molecule with a radius of gyration of 10 nm or less, more compact than branched dextran or polystyrene of comparable molecular weights. Studies of solution viscosity as a function of ionic strength indicated that spatial expansion was not responsible for viscosity increases and suggested that electroviscous effects might offer an explanation. Because this study did not use fractionated GA, the results were probably dominated by the AG fraction (Swenson and others 1968).

The values of hydrodynamic radius determined by Al-Assaf and others (2005) are somewhat greater than those reported by others (Swenson and others 1968, Randall and others 1989). All these studies used light scattering to measure the molecular diffusion constants in solution, although different instruments were used in different ways. The hydrodynamic radius is somewhat dependent on the ionic strength and concentration of the solution; however, the publications do not contain sufficient information to reconcile the differences.

A comprehensive and sophisticated study of GA solution rheology was performed by Goycoolea and others (1995). They also simultaneously examined the behavior of mesquite gum, which has a composition and chemical structure similar to that of the AG fraction of GA. A study of GA solution rheology was interpreted in view of a model of molecular association (Li and others 2009). Both gum solutions exhibited only slight shear thinning (reduction in viscosity) as the solution concentration was increased up to the highest accessible concentrations (≈50%). The "hydrodynamic radius" of mesquite gum (i.e., the effective volume occupied by the molecule in solution) determined by light scattering is 8.5 nm. This is similar to the 9.2-nm hydrodynamic radius determined for the AG fraction of GA (Randall and others 1989), but it is appreciably smaller than the volume occupied by the gum arabic AGP fraction of 22.8 nm (Randall and others 1989).

The intrinsic viscosity of charged macromolecules in solution normally decreases as salt is added to the solution (Morris 1990, Morris and others 1981). This is caused by progressive shielding of intramolecular electrostatic repulsions allowing the molecules to contract to a less expanded conformation. However, there was no systematic change in the intrinsic viscosity of mesquite gum at ionic strengths ranging from 0.05 to 2.0 mole/L solution. This indicates that the compact solution structure has limited capability of contraction and reaffirms the previously mentioned study (Swenson and others 1968).

However, both GA and mesquite gum exhibit solution behavior at high concentration that is considered typical for linear polysaccharides at much lower concentrations. This is interpreted to mean that these molecules in solution behave as compact spheres with minimal interaction until the concentration is high enough to reach the noninteraction fractional volume limit. Typical linear polysaccharides have more open solution structures that interpenetrate as concentration is increased. These interpenetrations act as labile cross-links, which cause the molecules to act as if their molecular size is much larger.

At low concentrations, both GA and mesquite gum solutions show identical rheological behavior. At higher concentrations, where intermolecular contacts occur, GA solutions exhibit more intermolecular interaction. This is attributed to the disproportionate contribution of the AGP fraction to solution rheology. Although the AGP fraction constitutes only ~10% of the total mass, its much larger hydrodynamic volume dominates the solution behavior at high concentrations.

Dror and others (2006) studied the structure of GA in aqueous solution using a combination of neutron scattering, x-ray diffraction, and transmission electron microscopy in frozen solution. Compact spheroidal structures with diameters that appear to be less than 10 nm were observed. They determined that the electrostatic interaction between the ionized structures in solution maintains the distance between the GA spheres. They contrasted the stabilizing properties of GA to those of AG isolated from larch wood. The larch AG does not exhibit surfactant behavior, has fewer uronic acid groups, and is also devoid of protein (Dror and others 2006).

A study of aqueous solutions of the AG component using small angle neutron scattering and cryo-transmission electron microscopy concluded that the AG molecule is a thin oblate ellipsoid in solution (Sanchez and others 2008). It was difficult for us to follow this argument, which attempts to fit models to the neutron scattering data. It appears that a spherical shape provides a better fit to the data. Further support for the thin disk model from electron microscopy appears to be tainted by excessive manipulation of the image data.

The relationship between molecular structure and the formation of viscous gels for some polysaccharides has been described (Rinaudo 2001). The polysaccharides discussed are very different in composition from those of GA. Galactomannans (plant carbohydrates) have a linear molecular structure, which can form gel networks at high concentration by intermolecular hydrogen bonds. Gellan and κ-carrageenan are bacterial polysaccharides that adopt a helical conformation in solution, which results in high viscosity. The helical conformation is melted at higher temperature resulting in a low solution viscosity. Another important factor is the presence of polyvalent cations, e.g., calcium, which can serve as cross-links between polysaccharides with an anionic charge.

Natural Product Variation

GA is an exudate from Acacia trees that are under stress. To a good approximation, GA consists of the three major components previously discussed: AGP, AG, and GP; however, the amounts of each component are variable. Studies show that there is variation in composition both from tree to tree and between commercial suppliers.

As an example, eight GA nodules (exudate sites on the tree) from different *A. senegal* trees were examined by gel permeation chromatography, solution viscosity, light scattering, and optical rotation (Vandevelde and Fenyo 1985). In examining this study from the general composition previously described, it is apparent that there is considerable variation in the proportions of AGP to AG from tree to tree. In some cases, there was sufficient material to isolate fractions by preparative chromatography and to characterize the fractions. It was observed that optical rotation for AGP and AG fractions would be nearly the same, –30 degrees. This is because the sugar portion of these components is the same. However, there should be different values for intrinsic viscosity and nitrogen content because the molecular

weights and protein contents of the components are different.

Six commercial GA samples were compared with authenticated samples of *Acacia senegal* and *Acacia seyal* (Osman and others 1993). Specific polarized light optical rotation, sugar composition, nitrogen and amino acid content, and molecular mass distribution were measured. The amounts of AGP and AG varied inversely among the samples, i.e., if AGP was particularly high then AG would be low. The sugar composition, amino acid composition, specific rotation, and nitrogen content among the *Acacia s.* samples were very similar (except for one sample that had about three times more nitrogen). An immunoassay was examined as a test for GA; however, the immunoassay was much more responsive to the GP component than to the important AGP component.

Sixty-seven commercial GA samples from eight different suppliers were compared using a set of five fully authenticated *A. senegal* var. *senegal* samples and an unprocessed sample (Al-Assaf and others 2005). Gel permeation chromatography coupled to a multi-angle light scattering detector, a refractive index detector, and a UV detector operated at 214 nm were used to characterize these materials. Extensive variation was found among the samples, and 15 were outside of the selected normal distribution. Some variation was suspected of being caused by processing methods (spray drying) or blending with a higher molecular weight variant of *A. senegal* var. *karensis*.

Some properties of more than 1,500 GA samples from 32 different areas of Sudan were measured (Karamalla and others 1998). About half of the samples were from individual trees (authentic samples), and the other half were commercial samples. The data obtained indicate the following average values: moisture (10.8%), ash (3.8%), nitrogen (0.33%), specific rotation (–31.3°), pH (4.66), equivalent weight (1,436 Daltons), and total uronic acid content (13.7%), with modest variation about these values. The authors observed wide variation in intrinsic viscosity, the resulting viscosity, and average molecular weight and concluded that these variations preclude using these parameters as a useful specification. This may have been self-serving since the study was conducted by the University of Khartoum and supported by the Gum Arabic Company and Khartoum Gum Arabic Processing Company. In fact, as mentioned, the variation in intrinsic viscosity appears to be related to the relative abundance of AGP, which is often the active component.

In summary, the extensive literature has shown that much can be learned about GA composition and properties, but the natural variability limits even sophisticated methods from providing clear conclusions. Although this information is useful in understanding more about GA, these methods tend to be too sophisticated for normal product testing and none give any indication of how they perform as a binder in the primers.

Super Gum™

One result from examining the characteristics of GA from *Acacia senegal* trees of different ages was an observation that the proportion of high molecular weight component—apparently AGP—increased with the age of the tree (Idris and others 1998). Subsequently, it was discovered that this aging effect could be mimicked by a heat treatment process (Al-Assaf and others 2007; Aoki and others 2007a, 2007b; Cui and others 2007; Pickles and others 2007; Phillips and others 2008). A patent was obtained for this process (Al-Assaf and others 2004).

This maturation process consists of heating GA at 110 °C for several hours. Gel permeation chromatograms show the difference for various GAs that were heated for different lengths of time. These illustrated a gain in high molecular weight fraction which elutes first and an associated decrease in the lower molecular weight fractions. The previously mentioned studies attribute this to the formation of more AGP component from GP and AG species.

Matured GA is available as a commercial product. There are two product lines: Acacia (sen) SUPER GUM™, which is matured GA from *Acacia senegal* trees, and Acacia (sey) SUPER GUM™, which is matured GA from *Acacia seyal* trees (San-Ei Gen F.F.I., Inc., Osaka, Japan).

The mechanism suggested by some authors of the previously mentioned studies does not seem accurate because they indicate that there is no chemical change involved in the maturation process. It appears that there is some rearrangement of components and formation of super-molecular aggregates that are sufficiently tenacious to remain intact in solution. The components that elute in the sharp first peak of the gel permeation chromatograph are large species, which do not fit within the pores of the column packing. There is no size discrimination for this component; i.e., everything that is larger than the pore size is excluded. There could easily be several different species contained in this fraction. This calls into question the conclusion suggested in the previously mentioned studies that this peak represents only AGP species. It is more likely that various aggregates composed of AG and GP species with AGP are formed by the maturation process. This model is illustrated in Figure 1-4, in which digestion to remove the protein with portease shows similar results.

The SUPER GUM™ products appeared to have better performance as emulsifiers than the unprocessed GA from which they were derived (Aoki and others 2007b). Because the experimental evidence links better adhesive strength with a greater amount of AGP fraction, such products might perform better as primer binders as well.

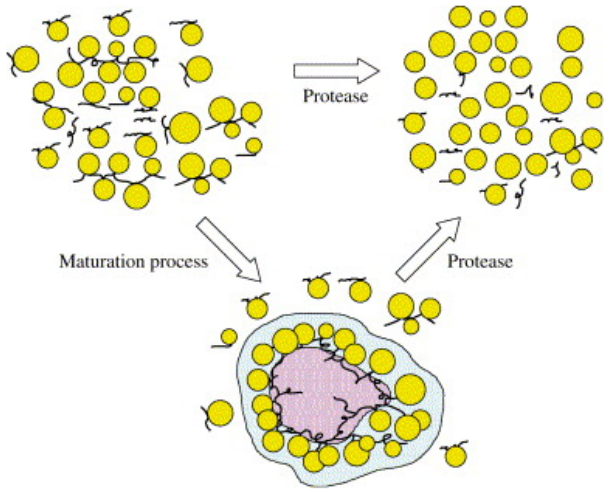

Figure 1-4. A suggested model for the super-molecular aggregation formed by the maturation process (Used with permission of Elsevier Science & Technology Journals, from Aoki and others (2007a); permission conveyed through Copyright Clearance Center, Inc.).

This suggests that heating GA in the solid state promotes mobility of the components, allowing aggregation to occur. It is not clear whether there is a sharp initiation point for this reaction. There is indication that treatment at lower temperatures for longer amounts of time also results in "maturation". It is reasonable to assume that maturation could be produced in manufacturing or laboratory heat treatments of GA. Simply drying samples overnight in an oven should increase the amount of molecular association, which could result in surprising variations in performance.

Although the improved surfactant properties and the higher molecular weight could improve binder properties, no work has been done in this area.

Understanding Related to Binders

Although this information is useful for understanding the composition and structure of GA samples, along with their interaction with hydrophobic materials, it does not directly relate to the binder application. In fact, despite the numerous studies on characterizing the chemistry, morphology, and surfactant properties of GA, no information could be found on either binder or adhesive properties. The carbohydrate components may play more of a role in bonding the explosives because these tend to be more polar than the proteins, and carbohydrates are often used as binders. Although these literature characterization methods are useful in understanding GA, they are too technically complicated to provide useful improved product specifications.

Literature Cited

Al-Assaf, S.; Phillips, G.O.; Williams, P.A. 2005. Studies on acacia exudates gums. Part I: the molecular weight of *Acacia senegal* gum exudates. Food Hydrocolloids. 19(4): 647-660. https://doi.org/10.1016/j.foodhyd.2004.09.002.

Al-Assaf, S.; Phillips, G.O.; Aoki, H.; Sasaki, Y. 2007. Characterization and properties of *Acacia senegal* (L.) Willd. var. *senegal* with enhanced properties [Acacia (*sen*) SUPER GUM™]: Part 1—Controlled maturation of *Acacia senegal* var. *senegal* to increase viscoelasticity, produce a hydrogel form and convert a poor into a good emulsifier. Food Hydrocolloids. 21: 319-328. https://doi.org/10.1016/j.foodhyd.2006.04.011.

Al-Assaf, S.; Phillips, G.O.; Sasaki, Y.; Katayama, T. 2004. Modified gum arabic. WO/2004/089991. https://patentscope.wipo.int/search/en/detail.jsf?docId=WO2004089991.

Anderson, D.M.W.; Hirst, E.; Stoddart, J.F. 1966. Studies on uronic acid materials. Part XVII. Some structural features of *Acacia senegal* gum (gum arabic). Journal of the Chemical Society C. 1959-1966. https://doi.org/10.1039/j39660001959.

Aoki, H.; Al-Assaf, S.; Katayama, T.; Phillips, G.O. 2007a. Characterization and properties of *Acacia senegal* (L.) Willd. var. *senegal* with enhanced properties (Acacia (*sen*) SUPER GUM™): Part 2—Mechanism of the maturation process. Food Hydrocolloids. 21(3): 329-337. https://doi.org/10.1016/j.foodhyd.2006.04.002.

Aoki, H.; Katayama, T.; Ogasawara, T.; Sasaki, Y.; Al-Assaf, S.; Phillips, G.O. 2007b. Characterization and properties of *Acacia senegal* (L.) Willd. var. *senegal* with enhanced properties (Acacia (*sen*) SUPER GUM™): Part 5—Factors affecting the emulsification of *Acacia senegal* and Acacia (*sen*) SUPER GUM™. Food Hydrocolloids. 21(3): 353-358. https://doi.org/10.1016/j.foodhyd.2006.04.014.

Connolly, S.; Fenyo, J.C.; Vandevelde, M.C. 1987. Heterogeneity and homogeneity of an arabinogalactan-protein: *Acacia senegal* gum. Food Hydrocolloids. 1: 477-480. https://doi.org/10.1016/S0268-005X(87)80045-0.

Connolly, S.; Fenyo, J.C.; Vandevelde, M.C. 1988. Effect of a proteinase on the macromolecular distribution of *Acacia senegal* gum. Carbohydrate Polymers. 8: 23-32. https://doi.org/10.1016/0144-8617(88)90033-1.

Cui, S.W.; Phillips, G.O.; Blackwell, B.; Nikiforuk, J. 2007. Characterisation and properties of *Acacia senegal* (L.) Willd. var. *senegal* with enhanced properties (Acacia (*sen*) SUPER GUM™): Part 4—Spectroscopic characterisation of *Acacia senegal* var. *senegal* and Acacia (*sen*) SUPER GUM™ arabic. Food Hydrocolloids. 21(3): 347-352. https://doi.org/10.1016/j.foodhyd.2006.05.009.

Dror, Y.; Cohen, Y.; Yerushalmi-Rozen, R. 2006. Structure of gum arabic in aqueous solution. Journal of Polymer Science Part B: Polymer Physics. 44(22): 3265-3271. https://doi.org/10.1002/polb.20970.

Fincher, G.B.; Stone, B.A.; Clarke, A.E. 1983. Arabinogalactan-proteins: structure, biosynthesis, and function. Annual Review of Plant Physiology. 34: 47-70. https://doi.org/10.1146/annurev.pp.34.060183.000403.

Goycoolea, F.M.; Morris, E.R., Richardson, R.K.; Bell, A.E. 1995. Solution rheology of mesquite gum in comparison with gum arabic. Carbohydrate Polymers. 27(1): 37-45. https://doi.org/10.1016/0144-8617(95)00031-2.

Idris, O.H.M.; Williams, P.A.; Phillips G.O. 1998. Characterisation of gum from *Acacia senegal* trees of different age and location using multidetection gel permeation chromatography. Food Hydrocolloids. 12(4): 379-388. https://doi.org/10.1016/S0268-005X(98)00058-7.

Islam, A.M.; Phillips, G.O.; Sljivo, A.; Snowden, M.J.; Williams, P.A. 1997. A review of recent developments on the regulatory, structural and functional aspects of gum arabic. Food Hydrocolloids. 11(4): 493-505. https://doi.org/10.1016/S0268-005X(97)80048-3.

Karamalla, K.A.; Siddig, N.E.; Osman, M.E. 1998. Analytical data for *Acacia senegal* var. *senegal* gum samples collected between 1993 and 1995 from Sudan. Food Hydrocolloids. 12(4): 373-378. https://doi.org/10.1016/S0268-005X(98)00005-8.

Li, X.; Fang, Y.; Al-Assaf, S.; Phillips, G.O.; Nishinari, K.; Zhang, H. 2009. Rheological study of gum arabic solutions: Interpretation based on molecular self-association. Food Hydrocolloids. 23(8): 2394-2402. https://doi.org/10.1016/j.foodhyd.2009.06.018.

Mahendran, T.; Williams, P.A.; Phillips, G.O.; Al-Assaf, S.; Baldwin, T.C. 2008. New insights into the structural characteristics of the arabinogalactan-protein (AGP) fraction of gum arabic. Journal of Agricultural and Food Chemistry. 56(19): 9269-9276. https://doi.org/10.1021/jf800849a.

Morris, E.R. 1990. Shear-thinning of 'random coil' polysaccharides: characterisation by two parameters from a simple linear plot. Carbohydrate Polymers. 13(1): 85-96. https://doi.org/10.1016/0144-8617(90)90053-U.

Morris, E.R.; Cutler, A.N.; Ross-Murphy, S.B.; Rees, D.A.; Price, J. 1981. Concentration and shear rate dependence of viscosity in random coil polysaccharide solutions. Carbohydrate Polymers. 1(1): 5-21. https://doi.org/10.1016/0144-8617(81)90011-4.

Osman, M.E.; Williams, P.A.; Menzies, A.R.; Phillips, G.O. 1993. Characterization of commercial samples of gum arabic. Journal of Agricultural and Food Chemistry. 41(1): 71-77. https://doi.org/10.1021/jf00025a016.

Phillips, G.O.; Ogasawara, T.; Ushida, K. 2008. The regulatory and scientific approach to defining gum arabic (*Acacia Senegal and Acacia seyal*) as a dietary fibre. Food Hydrocolloids. 22(1): 24-35. https://doi.org/10.1016/j.foodhyd.2006.12.016.

Pickles, N.A.; Aoki, H.; Al-Assaf, S.; Sakata, M.; Ogasawara, T.; Ireland, H.E.; Coleman, R.C.; Phillips, G.O.; Williams, J.H.H. 2007. Characterization and properties of *Acacia senegal* (L.) Willd. var. *senegal* with enhanced properties [Acacia (sen) SUPER GUM™]: Part 3—Immunological characterisation of Acacia (sen) SUPER GUM™. Food Hydrocolloids. 21(3): 338-346. https://doi.org/10.1016/j.foodhyd.2006.06.005.

Randall, R.C.; Phillips, G.O.; Williams, P.A. 1988. The role of the proteinaceous component on the emulsifying properties of gum arabic. Food Hydrocolloids. 2: 131-140. https://doi.org/10.1016/S0268-005X(88)80011-0.

Randall, R.C.; Phillips, G.O.; Williams, P.A. 1989. Fractionation and characterization of gum from *Acacia senegal*. Food Hydrocolloids. 3(1): 65-75. https://doi.org/10.1016/S0268-005X(89)80034-7.

Renard, D.; Lavenant-Gourgeon, L.; Ralet, M.C.; Sanchez, C. 2006. *Acacia senegal* gum: continuum of molecular species differing by their protein to sugar ratio, molecular weight, and charges. Biomacromolecules. 7(9): 2637-2649. https://doi.org/10.1021/bm060145j.

Rinaudo, M. 2001. Relation between the molecular structure of some polysaccharides and original properties in sol and gel states. Food Hydrocolloids. 15(4-6): 433-440. https://doi.org/10.1016/S0268-005X(01)00041-8.

Sanchez, C.; Schmitt, C.; Kolodziejczyk, E.; Lapp, A.; Gaillard, C.; Renard, D. 2008. The acacia gum arabinogalactan fraction is a thin oblate ellipsoid: a new model based on small-angle neutron scattering and ab initio calculation. Biophysical Journal. 94(2): 629-639. https://doi.org/10.1529/biophysj.107.109124.

Showalter, A.M. 2001. Arabinogalactan-proteins: structure, expression and function. Cellular and Molecular Life Sciences. 58: 1399-1417. https://doi.org/10.1007/PL00000784.

Snowden, M.J.; Phillips, G.O.; Williams, P.A. 1987. Functional characteristics of gum arabic. Food Hydrocolloids. 1(4): 291-300. https://doi.org/10.1016/S0268-005X(87)80017-6.

Swenson, H.A.; Kaustinen, H.M.; Kaustinen, O.A.; Thompson, N.S. 1968. Structure of gum arabic and its configuration in solution. Journal of Polymer Science Part A-2: Polymer Physics. 6(9): 1593-1606. https://doi.org/10.1002/pol.1968.160060904.

Tryfona, T.; Liang, H.-C.; Kotake, T.; Tsumuraya, Y.; Stephens, E.; Dupree, P. 2012. Structural characterization of arabidopsis leaf arabinogalactan polysaccharides. Plant Physiology. 160(2): 653-666. https://doi.org/10.1104/pp.112.202309.

Vandevelde, M.C.; Fenyo, J.C. 1985. Macromolecular distribution of *Acacia senegal* gum (gum arabic) by size-exclusion chromatography. Carbohydrate Polymers. 5(4): 251-273. https://doi.org/10.1016/0144-8617(85)90034-7.

Yadav, M.P.; Igartuburu, J.M.; Yan, Y.; Nothnagel, E.A. 2007. Chemical investigation of the structural basis of the emulsifying activity of gum arabic. Food Hydrocolloids. 21(2): 297-308. https://doi.org/10.1016/j.foodhyd.2006.05.001.

Chapter Two
Characterization of Three Gum Arabics

As part of the Phase One program to establish improved specifications for gum arabic (GA), the USDA Forest Service, Forest Products Laboratory (FPL) characterized the properties of three different commercial GAs. Since this project began, we have learned much more about GA by gathering and analyzing literature (see Chapter One). The food uses of GA have been the driving force for many of these investigations. Although a few of these applications have some relevance to the use of GA as a binder in primer formulation, many do not. This is because food applications typically involve surfactant properties in aqueous solutions, whereas binder performance mainly involves solid state adhesion performance. Analysis of this literature transformed what was initially just a list of possible new test methods into a series of tests that are more interrelated, with some directly related to performance criteria. The characterizations of GA in this section fall into two main classes: those that measure a physical property and those that relate to GA chemical composition. It should be noted that the chemical composition influences the physical properties, as indicated in Chapter One.

For most of these analyses, the Colony and Hummel GA products were very similar. However, there were differences in the apparent viscosity measurements, dry particle sizes, and dissolution rates. In contrast, the Brenntag (Quadra) GA is quite different in several of the analysis methods because it is a gum sourced from Eritrea, whereas the other two products were sourced from Chad. However, in some cases, the Brenntag was similar to the Colony in cases where the Hummel was different. Some of these differences could very well relate to the performance of the GA as a binder, but this evaluation was not part of the Phase One program and the binder test was not developed until much later in the program (see Chapter 6, which also contains information on the current pellet manufacturing process).

Overall Perspective

The work reported in this chapter was performed in Phase One of the project to understand how the samples from several GA sources differed in properties. The goal was to select analytical measurements that would identify simple property differences between GA batches that performed well as primer binders and GA batches that were more problematic. Unfortunately, we did not have an explicitly "bad batch" compared with a "good batch" from the same manufacturer; thus, we had to surmise the effect of different analysis on actual performance. These measurements could then lead to improved product specifications. As is true with the current specifications for GA, most of these additional tests related to the general properties and purity of the material and not to specific performance criteria for the binder application. However, the differences between the GAs from the three producers in most of these tests should help determine which factors may be used as additional specification criteria. In addition, knowing the process used in mixing the primer ingredients and what is expected of the binder can also help to understand which tests may be more significant.

Although GA appears to form a clear solution when mixed in water, both the literature and our observations clearly indicate that it forms a dispersion in water. This is because the gum is suspended as droplets that are so fine that they scatter only a very small amount of visible light. This provides aqueous dispersions with low viscosity. Several data indicate that there are significant changes in these dispersions between one and three days after mixing, as illustrated in the subsequent section Rotational Apparent Viscosity using a Brookfield Viscometer, which is a procedure that is used in the commercial approval process.

To perform as a binder, the GA must have specific properties for both the mixing step and the final dry state. In the mixing step, the gum dispersion needs to be well distributed among the wet solid particles of the reactive chemicals and the gum molecules need to contact these reactive particles at the molecular level in order to work well as a binder. In addition, this dispersion needs to have sufficiently low viscosity at high solids to incorporate as much GA as possible in the wet primer formulation, which needs to bond all the primer components as the primer dries during many months of ambient storage, which can entail wide variations in temperature depending on location. Thus, potentially important properties of GA for the binder application are likely to be dispersion viscosity and surfactant properties because the gum needs to rapidly distribute among the other materials under the mild agitation of the blending process.

Differences were observed in the apparent viscosity, but at this point, there is not enough information to know if these differences relate to actual performance. The Hummel gum had a high apparent viscosity under very low shear conditions. This high viscosity in both Brookfield and fluid rheometer measurements may reflect large domains in the dispersion, which result in greater domain–domain interaction. This in turn could reflect interaction of dispersion particles or higher molecular weight components. This high viscosity may inhibit the gum's ability to evenly

distribute in the mixing step. There did not seem to be large differences in the surface wetting properties. For the final dry state, the gum needs to bond the particles together sufficiently so that the primer pellets do not fracture to create dust, which has been considered a possible reason for misfiring. In the preliminary adhesive tests that we developed, we did not see any large differences. However, the Hummel material exhibited slightly higher bonding strength in the peel test, which again could be a reflection of either higher molecular weight or higher protein content.

All tests were done in a blind manner in that the analyst did not know the source of each sample. These additional tests fell outside of the standard GA qualification testing, but evaluation of the literature helped define the procedures that we used in some cases. In other cases, completely new tests had to be developed based on our past experiences. In any case, tests selected for the next phase may need to be investigated more thoroughly to establish a procedure more closely related to actual performance needs. Particle size of the dispersion droplets was not part of the program due to lack of appropriate equipment but could be part of future analyses.

Physical Properties

Sample Specification Analysis

The first step was to evaluate the GA samples that we received from GA suppliers that have been used commercially and had been evaluated at U.S. Army Armament Research Development and Engineering Center (ARDEC) to make sure that they met the standard specification (Appendix A). Secondary testing involved obtaining some additional information on the characteristics of the solids (Appendix B). The detailed procedures and data are given in these appendices.

From these data, we learned that the GA samples from the three suppliers met the standards with only minor differences. However, the extra tests on the materials indicated that the Colony had the smallest particle size, and in the scanning electron microscopy images, it looked as though it had been pulverized. The Quadra and Hummel had larger particle sizes than the Colony and were mainly spherical, almost as if they were spray-dried. What was confusing from these data was that the surface area analysis was opposite of what would be expected by the particle size and scanning electron microscopy data.

Rotational Apparent Viscosity using a Brookfield Viscometer

Alliant Techsystems Inc. (Arlington, Virginia, USA) (ATK) performed some standard Brookfield rotational apparent viscosity studies of GA and observed some unusual phenomena in the time and temperature dependences (ATK 2006). The FPL work plan was to measure the viscosities of the six samples using 40% solid dispersions on the third day after the initial mixing, as is used in normal plant qualification testing. We decided to add a measurement at one day after mixing to determine if any time-dependent changes in the apparent viscosity existed. The measurements were done using a Brookfield rotational LVT viscometer (AMETEK Brookfield, Inc., Middleboro, Massachusetts, USA) with a #3 spindle at 25 °C and 60 rpm for 5.5 min after beginning agitation in the viscometer. The prior ATK studies were done using similar conditions except that a #4 spindle was used to measure 48% solid dispersions at 21 °C. It was noted in the ATK studies that this temperature was hard to control. The current data are given in Table 2-1 using GA-1 to GA-6 as the blind sample labels in our work.

Of note is that the Hummel tests demonstrated higher one-day apparent viscosities for our sample compared with the two Colony samples, Brenntag sample, and Quadra sample. All samples showed an apparent viscosity drop between the one-day and three-day measurements. We wondered if the entrapped air from the original mixing of the powdered samples led to the high one-day apparent viscosities and if the degassing during the next two days of sitting led to the decrease or whether it was just better dispersion over time. The surfactant properties of the GA and the high apparent viscosities would slow the deaeration of the samples. To determine if the entrapped air led to the higher one-day apparent viscosities, a sample of the Colony (GA-1) was dissolved in water. After a half hour of mixing, the apparent viscosity was 1,426 centipoise in the Brookfield viscometer and 1,260 centipoise after 30 seconds of agitation in the cup. This sample was then transferred to a beaker and degassed in an aspirator vacuum for 2 hours. The apparent viscosity of the sample increased after degassing, with 1,654 and 1,398 centipoise for the immediate and 30-second viscosities, respectively. Thus, because the deaeration raised the apparent viscosity, it was rejected as an explanation for the drop in viscosities between the one- and three-day measurements. We also added studies of the pH effect on the measured viscosities and found that the apparent viscosity was insensitive to pH between 3.5 and 9.8.

Table 2-1—One- and three-day apparent viscosities of gum arabic (GA) samples at 25 °C

	Apparent viscosity (centipoise)[a]	
Gum arabic sample	1-day	3-day
Colony (current) (GA-1)	1,170	818
Colony (prior) (GA-4)	1,174	782
Hummel (current) (GA-6)	1,456	921
Hummel (repeat) (GA-2)	1,486	886
Brenntag (GA-3)	1,104	944
Quadra (GA-5)	1,142	750

[a]The pooled standard deviation was ±25 centipoise.

These results may be explained by changes in the distribution of the GA components over time. Although the GA appears to form a solution, most of the material is dispersed as a colloid. The size of these particles and the molecules on the particle surfaces can take time to reach an equilibrium state. This unusual Brookfield viscosity behavior supported our original plan to use more sophisticated rheological techniques. Although the Brookfield is widely used laboratory equipment for measuring viscosity, it does not provide an understanding of the properties of non-Newtonian (flow dependent on shear rate) systems. The use of a fluid rheometer to provide a better understanding of the rheology is discussed in the next section.

Rotational Viscosity using a Fluid Rheometer

The plans for more sophisticated rheological measurements changed from the original proposal because the GA dispersions were much more complicated than originally anticipated. The original plan was to use an oscillatory rheometer to look at both the flow and elastic properties of the GA dispersions, but given their non-Newtonian behavior, we felt a rotational shear method with emphasis on shear rate was more important in relation to end use. The rheometer that we used was a TA Instruments (New Castle, Delaware, USA) AR1000 unit operated under controlled shear rate that allowed us to control the shear rate for many decades. FPL did not have such a unit, so this work was contracted out to Arizona Chemical in Savannah, Georgia, USA. Because the dispersion forms a structure after sitting for long periods that is removed by mixing, the samples needed to be presheared prior to analysis to obtain the desired data. In Figure 2-1, the viscosity curves are shown for samples GA-1 to GA-6. The viscosity and shear rates were plotted as the log values, which caused the ranges to be a lot wider than they seem.

The most important observation is that the Hummel material (GA-2 and GA-6) had a much higher viscosity at the low shear rates than the Colony (GA-1 and GA-4), Brenntag (GA-3), and Quadra (GA-5) samples. This is important for the binder application because the high viscosity of the Hummel GA may limit its ability to distribute evenly when mixing with the explosive components because the mixing is low shear. In addition, this result was repeatable with the only Hummel sample that we had. This high viscosity may be a reflection of higher molecular weight components or greater protein content and could lead to poor distribution of GA in the pellet. Conversely, the higher molecular weight could result in better bond strength for holding the primer pellet together. Obviously, more testing needs to be done. In general, the Colony, Brenntag, and Quadra samples were unusual because they showed both shear thickening and shear thinning depending on the shear rate. The complex behavior of GA dispersions has been discussed in the literature (Sanchez and others 2002).

With the observed viscosity measurements and the literature data, there is ample evidence that more studies on the rheological properties could be done. However, the literature has indicated that the measurement of these properties is not very straightforward. Surface tension properties can also interfere with the rheological determinations (Sanchez and others 2002).

Moisture Adsorption of Dried Gum Arabic

Moisture absorption of the GA could lead to its inconsistent charging because the current protocol does not correct for the moisture content of the GA. Thus, it is valuable to understand the hydroscopic nature of the gum samples. The method selected for this determination was to dry the GA samples in an oven, then to spread them in a thin layer in a weighing dish that was placed in a room at 22 °C and 42% relative humidity. The weight was measured at different

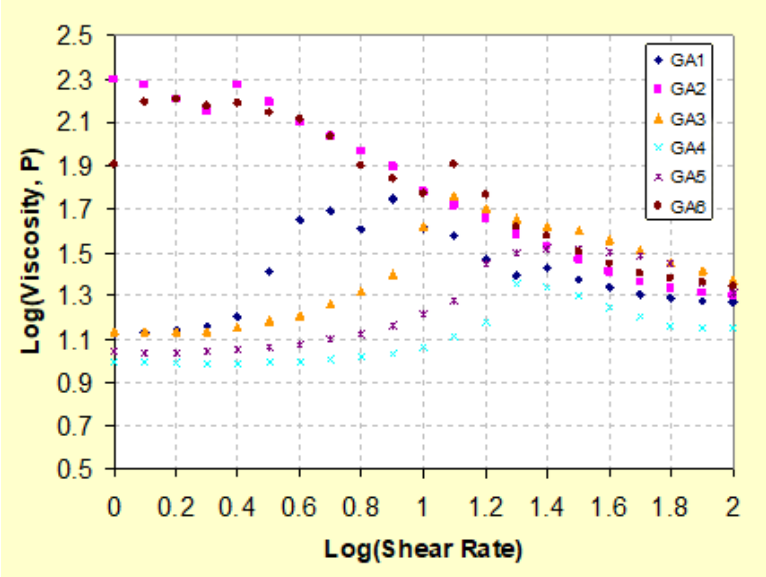

Figure 2-1. Gum arabic (GA) rheology (42% solids) of log viscosity versus log of shear rate for the different gum arabics.

times, and the increase in weight was plotted against time (Fig. 2-2).

The weight gain was much higher for the Colony gum (GA-1 and GA-4) than for the other gums. This may have been caused by the higher surface areas for Colony based on its fine and more irregular surface area (ARDEC 2007) compared with the other samples, rather than any great difference in the chemical hydrophilicity of the different GA samples themselves. Because the weight gain was rapid initially before leveling off changes in moisture content during normal handling apparently are not an issue. However, the difference between Colony and other gums could cause a little bit less binder being present if the moisture content is not taken into consideration.

Rate of Dissolution

Another area of concern is that the different GAs vary in their rate of being dissolved in water. The rate of dissolution of the GA was carried out by adding 100 mL of deionized water to 17.5 g of the gum sample in a 250-mL beaker. The samples were gently stirred using a magnetic stir bar and a stir plate. Aliquots were removed at 0.5, 1.0, 1.5, 2.0, 3.0, 5.0, 22.0, 23.0, and 24.0 hours to measure their refractive index (RI). RI was used to have an intensive property compared with a strictly visual observation. The RI values generally had a maximum value before a small decline. The complete dissolution of the gum was obtained by determining when the RI value had virtually leveled off or had reached a maximum. These times and the maximum RI values are given in Table 2-2.

An example of the dissolution data is given in Figure 2-3 for the Colony sample GA-1 with the value at zero hours being the RI of the water.

The rate of dissolution did not provide any likely differences among the gum samples. The dissimilarities were small after the first half hour, and we could not assess if suspended insolubles and gas bubbles may have interfered with the measurements. Visual determination of the dissolution during these tests was also done, and the results are discussed in the Color Analysis section.

Table 2-2—Changes in refractive index (RI) to measure solution rate in 22 °C water of gum arabic (GA) samples

Sample	Time (hours)		Maximum value of RI
	Virtual	Max in RI	
Colony (current) (GA-1)	1.5	3	1.3680
Colony (prior) (GA-4)	1	1	1.3700
Hummel (current) (GA-6)	1	1	1.3700
Hummel (repeat) (GA-2)	1.5	3	1.3706
Brenntag (GA-3)	1	1	1.3721
Quadra (GA-5)	0.5	0.5	1.3720

Optical Rotation

Organic compounds of the same formulation, especially those from natural sources, can have different attachment of atoms in such a way that they can differ in the degree that they rotate polarized light. Thus, a pure single compound may have a defined degree of rotation. The light rotation of a sucrose solution in water depends on the purity of the sucrose and the solution concentration. Addition of other carbohydrates will alter the optical rotation of the solution. For a long time, optical rotation was used as a measure of purity of natural materials, including GA. For our tests, we used a Perkin-Elmer (Beaconsfield, Buckinghamshire, England) Model 141 polarimeter with a 589-nm lamp and 10-mm-length cell at 20 °C. Sucrose solutions of different concentrations in distilled water were measured as a control. The optical rotations of the gums were measured at 2% and 10% concentration. The polarimeter values in Table 2-3 show that the Hummel and Colony material were similar but the Brenntag and Quadra had very different values. We

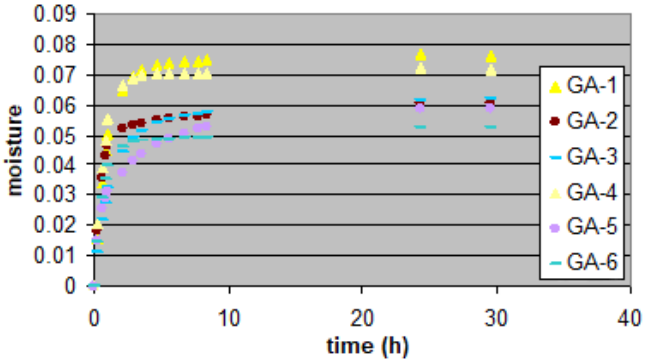

Figure 2-2. Normalized moisture (weight) gain of oven-dried gum arabic (GA) at 42% relative humidity at 22 °C.

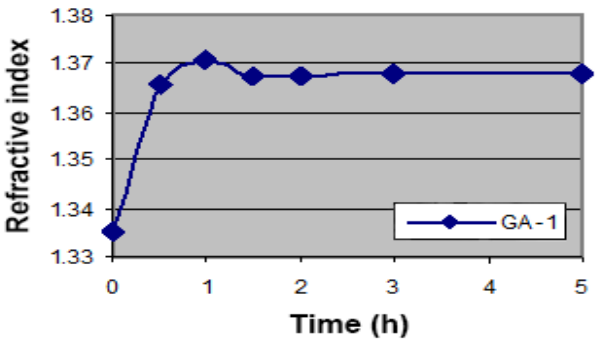

Figure 2-3. Changes in refractive index to measure solution rate in 22 °C water.

attribute this to the fact that Brenntag and Quadra are *Acacia seyal* gums, whereas the other two are *Acacia senegal* gums. Although the optical rotation values have been long used as a purity criterion, we agree with Anderson and others (1991) that blending of different gums or additives could lead to the target optical rotation without indicating purity. Anderson and others have proposed using a nuclear magnetic resonance spectroscopy method as a better alternative for measuring purity. This is covered in the subsequent section Nuclear Magnetic Resonance Spectroscopic Analysis within the following Chemical Properties discussion.

Surface Tension by Contact Angle

The ability of a liquid to wet a surface is important for many processes, including adhesive bonding. A standard way to determine the ability of a liquid to wet or flow over a surface is to place a drop on a flat surface and measure the angle between the surface and the droplet with respect to air: the lower the contact angle (θ_c), the better the wetting (Fig. 2-4). The polarity properties of both the surface and the liquid influence this angle.

After testing a number of variables, we established a method using a pocket goniometer and dynamic absorption tester unit (Fibro System, Capelle a/d Ijssel, the Netherlands) with 10-µL drops of solution (20% GA in water) dropped onto an unpolished aluminum surface. The contact angle for each sample was measured five times and the average is presented in Table 2-4. As a control, two samples of water had contact angle values of 78.3 and 78.5 degrees.

Given the large variability in the measurements, there were no significant differences among the gum dispersions. It was interesting that the Colony and Hummel samples decreased in contact angle whereas the Brenntag and Quadra increased in contact angle between the data measured one day after mixing and the data measured three days after mixing.

Adhesion Tests – Shear

With the gum as the binder holding the other particles together in the primer, an adhesion test should be an

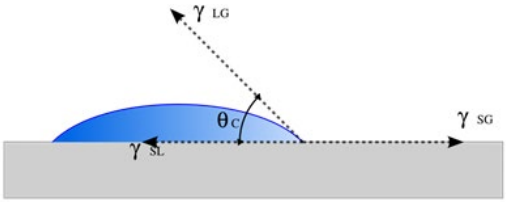

Figure 2-4. Abbreviations used in describing contact angles for a drop on a flat, level surface.

important performance measure. A number of methods were examined because we were unable to find any information in the literature on the testing of GA adhesion or any appropriate standard adhesion method used for any similar materials. We ended up using two very different methods to evaluate the overall bond strength. This first test was aimed at examining differences in cohesive strength of the GA samples, and the second test was aimed more at adhesive strength. For both cases, at least one of the substrates in the test needed to be porous for drawing the water away from the bondline to produce a solid GA film for adhesive testing.

A common way to test adhesive strength is to do a shear test in which two pieces of the substrate are bonded at the sections of both pieces that overlap. The shear test involves pulling on the unbonded ends of each piece with increasing force until either the bond or the substrate fails. For this lap shear test, the substrates should be stiff. To have stiff, easily bonded, and moisture-absorbing substrates, pairs of rectangular pieces of maple veneer (2.0 by 11.7 cm and 0.08 cm thick) were used. They were bonded with a small overlap (0.5 cm) giving a bonded area of one square centimeter. About 0.02 g of a 40% GA dispersion was applied to an end of one of the pieces. The samples were bonded under two conditions: 120 °C for 2 min and 23 °C for 10 min. Both conditions were placed under 9.1 kg/cm pressure. The samples were then stored overnight, and the strength was tested by pulling on the ends of the bonded specimens. The strength of the bond was measured as an average of three specimens. As shown in Figure 2-5, there was not a large difference among the samples for each of the

Table 2-3—Optical rotation of gum arabic (GA) samples with a 589-nm lamp and 10-mm-long cell at 20 °C

	Optical rotation (deg)	
Sample	2% concentration	10% concentration
Colony (current) (GA-1)	–0.60	–3.20
Colony (prior) (GA-4)	–0.51	–3.14
Hummel (current) (GA-6)	–0.55	–2.90
Hummel (repeat) (GA-2)	–0.57	–3.14
Brenntag (GA-3)	0.85	4.55
Quadra (GA-5)	1.00	4.74

Table 2-4—Contact angle in degrees at ambient temperature for the three gum arabics (GA)

	Contact angle (deg)	
Sample	1-day	3-day
Colony (current) (GA-1)	78.6	68.5
Colony (prior) (GA-4)	71.7	66.2
Hummel (current) (GA-6)	72.1	69.5
Hummel (repeat) (GA-2)	81.1	72.6
Brenntag (GA-3)	68.0	76.0
Quadra (GA-5)	64.7	69.3

two methods, although the lowest strengths were for the Brenntag (G-3) and Quadra (GA-5) samples. We also observed greater strengths for the room temperature bonds compared with the hot bonding method.

The good development of strength across a wide temperature range shows that the binder has sufficient cohesive strength to help form a strong matrix and is unlikely to be the reason for the pellet dusting after storage. However, a wood surface is quite different from the explosive materials used in primer pellets.

Adhesion Tests – Peel

In addition to the shear test used to determine the cohesive strength of the adhesive, we also wanted to use a peel test to measure the strength of the adhesive to the substrate because it applies a different type of force on the bond. Again, we needed one substrate to be porous to allow the water in the GA dispersion to be drawn away from the bondline. Thus, using wood as one of the substrates made sense. We tried several other materials as the second substrate, including white office paper, glassine, and Tyvek (DuPont, Wilmington, Delaware, USA) (a type of flashspun high-density polyethylene fiber). The bond strength was so great that white office paper and glassine tore before we observed failure in the bondline. Conversely, the Tyvek was strong enough to give us bondline failure. The bonds were made by applying 0.21 g of a 40% GA dispersion to a rectangular piece of wood (2.0 by 11.7 cm and 0.08 cm thick). A piece of Tyvek was then placed on the surface leaving about 1 cm unbonded on one end, and 500 g of weight was placed on the assembly. The sample was then left overnight. We examined several angles and rates of peel before settling on 180° and 1.52 m/min pulling on the unbonded portion of the Tyvek toward the bonded section. This procedure was then used for all six samples (Table 2-5). The wood sides of the samples were bonded to a metal plate using double-sided tape and tested using a peel tester (model TL-2200, IMASS, Inc., Accord, Massachusetts, USA). The results were analyzed with IMASS peel software v0-9c.

The results show that the Hummel had greater peel strengths than the other samples, although for any future testing, we would probably test more specimens to improve the repeatability. The Brenntag adhesive had the lowest results in both adhesive strength and cohesive strength. Again, higher bond strength may reflect greater concentration of high molecular weight components and/or higher protein content since either of these qualities is consistent with bond strength. However, these tests used an adhesive film, whereas the actual use is more of a spot weld of particles. Of greater importance is that we did not find at that time any way to test bonded surfaces that represented the actual chemical composition of the particles being bonded in the primer application.

Color Analysis

Color measurements are often used as a measure of purity. Especially with a white-colored material, even small amounts of impurity readily show up in the solid form and even more so in the dispersion. However, it should be remembered that any colored impurity may be a very small amount of the product and may play no role in the performance of the product.

The ultraviolet (UV)-visible spectra from 200 to 1,000 nm were measured for each of the samples. The graphs for the three main samples from each supplier are shown in Figure 2-6. The Brenntag and Quadra gums were distinctive in having higher relative absorbance of the light above 240 nm. All GA samples had a main peak in the 210- to 220-nm range, which is normal for carbonyl-containing organics, and the gums contained both organic acids and proteins. The greater absorbance at the longer wavelengths gave the Brenntag gum dispersions a distinctive light yellowish color. The spectra shown in Figure 2-6 are for samples at 30 wt% dispersions measured on a U-3010 spectrophotometer (Hitachi, Ltd., Chiyoda, Tokyo, Japan).

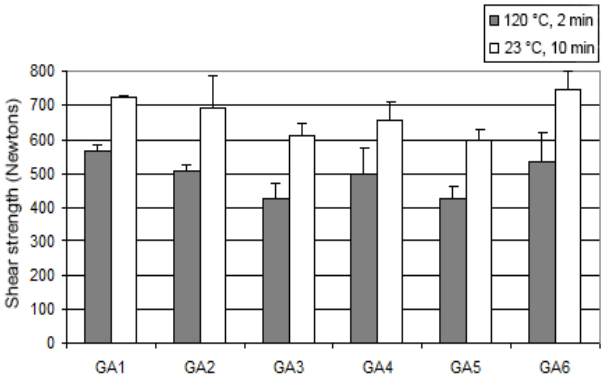

Figure 2-5. Automated bonding evaluation system (ABES) shear strength dry after bonding under two different conditions for the three gum arabics (GA).

Table 2-5—Peel force of gum arabic (GA) in Newtons of Tyvek bonded to wood peeled at 180° and 1.52 m/min at ambient temperature

	Peel force (N)	
Sample	Average	Standard deviation
Colony (current) (GA-1)	2.6	0.2
Colony (prior) (GA-4)	2.9	0.5
Hummel (current) (GA-6)	3.7	0.3
Hummel (repeat) (GA-2)	3.1	0.4
Brenntag (GA-3)	2.3	0.2
Quadra (GA-5)	2.6	0.3

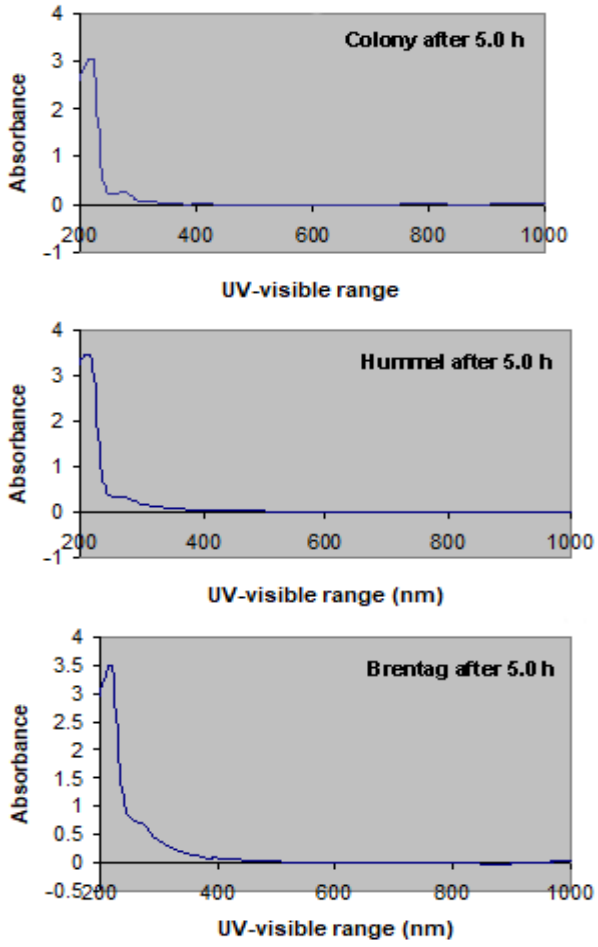

Figure 2-6. Ultraviolet (UV) absorbance of the three gum arabics as 30 wt% aqueous solutions.

The Colony and Hummel were very similar in the UV-visible spectra, with the main absorbance being around 220 nm, which is typical for organic acids. On the other hand, the Brenntag/Quadra had increased absorbance in the 300- to 400-nm range that would indicate other compounds being present.

Although not part of the original plan, we also recorded the visual appearance of the samples when we were doing the dissolution experiments as described in the section Rate of Dissolution. It was interesting that two operators could tell one pair of samples from the other two pairs on the basis of visual appearance of the dispersions. The observed yellowness of the Brenntag and Quadra dispersion is illustrated in the UV-visible spectra in Figure 2-6, and the insolubles of the Hummel dispersions were darker than that for the Colony dispersions. The Colony showed a translucent, cloudy, gel-like behavior. The Hummel and Brenntag–Quadra formed a more opaque, chalky-like mixture. This may relate to the particle size in the dispersions, but this determination was not part of the original study plan.

Chemical Properties

Compositional Analysis

Although the composition of GA is mainly polysaccharides, there are also protein components that have been shown to be important to its surfactant properties, as discussed in Chapter One. Thus, the analysis of the nitrogen content is more informative than the carbon and hydrogen content in that it relates to the protein content of the GA. We had the samples analyzed at the USDA Agricultural Research Service Dairy Forage Research Center using a varioMAX (Elementar Analysensysteme GmbH, Langenselbold, Germany) with each sample run in duplicate as indicated in Table 2-6. This equipment uses the Dumas protein method, which is different from that used by the ATK analyzer but is a different chemistry from the Kjedahl method.

Carbon, hydrogen, and nitrogen analysis was done by ATK. Elemental analysis for carbon, hydrogen, and nitrogen was performed on a PerkinElmer 2400 series II CHNS/O Analyzer (PerkinElmer, Inc., Waltham, Massachusetts, USA) with each sample being analyzed six times (Tanner 2007). Although the absolute values given in Tables 2-6 and 2-7 differ between the two methods, both supported a lower

Table 2-6—Nitrogen content using the Dumas protein method with a varioMAX with each sample being run in duplicate

Sample	Nitrogen content (%)	Standard deviation
Colony (current) (GA-1)	0.3743	0.0082
Colony (prior) (GA-4)	0.3452	0.0014
Hummel (current) (GA-6)	0.3887	0.0017
Hummel (repeat) (GA-2)	0.3954	0.0000
Brenntag (GA-3)	0.1661	0.0041
Quadra (GA-5)	0.1608	0.0040

Table 2-7—Carbon, hydrogen, and nitrogen content on a PerkinElmer 2400 series II CHNS/O analyzer with each sample being run six times

Supplier	Element	Average ± 2 standard deviation
Hummel	Carbon	39.64 ± 0.14
Brenntag	Carbon	40.82 ± 0.10
Colony	Carbon	38.38 ±0 .16
Hummel	Hydrogen	6.22 ± 0.10
Brenntag	Hydrogen	5.97 ± 0.10
Colony	Hydrogen	6.26 ± 0.30
Hummel	Nitrogen	0.60 ± 0.06
Brenntag	Nitrogen	0.43 ± 0.08
Colony	Nitrogen	0.54 ± 0.06

nitrogen content for the Brenntag gum and a slightly higher nitrogen (protein) content in the Hummel sample with the nitrogen content reflecting differences in the protein content.

Molecular Weight by Gel Permeation Chromatography

The molecular weights (MW) of the gum components were investigated because the higher MW portion tends to contain most of the protein–carbohydrate component (Randall and others 1989). These proteins are often considered to positively influence the surface-active properties (Jayme and others 1999). The different components of GA can be separated by MW using gel permeation chromatography (GPC), as discussed in Chapter One. Although several methods have been used, the procedure of Osman and others (1993) seemed to be the most useful. The use of a UV detector with GPC gave a relative distribution of the different MW components that was close to that obtained using a multi-angle light scattering detector compared with using a refractive index detector (Al-Assaf and others 2007). This is somewhat surprising because the UV detector is more specific for proteins, whereas a refractive index is a more general detector of organic materials. The GPC method was used with an Agilent 1100 HPLC system (Agilent Technologies, Inc., Santa Clara, California, USA). The GA dispersions (1% w/v dry wt) in 0.5 *M* NaCl were filtered through 0.45-nm membrane filters before injecting 100 µL with the autosampler onto a Superose 6 column (GE Healthcare Bio-Sciences Corp, Piscataway, New Jersey, USA). The samples were eluted with 0.5 *M* NaCl at a flow rate of 0.5 mL/min and monitored by UV at 206 nm.

Figure 2-7 shows GPC chromatograms of two Colony (GA-1 and GA-4), Brenntag (GA-3), Quadra (GA-5), and two Hummel (GA-2 and GA-6) samples.

Table 2-8 contains the areas of the peaks as a percentage of the total sample. The areas were calculated by the HP ChemStation integrator, which is part of the Agilent 1100 system. The three peaks that eluted in the first 30 min correspond with the three major fractions determined by Osman and others (1993). These three fractions were added together to give the high molecular weight (HMW) total. As shown in the HMW column in the table, the samples were separated into two groups, those with an HMW total above 73% and those below 73%. The remaining peaks eluted after 40 min, which corresponded with an MW below 14 kD. These lower MW peaks were not found in any of the samples analyzed by Osman and others (1993). The samples analyzed by Osman and others and reported on in 1993 were in a kibbled or nodule form. Perhaps our samples, which were in a powdered form, contained lower-weight fractions because of having been processed more extensively.

We observed that the two Colony GA samples (GA-1 and GA-4) showed slightly different MW distributions from each other but that the Brenntag (GA-3) and Quadra (GA-5) were quite different from the Colony GA-4 and Hummel (GA-2 and GA-6) samples. The Hummel sample had more HMW components than the other GA samples. This factor could be underlying the high viscosity and peel strength results for the Hummel GA.

Infrared Spectroscopy

The GA samples were examined by infrared spectroscopy because these spectra can be sensitive to the chemical composition of certain functional groups. The spectra of carbohydrates are rather complex and tend to be similar because different carbohydrates usually contain the same numbers of the same functional groups.

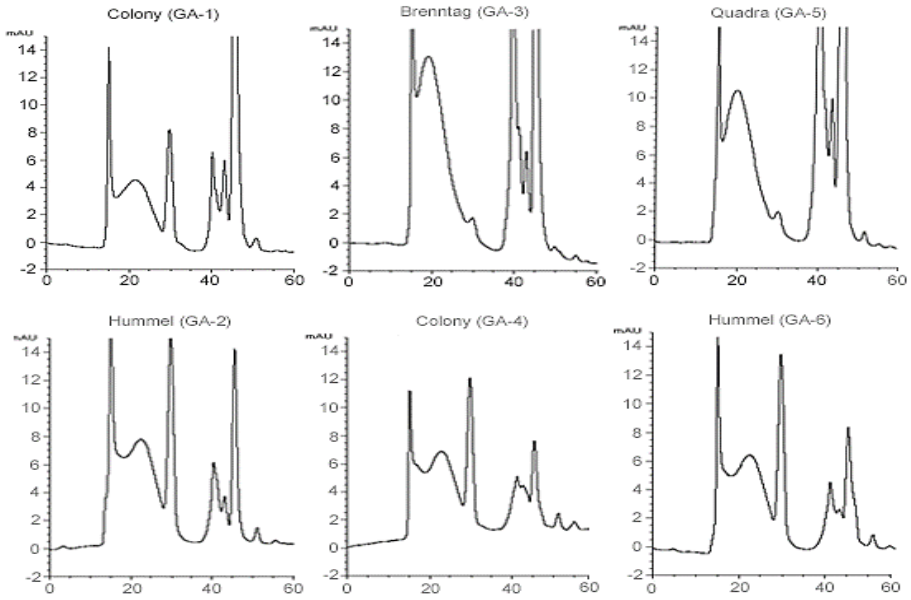

Figure 2-7. Gel permeation chromatography method using an Agilent 1100 HPLC system (Agilent Technologies, Inc., Santa Clara, California, USA) with an ultraviolet (UV) detector at 206 nm for the gum arabics (GA).

Table 2-8—The areas of the peaks at different elution times as a percentage of the total sample for the gum arabic (GA) samples[a]

	Areas of peaks at different elution times (%)							
Sample	15.1 min	21.7 min	29.8 min	40.1 min	43.0 min	45.5 min	50.9 min	High molecular weight total (<29.8)
Colony (GA-1)	10.6	28.7	11.0	10.2	6.9	31.3	0.9	50.3
Brenntag (GA-3)	10.5	43.0	3.2	18.2	4.0	19.7	0.9	56.7
Quadra (GA-5)	6.8	33.0	2.8	21.7	5.1	29.6	0.7	42.6
Hummel (GA-2)	27.8	31.2	15.4	8.7	3.1	11.3	1.3	74.4
Colony (GA-4)	19.6	36.2	17.6	8.8	5.5	9.5	1.7	73.4
Hummel (GA-6)	19.6	37.7	17.6	8.3	3.0	12.2	1.3	74.9

[a]For reference, Osman and others (1993) determined the following molecular weights: 1,450,000 (10.4 wt%) for arabinogalactan-protein (AGP), 279,000 (88.4 wt%) for arabinogalactan (AG), and 250,000 (1.0 wt%) for glycoprotein (GP).

The infrared spectra of the six samples are very similar. To test this, the spectrum of each sample was overlapped with that of the Hummel (GA-2) (Fig. 2-8). The spectral intensities were matched at 1435 cm^{-1}. This absorbance band is largely attributed to skeletal motions of the carbon rings, CH and CH_2 wagging motions, all of which should be relatively common among the samples. The largest mismatch was observed between the Colony (GA-1) and the Hummel (GA-2) (Fig. 2-8). This is judged to be a small difference, which is mainly attributable to C–O vibrations in the 1670-1820 cm^{-1} range (Fig. 2-8). These peaks may be related to the carboxylic acid content but could also be attributed to the protein functional groups. The peaks in the 1000 to 1200 cm^{-1} range are due to many absorptions but particularly to the C–O stretch of the alcohols.

Nuclear Magnetic Resonance Spectroscopic Analysis

Concern about the purity of GA for food uses has led to extensive research on identifying the quality of these gums. Of the methods examined, Anderson and others (1991) recommended the use of ^{13}C nuclear magnetic resonance spectroscopy (^{13}C NMR) as the most powerful method for measuring purity. Many of the other methods either are too dependent on the specific gum source or cannot distinguish between the pure GA and blends of different gums. For example, blends of gums can be used to match the optical rotation of the pure gum. However, the ^{13}C NMR can provide semiquantitative analysis of the carbohydrates in the gum, which is likely to detect adulteration. This method is fairly rapid and effective because each type of gum has different types and ratios of carbohydrate segments that make up the carbohydrate polymers. It is virtually impossible to make blends of gums that will match the NMR spectra for GA, and thus to make a fake or adulterated GA.

The procedure described by Anderson and others (1991) was followed for this project. The GA samples (GA-1 to GA-6) were analyzed via NMR using a 10% dispersion of each sample in D_2O. The NMR parameters were kept constant for all samples with some variation in the number of scans because of attempts to equalize signal-to-noise for all samples. All spectra were run on the FPL Bruker

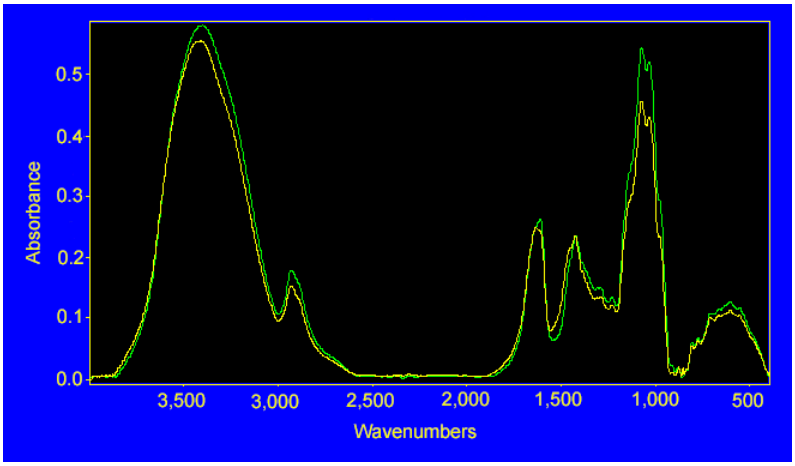

Figure 2-8. Overlap of infrared spectrum of GA-1 (Colony) and GA-2 (Hummel) to show representative similarity of absorptions.

250-MHz NMR spectrometer (Bruker Corporation, Billerica, Massachusetts, USA) at room temperature. For reference, 5 µL of a mixture of 1,3-^{13}C-acetone in D_2O was added. Thus, all ^{13}C spectra were referenced to the 1,3-^{13}C-acetone singlet at 30.56 ppm. There appeared to be two structurally different gums; GA-1, 2, 4, and 6 were very similar, whereas GA-3 and 5 were very similar to each other but different from the other GAs. The two groups differed in every region, including carbonyls, anomerics, and aliphatics. GA-1, 2, 4, and 6 showed identical peaks with slight variation between some peak intensities. Figure 2-9 is an overlay of GA-1 (Colony), 6 (Hummel), and 3 (Brenntag). Again, the Colony and Hummel GAs were from *Acacia senegal*, whereas Brenntag and Quadra (GA-3 and GA-5) were from *Acacia seyal*. From the NMR analysis, we can confirm that these two distinct *Acacia* spp. trees showed different gum exudate polysaccharide types and quantities (Fig. 2-9). The most appreciable differences among the GA samples from *A. senegal* and *A. seyal* were visualized in the polysaccharide anomeric region. For example, the anomeric region for *A. senegal* GA samples showed two arabinan peaks (108-110 ppm), with a set of three galactan peaks (103-104 ppm) and two sharp rhamnan peaks (100-102 ppm) compared with the *A. seyal* GA samples, which showed a single arabinan peak (110 ppm), a complex set of galactan peaks (97-105 ppm), and weaker rhamnan peaks (100-102 ppm). The uronic acid carbonyl peaks showed distinct differences as well, with the *A. senegal* GA samples having a single peak at 175 ppm compared with the *A. seyal* GA samples having multiple peaks between 175 and 181 ppm. The individual ^{13}C spectra of all the samples are given in Figure 2-10. This NMR method is very specific and informative, but the cost of the equipment is high and requires an experienced operator.

Carbohydrate Analysis

Sugar and total carbohydrates were measured using a standard FPL wood sugar procedure (Petterson and others 1984). Vacuum-dried GA samples were hydrolyzed in a 72% sulfuric acid solution and then diluted with distilled water. A fructose internal standard was added, and samples were hydrolyzed again by heating the diluted samples (to about 100 °C) in an autoclave. Samples were allowed to reach room temperature and aliquoted for analysis by ion chromatography (IC). IC samples were measured by pulsed amperometric detection (PAD) and measured against an internal standard curve. Sugar values are reported in Table 2-9 as a percentage of the dried GA samples. Total carbohydrate percent is the additive value of the five measured sugars.

Sugar analysis indicated somewhat similar composition in the major sugars detected (arabinose, galactose, and rhamnose) for the Colony and Hummel samples. The Brenntag and Quadra samples (GA-3 and GA-5) contained significantly lower levels of rhamnose and higher amounts of arabinose compared with the other four GA samples. Total carbohydrate amounts were similar in all samples. As noted previously, Colony and Hummel GAs were sourced from *Acacia senegal*, whereas Brenntag and Quadra (GA-3 and GA-5) were sourced from *Acacia seyal*. Thus, these results illustrate the sensitivity of sugar analysis as a means of identifying the source of GA.

Uronic Acid Content

One specific sugar of interest is uronic acid because organic acid groups on this sugar may play a role along with the divalent metals in causing cross-links between the chains. Uronic acids were measured by a method reported by Bitter and Muir (1962) often referred to as “the carbazole method” in the literature. The vacuum oven-dried GA samples were

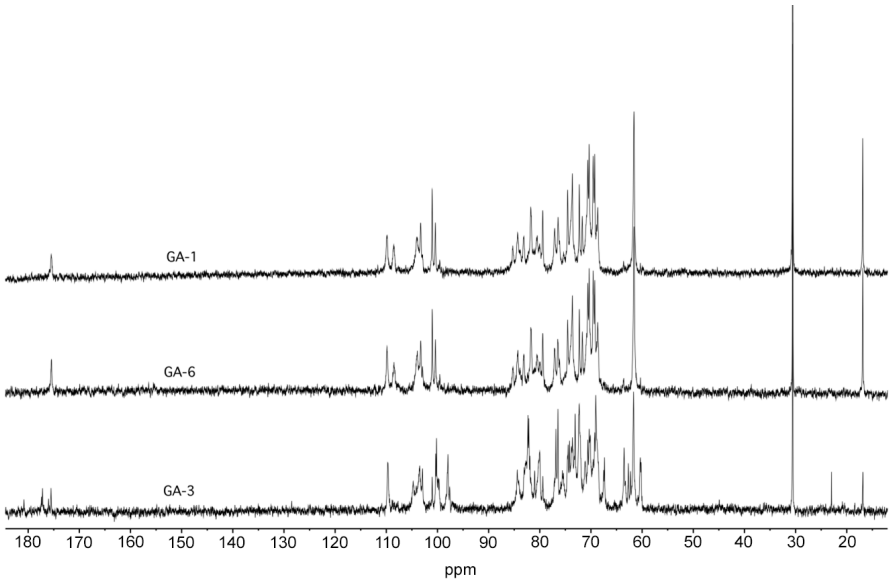

Figure 2-9. Overlay of ^{13}C spectra of GA-1 (Colony), GA-6 (Hummel), and GA-3 (Brenntag) gum arabic (GA) samples in D_2O showing the differences in the nuclear magnetic resonance spectra when the different tree species from different countries are used for preparing the GA.

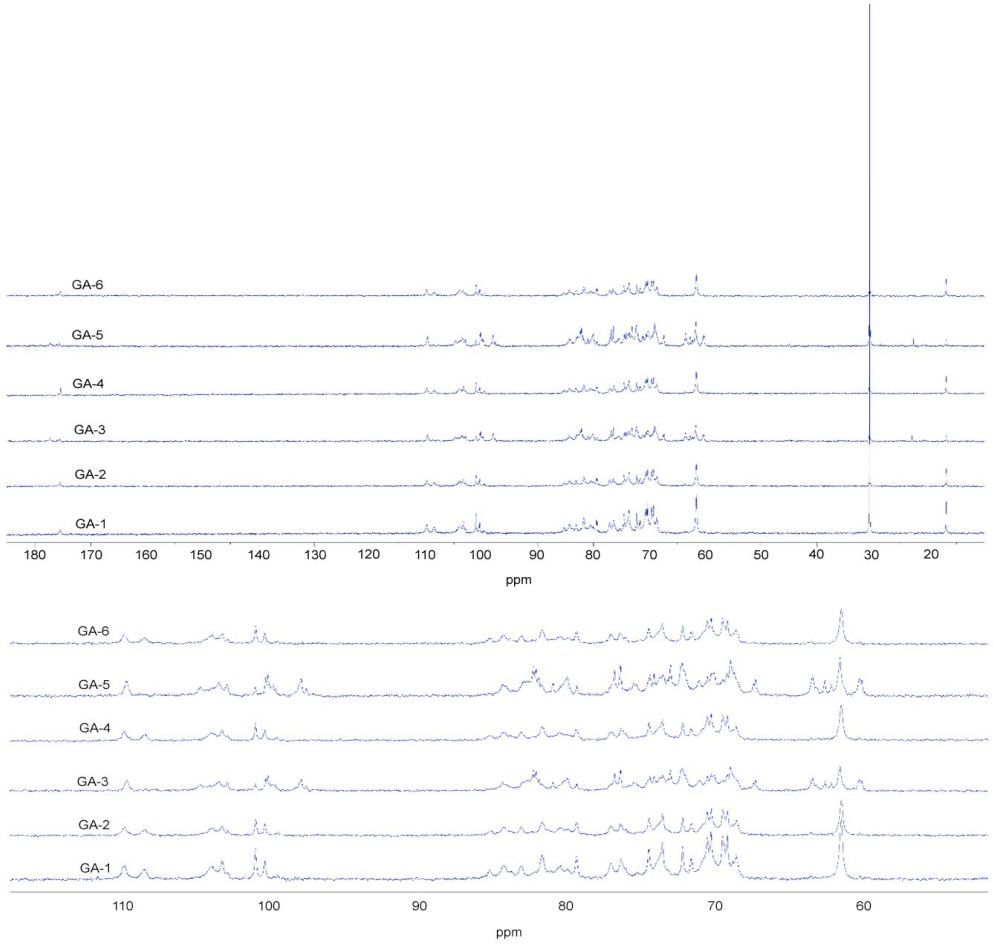

Figure 2-10. The ^{13}C spectra of each gum arabic (GA) sample in D_2O.

dissolved in distilled water (10% wt./vol.). Samples were aliquoted and digested for 10 min (at 100 °C) in a sodium tetraborate–sulfuric acid solution in a heating block. Carbazole reagent was added, and the samples were heated for another 15 min in the heating block and allowed to cool to room temperature. Sample absorbances were read at 530 nm in a UV-visible spectrophotometer. Glucuronic acid standards (10 through 100 ppm) were prepared identically to the GA samples and measured on the UV-vis to quantify total uronic acid concentrations. Uronic acid values (expressed as weight percentage) are reported in Table 2-10. There were no significant differences in uronic acid levels in the six GA samples analyzed by the carbazole method. Values ranged from 1.8% to 2.1%.

Metals Analysis

Gum arabic is a complex calcium, magnesium, and potassium salt of arabic acid (Colony Gums 2020). Metal contents of the gums can be important to their performance because the metal ions can influence the interactions

Table 2-9—USDA Forest Service, Forest Products Laboratory wood sugar analysis of the six gum arabic (GA) samples measured as percentage against a fructose standard

Sample	Arabinan (%)	Galactan (%)	Rhamnan (%)	Glucan (%)	Xylan (%)	Mannan (%)	Total carbon (%)
GA-1 (Colony)	24.4	38.1	10.1	nd[a]	0.0	nd	72.6
GA-2 (Hummel)	24.9	38.6	11.1	nd	0.0	nd	74.7
GA-3 (Brenntag)	33.3	35.5	2.8	0.03	0.1	nd	71.7
GA-4 (Colony)	24.3	38.0	10.9	nd	nd	nd	73.2
GA-5 (Quadra)	34.7	36.6	2.4	nd	0.0	nd	73.6
GA-6 (Hummel)	24.4	37.9	10.9	nd	0.1	nd	73.3
Standard deviation of assay	0.0	0.1	0.0	0.4	0.1	0.2	0.6

[a]nd, none detected.

Table 2-10—Uronic acid (UA) content of gum arabic (GA) samples as measured with the carbazole method

Sample	Total UA recovered (mg)	Total dried GA wt. (mg)	UA (%)
GA-1 (Colony)	3.5	189.7	1.8
GA-2 (Hummel)	3.3	186.4	1.8
GA-3 (Brenntag)	3.9	185.2	2.1
GA-4 (Colony)	3.2	155.8	2.0
GA-5 (Quadra)	3.8	189.8	2.0
GA-6 (Hummel)	3.5	185.4	1.9

between chains. Monovalent metal salts, such as sodium (Na) and potassium (K), do not promote interchain interactions. However, divalent and trivalent metal salts probably tie the chains together. The data using inductively coupled plasma optical emission spectroscopy for the gums is given in Table 2-11.

As with many of the other tests, the Colony and Hummel samples provided very similar results for the concentrations of the metals. But the measured metals were different for the Brenntag and Quadra compared with the Colony and Hummel samples. The types and amounts of metal ions appear to be related to the species of tree from which the GA is harvested.

Summary

It would be instructive to revisit these measurements after evaluating these GA samples as adhesives in the inert model system (Chapter 6). There, we found that the Hummel GA was superior to the other two as a binder.

The physical property that distinguishes the Hummel GA from the others is its greater amount of arabinogalactan-protein (AGP) fraction. This accounts for the high viscosity at low shear rate as well as the shear thinning rheology. The presence of this larger AGP fraction could also lead to better adhesive performance compared with the other GAs. Either the high MW or the presence of protein, or both, could lead to its improved adhesion compared with the Colony, Quadra, or Brenntag GAs. The food and beverage industry prizes the AGP component of GA for colloid stabilization. The largely hydrophobic protein portion, which is attached to the very hydrophilic carbohydrate, appears to act as a macromolecular surfactant.

The following measurements were found to be the most effective in distinguishing the differences in the three GAs. Gel permeation chromatography isolated and quantified the GA components. Brookfield and rotational viscosity were effective in demonstrating the presence of high MW species by their effect on rheology. Finally, the shear force and peel force measurements directly demonstrated the difference in adhesion strength.

Some measurements appeared to be very effective in differentiating between GA from different tree species. These include NMR spectroscopy, sugar analysis, and optical rotation, all of which differentiated on the basis of inherent molecular characteristics. Some measurements showed differences but were based on coincidental characteristics. These include elemental analysis (which quantified metal counter ions), nitrogen content (which was mostly due to different amounts of protein), and solution color (which may not be a reliable characteristic). However, all of these either show no difference or would be difficult to relate to binder performance.

Literature Cited

Al-Assaf, S.; Phillips, G.O.; Aoki, H.; Sasaki, Y. 2007. Characterization and properties of *Acacia senegal* (L.) Willd. var. *senegal* with enhanced properties (Acacia (*sen*) SUPER GUM™): Part 1—controlled maturation of *Acacia senegal* var. *senegal* to increase viscoelasticity, produce a hydrogel form and convert a poor into a good emulsifier. Food Hydrocolloids. 21(3): 319-328. https://doi.org/10.1016/j.foodhyd.2006.04.011.

Anderson, D.M.W.; Millar, J.R.A.; Weiping, W. 1991. Gum arabic (*Acacia senegal*): unambiguous identification by ^{13}C-NMR spectroscopy as an adjunct to the revised JECFA specification, and the application of ^{13}C-NMR spectra for regulatory/legislative purposes. Food Additives & Contaminants. 8(4): 405-421. https://doi.org/10.1080/02652039109373991.

ARDEC. 2007. Material analysis on three gum arabic samples. U.S. Army, Armament Research, Development, and Engineering Center, Pyrotechnic Research & Technology Branch.

Table 2-11—Elemental concentration of different metal ions in the six gum arabic (GA) samples analyzed

Sample	Elemental concentration (mg/g)					
	Al	Ca	Cu	K	Mg	Na
Colony (current) (GA-1)	0.009	7.84	0.004	6.79	2.29	0.01
Colony (prior) (GA-4)	0.005	6.45	0.002	6.92	2.83	0.01
Hummel (current) (GA-6)	0.009	7.09	0.002	6.77	2.52	0.41
Hummel (repeat) (GA-2)	0.004	7.46	0.002	6.89	2.65	0.41
Brenntag (GA-3)	0.038	11.05	0.003	2.31	1.82	5.23
Quadra (GA-5)	0.041	10.52	0.002	2.04	1.85	5.74

ATK. 2006. Confidential report on primer mix binder study. Lake City, MO: Alliant Techsystems.

Bitter, T.; Muir, H.M. 1962, A modified uronic acid carbazole reaction. Analytical Biochemistry. 4(4): 330-334. https://doi.org/10.1016/0003-2697(62)90095-7.

Colony Gums. 2020. Gum arabic. https://glass.imgix.net/c642d8c6-f857-4d0b-8833-56ac63a0a81e/b9/2c/b92c040eb7804e31857e22b3956c2e2b-COLONYGUMS_GUM_ARABIC.pdf. Monroe, NC: Colony Gums. (Dec. 15, 2020).

Jayme, M.L.; Dunstan, D.E.; Gee, M.L. 1999. Zeta potentials of gum arabic stabilised oil in water emulsions. Food Hydrocolloids. 13(6): 459-465. https://doi.org/10.1016/s0268-005x(99)00029-6.

Osman, M.E.; Williams, P.A.; Menzies, A.R.; Phillips, G.O. 1993. Characterization of commercial samples of gum arabic. Journal of Agricultural and Food Chemistry. 41(1): 71-77. https://doi.org/10.1021/jf00025a016.

Pettersen, R.C.; Schwandt, V.H.; Effland, M.J. 1984. An analysis of the wood sugar assay using HPLC: a comparison with paper chromatography. Journal of Chromatographic Science. 22(11): 478-484. https://doi.org/10.1093/chromsci/22.11.478.

Randall, R.C.; Philips, G.O.; Williams, P.A. 1989. Fractionation and characterization of gum from *Acacia senegal*. Food Hydrocolloids. 3(1): 65-75. https://doi.org/10.1016/s0268-005x(89)80034-7.

Sanchez, C.; Renard, D.; Robert, P.; Schmitt, C.; Lefebvre, J. 2002. Structure and rheological properties of acacia gum dispersions. Food Hydrocolloids. 16(3): 257-267. https://doi.org/10.1016/s0268-005x(01)00096-0.

Tanner, R. 2007. Elemental analysis for carbon, hydrogen and nitrogen. Internal Alliant Techsystems memo to R. Blau, September 28, 2007.

Chapter Three
Structure and Rheology

In trying to develop a better understanding of the different gum arabic (GA) samples, we combined the literature information with our data and the likely mechanisms for using GA as a binder. A binder needs to distribute well to adhere to the other materials. Thus, in this chapter, we investigated the known structure and the related rheology of GA and found that these probably contributed to the binder effectiveness.

Introduction

Solution properties are important for the primer binder for two main reasons. The first is that the binder needs to have a high solids content because the wet pellets need to be stiff to maintain the pellet shape and they need to only minimally shrink when they are air-dried. The explosive ingredients are kept wet during processing for safety reasons, which adds additional water to the pellet. The second is that, because mixing of the binder with the explosive ingredients is done with low energy mixing, the binder solution needs to be of low viscosity to be well dispersed in the mixture under these conditions.

Most carbohydrates are linear in structure or have limited short branches. These molecules adopt a random coil configuration in solution (Witten and Pincus 2004). The volume that random coils occupy in solution depends on the square root of the degree of polymerization. Thus, typical high molecular weight (MW) carbohydrates in solution exhibit high viscosity because molecular entanglements occur even at relatively low concentrations. These entanglements act like momentary crosslinks, which cause molecules to behave like larger molecules (Fig. 3-1). Mobility is compounded when carbohydrates are dissolved in water because the many hydroxyl groups on the sugar monomers interact with the water through hydrogen bonds. This is commonly experienced in the slow pouring of syrups. Even carbohydrates with branched structure, such as starches, form viscous solutions at low concentration (ca. ~5%). Dextrins (low MW starch derivatives) exhibit appreciable viscosity at low concentration in water.

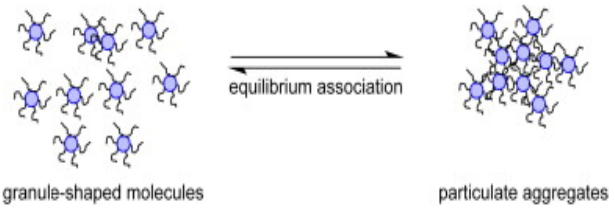

Figure 3-1. Aggregation of glycoproteins (Reprinted from Li and others (2009), with permission from Elsevier. https://www.sciencedirect.com/journal/food-hydrocolloids).

The structure and rheological behavior of GA is unusual among high MW carbohydrates. GA solutions in water do not exhibit high viscosity until about 30% concentration by weight. This is because GA is a mixture of protein bound carbohydrates with a highly branched structure that adopts a very compact form in water solution.

Rheology

The solution behavior of several GA samples was measured using a Brookfield viscometer (AMETEK Brookfield, Inc., Middleboro, Massachusetts, USA) as described in Chapter Two - Characterization of Three Gum Arabics. Some differences in initial viscosity were observed, which became smaller with time (Fig. 3-2). More distinct differences were observed using a TA Instruments AR1000 rheometer (TA Instruments, New Castle, Delaware, USA), which measures viscosity as a function of shear rate also using a cup and spindle design but with a much wider shear range than is possible with a Brookfield viscometer. The Hummel GA showed a distinctly different viscosity–shear rate relationship than did the Colony and Brenntag or Quadra GA samples. The high viscosity of the Hummel GA is not due to a problem in over-mixing because shear thickening usually involves log shear rate values greater than 1.

The solution viscosity can be related to differences found in MW distribution of these GA samples as determined by gel permeation chromatography. The Hummel GA samples had the largest fraction of high MW components, whereas Brenntag and Quadra GA samples had the smallest fraction of high MW components. The high viscosity measurements at low shear of the Hummel samples would indicate that wet binder pellets made with it would be more cohesive after they are formed into pellets than the other GA samples.

Molecular Weight Distribution

An ultraviolet detector was used to monitor the output from these gel permeation chromatograms. It was highly sensitive to the protein portion of the molecules and less sensitive to the carbohydrate branches, which constitute most of the GA. Therefore, the chromatograms are not a direct representation of the composition of the samples but give an approximation of the weight percent distribution of the major GA components as indicated in Table 3-1. This approximation is based on a graphical integration of the ultraviolet and refractive index traces for a typical GA gel permeation

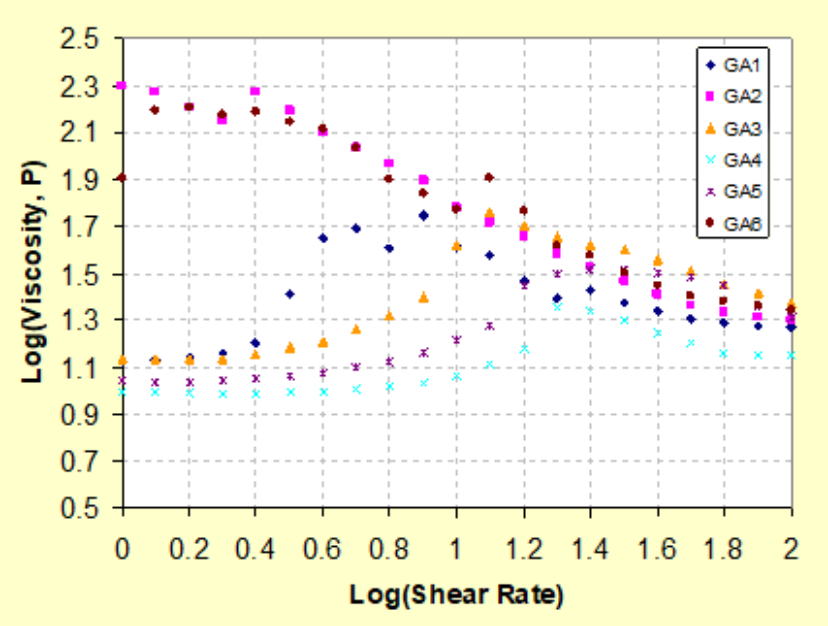

Figure 3-2. Solution rheology at high solids (42%). Brenntag (GA-3), Colony (GA-1 and GA-4), Hummel (GA-2 and GA-6), Quadra (GA-5).

chromatograph (Phillips 2009) to convert the ultraviolet signal to an approximate refractive index signal. The refractive index is a better indication of the mass distribution. These conversions were then applied to the graphically integrated components from the ultraviolet signal.

The high MW appeared to be an advantage in good adhesive strength and low pellet friability. Hummel GA performed better than the other samples in peel strength tests, and inert model pellets formulated using Hummel GA showed less weight loss in tumbling tests than pellets made with the other GA samples (Chapter Five: Pellet Manufacture and Integrity Testing).

We wanted to apply some of our information from studying the properties of different samples of GA to the search for a synthetic binder replacement (Chapter Four: Selection of Synthetic Replacements). In particular, the relationship between MW and adhesive strength is generally found to be positive in polymer applications (Flory 1945, 1953). However, the unusual solution property of GA, i.e., low viscosity at high solution concentration of a high MW polymer, is important for getting a good distribution of a small amount of binder in a primer formulation. The focus of the rest of this chapter is to confirm the gel permeation chromatography observations on molecular dimensions using other analytical methods.

Atomic Force Microscopy

Microscopy, particularly atomic force microscopy and transmission electron microscopy (TEM), has been used to describe the structure and size of complex carbohydrate polymers (Morris and others 1999). The approach was to extensively dilute an aqueous carbohydrate solution so that the individual molecules were well separated. The dilute solution was then dispersed on an atomically smooth background and dried for evaluation. The separated polymers were then imaged by TEM, but this required preparation of a replica of the dried polymer dispersion. It is the electron transparent replica that was examined in the TEM.

A more direct method is to examine the dried polymer dispersion directly by atomic force microscopy (AFM) (Morris and others 1999). This has been especially useful in describing the structure of carbohydrate molecules. These are most frequently linear structures with occasional branches. The frequency and length of the branches is difficult to determine with other methods, especially if the number of branches is small for each molecule. Intermolecular association is another property of carbohydrates that has been frequently studied by AFM. Carbohydrate polymers often combine among themselves or with other carbohydrates to form gel networks.

Atomic force microscopy creates a topographical image by scanning a very sharp tip over a specimen and monitoring

Table 3-1—Components of the gum arabic samples[a]

Sample	AGP (weight %)	AG (weight %)	GP (weight %)
Brenntag	0.03	99.7	0.3
Colony	1.2	97	1.8
Hummel	6.3	91	2.5

[a]AGP 1.45×10^6 Daltons, AG 2.79×10^5 Daltons, GP 2.5×10^5 Daltons.

the displacement needed to keep the tip in contact with the specimen. The high image resolution (lateral resolution of about 20 nm) is achieved by using a tip with a radius of about 10 nm. The displacement resolution (~0.1 nm) is achieved by suspending the tip from a cantilever with a very small spring constant and reflecting a laser from the cantilever to a position-sensitive optical detector. Figure 3-3 illustrates the use of a piezo-electrical scanner to move the specimen under a stationary tip. Similar results could be obtained by moving the tip and keeping the specimen fixed.

Carbohydrate Morphology

Hermansson (1989) studied the relationship between solution rheology and gel morphology of κ-carrageenan—a sulphated galactan from red algae. Solution specimens were cryo-frozen between mica plates and samples were examined by TEM. Comparative studies were also made with specimens prepared by spraying dilute solutions onto mica plates.

The development and application of scanning probe methods for describing the morphology of biological materials, including polysaccharides, is described by Morris and others (1999). Two methods for preparing dried carbohydrate dispersions for microscopy have evolved: the drop method and the spray method. For the drop method, a drop of very dilute solution can be applied to an atomically smooth surface, usually a freshly cleaved mica plate. However, as the drop dries, the remaining solution becomes more concentrated, which eventually leads to intermolecular association. The usual result is an undistinguished mass of material near the center of a dried drop and a "coffee ring" of aggregated molecules at the edge. In between these features, some isolated polymer molecules may be observed, but this method does not give an analysis that represents most of the material.

The spray method, which is the most promising, was originally developed for preparing protein specimens for TEM (Tyler and others 1980). A modified artist's airbrush (Model H-1, Paasche Airbrush Company, Chicago, Illinois, USA) was used as the nebulizer. The modification replaced the normal paint supply with a 100-µL Eppendorf (Hamburg, Germany) pipette tip that contained a dilute solution of polymer to be studied. The gas pressure and distance from the mica were adjusted so that droplets 25 to 150 µm diameter were produced. With the spray deposition technique, each atomized droplet may have contained one or only a few polymer molecules because the opportunity for aggregation was reduced (McIntire and Brant 1997).

A thin film of water is condensed on surfaces in air; this is especially the case for hydrophilic surfaces such as mica or carbohydrates. The scanning AFM tip experiences adhesive forces caused by this water film. This may not be significant for low resolution images, but at the nanometer scale required for describing molecules, it is a major contribution. Solid state physicists usually avoid this adhesive force by conducting AFM imaging in ultrahigh vacuum. Biologists have adopted another solution; they image materials under liquids such as alcohols, which inhibit desorption of the water molecules from the substrate (Kirby and others 1996a).

An alternative method for imaging biomolecules is to use noncontact or tapping mode AFM (Gunning and others 1996, Cowman and others 1998, McIntire and Brant 1997). Tapping mode AFM may also be used under a liquid.

Most polysaccharides are linear molecules and appear as long meandering raised features on the smooth mica surface (Fig. 3-4). The presence of branches and interactions between molecules can be observed in AFM images. Where molecules cross, there is a distinct increase in altitude. The width of these features in AFM images is not an accurate reflection of the molecular diameter. This is because the

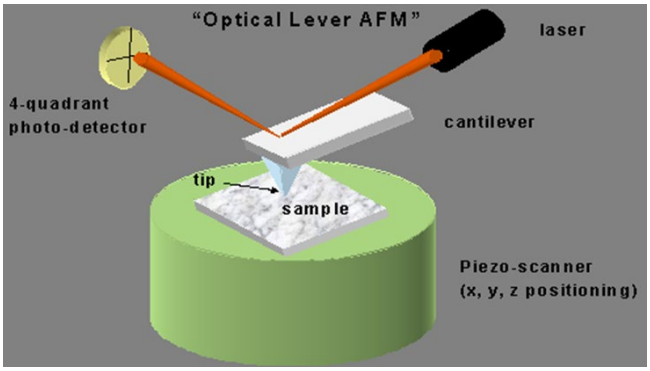

Figure 3-3. Schematic diagram of an atomic force microscope.

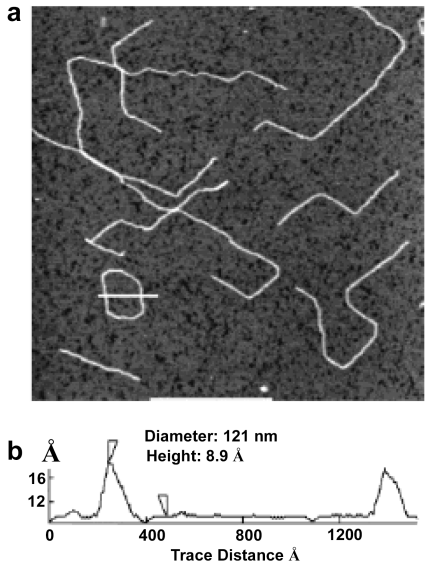

Figure 3-4. (a) Atomic force micrograph of a linear carbohydrate, scleroglucan; (b) vertical profile across the ring in lower left (from McIntire and Brant (1997); Copyright 1997 John Wiley & Sons, Inc. Used with permission).

AFM tip is pyramidal or cone shaped and the image width is a convolution of the tip profile and the molecular shape. However, the altitude (height) is usually an accurate measurement of the molecular diameter because only the extreme tip is in contact (or interaction) with either the mica surface or the molecular surface (McIntire and others 1995, Muller and Engel 1997, Muller and others 1999).

Studies have shown that the specimens prepared by the spray method are a good reflection of the molecular state in the solution (Kirby and others 1996b, Morris and others 1997, Gunning and others 1998). Thus, if molecular aggregation is present in solution (gel formation, salt effects), it will be observed on the dried plate (Cowman and others 1998).

Dextrans are random coil polysaccharides, and their AFM images show globular structures. The size of the globules has been shown to vary as the molecular weight changes (Tasker and others 1996; Frazier and others 1997a, 1997b). Besides just imaging the molecules, it is possible to quantify the data by generating contour length distributions, which can be converted into molecular size and dispersity (McIntire and Brant 1997, Ridout and others 1998).

The solution configuration, and thus the solid phase appearance, of these complex molecules sometimes depends on other factors. A change in solution pH, which would ionize functional groups on a polymer, would favor an extended chain configuration, which would separate like-charged ions. In the case of GA, deposition from aqueous solution results in spherical features. However, if a nonionic surfactant, e.g. Tween 20, is added, then extended chain features are found (Ikeda and others 2005).

A summary of the components, molecular structure, and solution behavior was described in Chapter One: Gum Arabic Overview. Only the salient features will be repeated here for convenience. Gum arabic is a mixture of three components: ~10% arabinogalactan-protein (AGP), 1.45×10^6 Daltons; ~88% arabinogalactan (AG), 2.8×10^5 Daltons; ~1% glycoprotein (GP), about half protein. The AGP component (Fig. 3-5) has been described as a long protein molecule with AG side chains attached (Mahendran and others 2008). These molecules have a very compact size in solution with a radius of gyration of about 20 nm or less. A rough estimate of size based on an assumed density of 1.0 g/mL suggests that an AGP molecule should occupy a sphere with a diameter of about 8 nm. The swollen volume in solution would be larger.

Experimental

Specimen Preparation

Aqueous solutions were prepared with GA (Hummel, Colony (GA-4), and Brenntag) at a concentration of 1 µg/mL. Specimens for AFM were prepared by spray deposition of these solutions onto ~5-mm square polished silicon wafers. An artist's airbrush (Paasche Model H-1) was used with compressed nitrogen at 193 kPa at a distance of 25 cm. The sample solutions were dispensed from a 100-µL Eppendorf pipette tip, which was fit into the modified airbrush. Additional specimens were prepared by drying single drops of the very dilute solution on cleaned, polished silicon plates. Although portions of the specimens prepared by the drop method consist of aggregated molecules, the numerical density of separated particles was greater than for the specimens prepared by the spray method. The silicon plates were used rather than the traditional mica plate because they offer a sufficiently featureless background while providing adequate conductivity to support examination by scanning electron microscopy. The plates were cleaned with cotton swabs soaked in acetone before use. The clean plates rarely had features greater than 0.1 nm.

Atomic Force Microscopy

Atomic force microscopy images were obtained using an atomic force microscope (Quesant Instrument Corporation, Agoura Hills, California, USA) in the intermittent contact "tapping" mode. A MikroMasch (Tartu, Estonia) NSC16 silicon cantilever probe with a tip radius of less than 10 nm was used at an operating frequency of about 163 kHz. A slow scan rate of 2.0 Hz was used to collect images at 600 × 600 resolution.

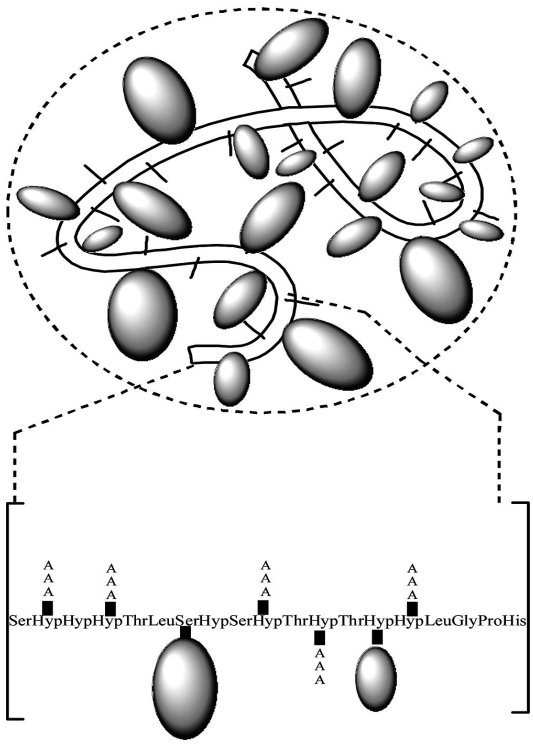

Figure 3-5. Graphical representation of arabinogalactan-protein (AGP) molecule from gum arabic (Reprinted from Mahendran and others (2008). Copyright 2008 American Chemical Society).

A representative AFM image of a GA specimen is shown in Figure 3-6. The grey scale in the AFM images is used to show vertical height, with the silicon support in black and the highest feature in white. The width of the features is not representative because it is distorted by the convolution of the shape of the pyramidal scanning tip and the roughly hemispherical particle shape.

The force on the scanning tip was optimized to provide a clear, stable image while avoiding damage to the specimen. Although repeated scanning was minimized to avoid damage, there was no evidence of change observed whenever scans were repeated.

Image Processing

The AFM images were acquired in a proprietary format using ScanAtomic software (Quesant Instrument Corporation). These images were subsequently converted to JPEG format and imported into Qplot version 4.06.alpha (Ambios Technology, Inc., Santa Cruz, California, USA) for image processing. The first step in image processing was to correct for sample tilt; this was done using a parabolic fit on a line-by-line basis. The vertical heights of the particles were determined from horizontal line profiles through the particles. More than 150 particles were systematically measured from several images for each of the GA samples. Every recognizable particle was measured within portions of each image.

These measurements are displayed in histograms (Figs. 3-7, 3-8, and 3-9) for each sample. The particle size from solution does not correlate to the particle size of the processed GA raw materials because the solid particles were produced with different processes.

Discussion

The particle size distribution from solution (Table 3-2) for each of the samples is similar to their molecular weight distribution (Table 3-1), as determined by gel permeation chromatography. The Brenntag sample had the smallest amount of high molecular weight component. The Hummel sample had the highest high molecular weight component and the broadest molecular weight distribution.

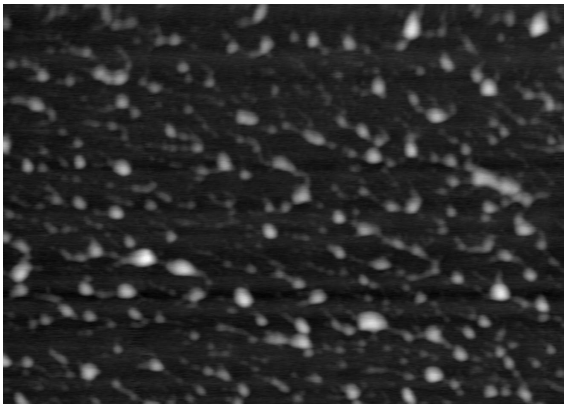

Figure 3-6. Atomic force microscopy image of a portion of a Hummel gum arabic specimen (4.3 × 4.3 µm).

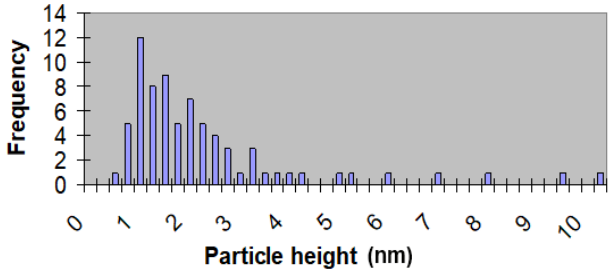

Figure 3-7. Particle height distribution for Brenntag gum arabic.

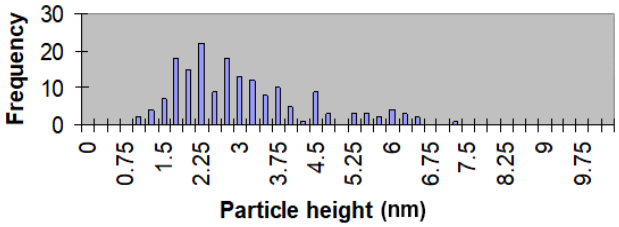

Figure 3-8. Particle height distribution for Colony gum arabic.

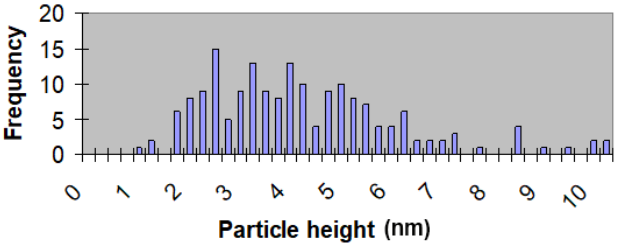

Figure 3-9. Particle height distribution for Hummel gum arabic.

These MW distributions are reflected in the solution rheology, especially using the rotational shear method. The unique shear thinning of the Hummel solution can be understood by the presence of high MW polymers. These large molecules form intermolecular contacts in concentrated solution, which makes the large molecules flow like even larger molecules as modeled in Figure 3-10. This high MW component, AGP, is favored for its performance as an emulsifier and adhesive (Randall and others 1988).

Table 3-2—Particle size statistics

Sample	Mean (nm)	Standard deviation	Median (nm)	Count
Brenntag	2.42	0.19	1.76	160
Colony	2.92	0.10	2.70	174
Hummel	4.15	0.15	3.88	180

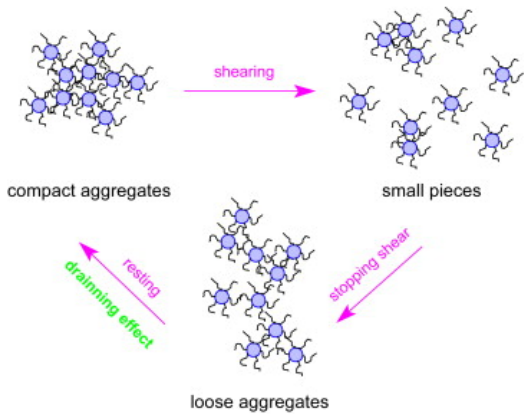

Figure 3-10. Graphical representation of aggregate formation and shear dissociation (Reprinted from Li and others 2009, with permission from Elsevier. https://www.sciencedirect.com/journal/food-hydrocolloids).

Two lessons learned from the GA studies are that these compact molecules have low solution viscosities and that high MW is desirable for adhesive strength. The low solution viscosity facilitates uniform distribution of a small amount of binder in a formulation. The adhesive strength results in good bonding with a small amount of binder. However, it is difficult to reconcile these features with solution polymers because the high MW implies low solubility and high viscosity solution (Witten and Pincus 2004).

One means of achieving such a combination of properties with synthetic polymers is through latex dispersions. Latexes have low viscosity at high solids concentration because the individual latex particles are stabilized colloids, which avoid interaction between particles. This low viscosity can be achieved even if the MW of the polymer in suspension is high. This is an important property in selecting synthetic materials for replacing the GA binder, which was Phase Two of the program and is discussed starting in Chapter 4: Selection of Synthetic Replacements.

Conclusions

Before we move away from Phase One, the objective was to develop improved specifications. The difficulty in doing this was that our cooperators were unable to provide both a GA that worked well and another that worked poorly for direct comparison. However, several observations could be crucial for new specifications. A key observation is that the GA should be from *Acacia senegal* trees rather than *Acacia seyal* trees. Some tests such as the nuclear magnetic resonance method are good, but they are not feasible as a control test for an industry with limited access to sophisticated analytical techniques. The gel permeation chromatography and peel test could be more practical methods to determine the quality of the GA for the binder application.

Literature Cited

Cowman, M.K.; Li, M.; Balazs, E.A. 1998. Tapping mode atomic force microscopy of hyaluronan: extended and intramolecularly interacting chains. Biophysical Journal. 75(4): 2030-2037. https://doi.org/10.1016/s0006-3495(98)77645-3.

Flory, P.J. 1945. Tensile strength in relation to molecular weight of high polymers. Journal of the American Chemical Society. 67(11): 2048-2050. https://doi.org/10.1021/ja01227a506.

Flory, P.J. 1953. Principles of polymer chemistry. Ithaca, NY: Cornell University Press.

Frazier, R.A., Davies, M.C.; Matthijs, G.; Roberts, C.J.; Schacht, E.; Tendler, S.J.B.; Williams, P.M. 1997a. High-resolution atomic force microscopy of dextran monolayer hydration. Langmuir. 13(18): 4795-4798. https://doi.org/10.1021/la970288e.

Frazier, R.A.; Davies, M.C.; Matthijs, G.; Roberts, C.J.; Schacht, E.; Tendler, S.J.B.; Williams, P.M. 1997b. *In situ* surface plasmon resonance analysis of dextran monolayer degradation by dextranase. Langmuir. 13(26): 7115-7120. https://doi.org/10.1021/la970382v.

Gunning, A.P.; Kirby, A.R.; Morris, V.J. 1996. Imaging xanthan gum in air by ac “tapping” mode atomic force microscopy. Ultramicroscopy. 63(1): 1-3. https://doi.org/10.1016/0304-3991(96)00032-0.

Gunning, A.P., Cairns, P.; Kirby, A.R.; Round, A.N.; Bixler, H.J.; Morris, V.J. 1998. Characterising semi-refined *iota*-carrageenan networks by atomic force microscopy. Carbohydrate Polymers. 36(1): 67-72. https://doi.org/10.1016/s0144-8617(97)00112-4.

Hermansson, A.M. 1989. Rheological and microstructural evidence for transient states during gelation of kappa-carrageenan in the presence of potassium. Carbohydrate Polymers. 10(3): 163-181. https://doi.org/10.1016/0144-8617(89)90009-x.

Ikeda, S.; Funami, T.; Zhang, G. 2005. Visualizing surface active hydrocolloids by atomic force microscopy. Carbohydrate Polymers. 62(2): 192-196. https://doi.org/10.1016/j.carbpol.2005.07.020.

Kirby, A.R., Gunning, A.P.; Morris, V.J. 1996a. Imaging polysaccharides by atomic force microscopy. Biopolymers. 38(3): 355-366. https://doi.org/10.1002/(sici)1097-0282(199603)38:3%3C355::aid-bip8%3E3.0.co;2-t.

Kirby, A.R., Gunning, A.P.; Waldron, K.W.; Morris, V.J.; Ng, A. 1996b. Visualization of plant cell walls by atomic force microscopy. Biophysical Journal. 70(3): 1138-1143. https://doi.org/10.1016/s0006-3495(96)79708-4.

Li, X.; Fang, Y.; Al-Assaf, S.; Phillips, G.O.; Nishinari, K.; Zhang, H. 2009. Rheological study of gum arabic solutions: interpretation based on molecular self-association. Food Hydrocolloids. 23(8): 2394-2402. https://doi.org/10.1016/j.foodhyd.2009.06.018.

Mahendran, T.; Williams, P.A.; Phillips, G.O.; Al-Assaf, S.; Baldwin, T.C. 2008. New insights into the structural characteristics of the arabinogalactan-protein (AGP) fraction of gum arabic. Journal of Agricultural and Food Chemistry. 56(19): 9269-9276. https://doi.org/10.1021/jf800849a.

McIntire, T.M.; Brant, D.A. 1997. Imaging of individual biopolymers and supramolecular assemblies using noncontact atomic force microscopy. Biopolymers. 42: 133-146. https://doi.org/10.1002/(sici)1097-0282(199708)42:2%3C133::aid-bip3%3E3.0.co;2-o.

McIntire, T.M.; Penner, R.M.; Brant, D.A. 1995. Observations of circular, triple-helical polysaccharide using noncontact atomic force microscopy. Macromolecules. 28: 6375-6377. https://doi.org/10.1021/ma00122a056.

Morris, V.J.; Gunning, A.P.; Kirby, A.R.; Round, A.N.; Waldron, K.; Ng, A. 1997. Atomic force microscopy of plant cell walls, plant cell wall polysaccharides and gels. International Journal of Biological Macromolecules. 21(1-2): 61-66. https://doi.org/10.1016/s0141-8130(97)00042-1.

Morris, V.J.; Kirby, A.R.; Gunning, A.P. 1999. Atomic force microscopy for biologists. London: Imperial College Press.

Muller, D.J.; Engel, A. 1997. The height of biomolecules measured with the atomic force microscope depends on electrostatic interactions. Biophysical Journal. 73: 1633-1644. https://doi.org/10.1016/s0006-3495(97)78195-5.

Muller, D.J.; Fotiadis, D.; Scheuring, S.; Muller, S.A.; Engel, A. 1999. Electrostatically balanced subnanometer imaging of biological specimens by atomic force microscopy. Biophysical Journal. 76: 1101-1111. https://doi.org/10.1016/s0006-3495(99)77275-9.

Phillips, G.O. 2009. Molecular association and function of arabinogalactan protein complexes from tree exudates. Structural Chemistry. 20: 309. https://doi.org/10.1007/s11224-009-9422-3.

Randall, R.C.; Phillips, G.O.; Williams, P.A. 1988. The role of the proteinaceous component on the emulsifying properties of gum arabic. Food Hydrocolloids. 2(2): 131-140. https://doi.org/10.1016/s0268-005x(88)80011-0.

Ridout, M.J.; Brownsey, G.J.; Gunning, A.P.; Morris, V.J. 1998. Characterisation of the polysaccharide produced by *Acetobacter xylinum* strain CR1/4 by light scattering and atomic force microscopy. International Journal of Biological Macromolecules. 23(4): 287-293. https://doi.org/10.1016/s0141-8130(98)00057-9.

Tasker, S.; Matthijs, G.; Davies, M.C.; Roberts, C.J.; Schacht, E.H.; Tendler, S.J.B. 1996. Molecular resolution imaging of dextran monolayers immobilized on silica by atomic force microscopy. Langmuir. 12(26): 6436-6442. https://doi.org/10.1021/la951087i.

Tyler, J.M.; Branton, D. 1980. Rotary shadowing of extended molecules dried from glycerol. Journal of Ultrastructure Research. 71(2): 95-102. https://doi.org/10.1016/s0022-5320(80)90098-2.

Witten, T.A.; Pincus, P.A. 2004. Structured fluids: polymers, colloids, surfactants. New York: Oxford University Press.

Chapter Four
Selection of Synthetic Replacements

The long-term objective of this program was to find a synthetic replacement for gum Arabic (GA), which comes exclusively from the politically unstable sub-Saharan Africa. This goal was the focus of Phase Two of this cooperative research. At the USDA Forest Service, Forest Products Laboratory (FPL), we went through several steps to select several likely candidates for testing in an inert primer formulation. The steps involved listing potential binders and then developing selection criteria to narrow the list of candidates. This process selected candidates for the next stage of testing to compare the performance with GA (Chapter Five: Pellet Manufacture and Integrity Testing).

Overall Perspective

The work reported in this chapter involved the selection process to find a replacement for GA. Because of the very complex nature of GA, we determined that making a synthetic GA was economically infeasible. Additionally, the possibility of trying to make new materials was considered not within the scope of this program. The directive was to investigate known binders or likely binders that were commercially available. Some of these known binders had obvious problems as GA replacements. We worked with the rest of the team to develop a list of formal criteria to apply to the selection process of the synthetic binder based on how the binder was used and performance expectations. At this point, the emphasis was on the mixing of the binder with the explosives using the cohesive strength of the primer pellets as the only performance criteria. The main ingredients of the primer are lead styphnate and barium nitrate, with smaller amounts of tetracene, antimony sulfide, aluminum powder, and pentaerythritol tetranitrate. The final formulation contains less than 3% GA binder (Chapter Five: Pellet Manufacture and Integrity Testing). With this formulation, the binder should have high polarity to bond to most of the other primer components. The binders passing these criteria made it to the next stage of actual binder performance testing (Chapter Five).

Binder Selection Criteria

The first step was to select a broad list of binders. The selection criteria were chosen through a joint process involving the entire team to ensure that the binder could operate with the existing primer formulation and binder production equipment and methods. The list in the next section includes the reasons why many of the binders were eliminated using the selection criteria.

Threshold (Minimum Requirements)

- Must be waterborne (the capability to dissolve, suspend, or emulsify in water)
    - At least 40% solids and six-month stability for purchased aqueous dispersions
    - Easily dispersed solids to make emulsions that are stable for at least a week if Alliant Techsystems, Inc. (ATK) makes dispersion
    - Easily dispersed and finely divided solid if the binder is dispersed during primer production process step
- Must be stable (no chemical breakdown) at less than 180 °C
    - Less than 5% weight loss excluding water from ambient to 180 °C as measured by thermogravimetric analysis; purchased dispersions are predried prior to analysis
- Melting point must be greater than 83 °C
    - Melting point would be measured by standard hot stage method or differential scanning calorimetry for pure materials; ring and ball softening point would be used for those polymers without a discrete melting point
- Must be greater than 40% solids as dissolved or suspended in water
    - Criteria only for those that are dispersed during primer production, whereas the predispersed need to be at least 40% solids
- Must be commercially available
- Available at standard production quantities (needed amount per year was not established at this time) and at a cost below the highest GA cost (not established at the time)

Preferred

- Has a defined structure
- Has a set molecular weight or representative formula (this was not clearly defined because most polymeric materials, including GA, are a mixture of molecular weights and structures)
- Water solubility preferred
- Available from multiple vendors
    - Two minimum with three or more preferred
- Comparable friability resistance with GA (will be used later in the screening process because a test would be required to evaluate this)

Downselection of Potential Binders

Based on prior team conference calls, we divided GA replacements into two classes: purchased solids and purchased dispersions. The solid binder can be either added as a dry solid to the primer mixing or predissolved as is currently done with GA. The dispersion binder would be added as a waterborne liquid to the primer mixture. Based on the agreed upon criteria, we eliminated many of the binders from the list of potential replacements. However, many binders still passed all the criteria, although a test for friability has not been developed yet, so that could not be tested. As will be discussed in Chapter Five, a friability test was developed for the nonexplosive primer, and it was applied later in the binder selection process. We decided to obtain binders representing different functionalities for exploring their performance properties but did not go into selecting alternative formulation variations within a class. The selected exploratory binders were dextrin solid, cationic starch solid, polyacrylamide solid, poly (vinyl acetate) dispersion, polyvinylpyrrolidone-vinyl acetate copolymer dispersion, acrylic dispersion, acrylic-styrene copolymer dispersion, polyurethane dispersion, and polyolefin dispersion.

The list of binders was divided into the aforementioned categories of those that are purchased as solids that readily dissolve in water and those purchased as stable dispersions, with notation for those added to the original list. Those recommended for dropping at this stage of the downselection process did not pass the threshold and preferred criteria (as subsequently noted for each chemical), including those that cannot form stable dispersions with high enough solids and/or were too hard to solubilize by mixing in the primer blending process.

Purchased Solids

- Mesquite gum (dropped because of its low commercial availability and ill-defined structure)
- Dextran (ordered from Aldrich, St. Louis, Missouri, USA)
- Cyclodextrin (ordered from Wacker Cavamax W6, Adrian, Michigan, USA)
- Starch (dropped because starch normally requires heat to disperse and the resulting high viscosity dispersion is not stable for a week)
- Cationic starch (ordered from National Starch, Bridgewater, New Jersey, USA)
- Sorbitol (dropped because of its low molecular weight and potentially low adhesion strength)
- Methyl cellulose (low priority because of very high viscosity)
- Sodium carboxymethylcellulose (dropped because of low solubility and difficulty in dissolving)
- Casein (dropped because it is too hard to obtain a stable high-solids dispersion)
- Soy proteins (dropped because it is too hard to obtain a stable high-solids dispersion)
- Wheat gluten (dropped because it is too hard to obtain a stable dispersion)
- Divinylbenzene (dropped because it is a liquid)
- Ethylene acrylic acid polymers (dropped because of its requirement of heat and caustic to disperse)
- Poly(vinylpyrrilidone) (ordered from ISP Plasdone K-12, Ashland, Ohio, USA)
- Vinylpyrrilidone-vinylacetate copolymer (ordered from ISP Plasdone S-630)
- Poly (vinyl alcohol) (dropped because it needs heat to go into solution and has solubility less than 30%)
- Polyacrylamide (ordered from Aldrich and Cytec PAM A-370, Ransbeek, Bruxelles, Belgium)
- Acrylamide-sodium acrylate copolymer (dropped because of inability to find a supplier)
- Maleated rosin (dropped because of its low water solubility)
- Phenolics, novalac (dropped because of its low water solubility except at high pH, which was undesirable)

Purchased Dispersions

- Poly (vinyl acetate) dispersions (ordered from Franklin Duracet 12B, Columbus, Ohio, USA)
- Partially hydrolyzed poly (vinyl acetate) (could not find a suitable one)
- Ethylene-vinyl acetate copolymers (added) (ordered from Air Products Airflex 400, Allentown, Pennsylvania, USA)
- Poly(amidoamine)-epichlorohydrin resin (dropped because of its low solids and instability at neutral pH)
- Poly(butadiene-styrene) latex (ordered from BASF Butanol NS 198, Freeport, Texas, USA)
- Acrylic latex (Rhoplex MC1834 and Robond PS2000, Dow, Midland, Michigan, USA)
- Acrylic-styrene copolymer (styreneated acrylics) (ordered from BASF Acronal NX 296)
- Acrylic-methyl methacrylate copolymer (added) (ordered from BASF Optive 120)
- Acrylic-butyl acrylate copolymer (added) (deferred selection)
- Natural rubber latex (deferred selection because of poor compatibility with polar primers)
- Phenolics, resol (dropped because of low water solubility at neutral pH)
- Styrene maleic anhydride copolymers (deferred selection)
- Dendritic polymers (dropped because of limited commercial availability and high cost)
- Polyolefin dispersion (added) (deferred selection because of poor compatibility with polar primers)
- Polyurethane dispersion (added) (ordered from Lubrizol Sancure 20025, Wickliffe, Ohio, USA)

Selected Primers for Further Investigation

Purchased Solids

- Dextran (ordered from Aldrich)
- Cyclodextrin (ordered from Wacker Cavamax W6)
- Cationic starch (ordered from National Starch)
- Poly (vinylpyrrilidone) (ordered from ISP Plasdone K-12)
- Vinylpyrrilidone-vinylacetate copolymer (ordered from ISP Plasdone S-630)
- Polyacrylamide (ordered from Aldrich and Cytec PAM A-370)

Purchased Dispersions

- Poly (vinyl acetate) dispersions (ordered from Franklin Duracet 12B)
- Ethylene-vinyl acetate copolymers (ordered from Air Products Airflex 400)
- Poly (butadiene-styrene) latex (ordered from BASF Butanol NS 198)
- Acrylic latex (Rhoplex MC1834 and Robond PS 2000, ordered from Dow)
- Acrylic-styrene copolymer (styreneated acrylics) (ordered from BASF Acronal NX 296)
- Acrylic-methyl methacrylate copolymer (ordered from BASF Optive 120)
- Polyurethane dispersion (ordered from Lubrizol Sancure 20025)

Further Elimination of Selected Primers

At this point, at FPL, we did not have a good method to eliminate any of the selected solids or dispersions. One potential problem that we ignored was that in some cases it is unlikely that the exact same product could be obtained from more than one supplier because each supplier makes a somewhat different product of the same type. Although we cannot be certain of this because most of these materials are grouped by their end use applications (e.g., architectural paints, industrial paints, water-treatment chemicals, paper coatings, etc.) rather than their polymer structure. Thus, it took a lot of digging including reading individual material data safety sheets to come up with the list that we had. This means that the list of solids and dispersions is probably missing potential binders and that we may not have selected the best one for each class. However, the program had to move forward, and we settled for what we had.

However, this still left us with the need for a test to determine the binder performance. The U.S. Army Armament Research Development and Engineering Center (ARDEC) at Picatinny Arsenal in New Jersey, U.S. Army Joint Munitions Command (JMC) in Rock Island, Illinois, and Lake City Army Ammunition Plant (LCAAP) of Alliant Techsystems, Inc. (ATK) in Independence, Missouri, had ways to determine pellet integrity of the actual primers, but we did not have the expertise and were not equipped to appropriately handle the safety issues of working with live explosives. As discussed in Chapter Five, we developed an inert primer formulation and several tests to determine the effect of the different binders on the primer pellet.

Chapter Five
Pellet Manufacture and Integrity Testing

The second part of the Phase Two Program was to narrow the selection for finding a replacement for gum arabic (GA). The USDA Forest Service, Forest Products Laboratory (FPL) developed and applied several methods to evaluate the mechanical integrity of pellets made with an inert primer formulation. These tests narrowed down the 35 identified synthetic polymer candidates to six: Ashland Chemical FlowStrength, WSB40 poly (acrylamide) solution, Omnova Solutions AcryGen D 471 poly (styrene-acrylate) latex, Cargill Plus 08702 dextrin solid, Franklin Duracet 12 DB poly (vinyl acetate) latex, and Rohm & Haas Rhoplex/Robond poly (vinyl acrylate) latex. Of these, the dextrin was found to be the most similar in use to GA and is likely to be the most economically attractive.

Overall Perspective

To determine the performance, FPL had to address two major items. Because the primer is made from explosive components, a formula was first developed in which each explosive component was replaced with a nonexplosive component using a similar structure. With this formula, a technique was used to make primer pellets with a method similar to the commercial process. Several methods were then developed to measure the mechanical integrity (friability) of these pellets with one showing excellent performance. These two steps of making a nonexplosive primer and reliably testing primer pellet friability provided two conclusions: first, that of the GA products, the Hummel material provided the best strength, and second, that three of the synthetic binders provided performance equal to or better than the best GA.

Introduction

In Chapter Four, the initial selection of 35 synthetic polymer binder candidates to replace GA in primer pellet formulation were decreased to 14 possible binder classes with 16 specific product candidates. The next step was to evaluate the performance of these polymers as binders. We did some adhesive testing in Chapter Four but were not convinced that these tests would be the best screening tools. Thus, this chapter focuses on the pellet binder tests that duplicate the actual cause of failure, fragmentation of the dried primer pellets.

The most direct method would be to substitute equivalent amounts of each binder for GA in the FA-956 primer formulation and perform some mechanical test that would measure the integrity of the pellet. Unfortunately, the FA-956 primer formulation is a very explosive mixture and FPL was not equipped or approved to work with such materials. In addition, testing explosive materials safely is an expensive and time-consuming process. Thus, our approach was to develop an inert mixture with chemical and physical characteristics that would closely mimic the FA-956 formulation. Using an inert mixture enabled efficient and economical screening of many candidate binders in a meaningful way.

A main concern was to select components that would approximate the surface chemistry of the ingredients in FA-956. Surface chemistry controls the spreading (wetting) of a polymer on the substrate surface. It is a fundamental necessity that a binder must at least partially coat the components of a mixture and form strong adhesion with the other components. This is a challenge because FA-956 contains rather hydrophobic materials such as tetracene as well as polar materials such as aluminum powder, which has an aluminum oxide exterior. In addition, there is a substantial amount of water-soluble material in FA-956 (32% barium nitrate). Table 5-1 gives a list of the FA-956 components along with the components of the inert mixtures that were selected as commonly available substitutes. Because we could not find a good way to determine the actual surface energy of the components, we used best guesses and had them verified by the rest of the team. One difference in our procedure was that we did not include a component for pentaerythritol tetranitrate (PETN). This was because we could not find a similar substitute and it is a small part of the formulation.

Primer pellets were manufactured using the same method used by ATK at the Lake City plant but substituting our inert formulation. A wet slurry with a paste-like consistency was forced into holes in a metal plate using a squeegee. The

Table 5-1—Inert formulation

Active ingredient	Amount (%)	Model ingredient	Weight[a] (g)
Lead styphnate	37 ± 5	Lead tartrate	3.50
Tetracene	4 ± 1	Naphthalene	0.35
Barium nitrate	32 ± 5	Barium chloride	3.02
Antimony sulfide	15 ± 2	Antimony sulfide	1.42
Aluminum powder	7 ± 1	Aluminum oxide	0.66
PETN[b]	5 ± 1	None	None

[a]Amount used in each batch, 8.95 ± 0.03 g.

[b]PETN, pentaerythritol tetranitrate.

mixture was allowed to dry for a short time before the individual pellets were pushed from the holes in the casting plate with a metal rod. The pellets were then air-dried at ambient temperature before mechanical testing.

Pellet Manufacture

Using the standard operating procedure for the Lake City Army Ammunition Plant as a basis, we scaled down their ratio of 4.55 kg GA per 5,000 mL H_2O to a more manageable laboratory scale of 0.91 g GA per 1 mL H_2O. GA solutions were produced based on this ratio and added to the other primer components. The resulting mixture, however, was too viscous for adequate mixing when producing the primer pellets in our small-scale laboratory tests. To reduce mixing problems, we lowered the viscosity by doubling the amount of H_2O. The final ratio that was applied to the different GA binders for production was 0.91 g GA per 2 mL H_2O. The additional water was necessary because we used dry primer components, but in actual manufacturing, the binder components are kept wet to make them safer to handle.

Casting Plate

FPL's machine shop prepared a 1/16-in.- (1.6-mm-) thick stainless steel plate with 1/8-in.- (3.2-mm-) diameter holes. This was used to cast the pellets in a way that was similar to commercial production. A squeegee was used to push the primer into the holes, and a rod was machined to push the pellets from the plate. Figure 5-1 depicts the casting plate, push rod, and silk screen squeegee that were used to manufacture inert primer pellets.

Formulation of Pellets

With the process used at ATK as reference, FPL developed a similar primer formulation and pellet-making process. From the ATK procedures, we took the ratios of the materials for the primer pellets and scaled them down to a lab-scale quantity. The final ratio was adjusted from 4.8 mL of GA per 453.6 g of pellet material to 0.1 mL GA per 9.45 g of pellet material. Using this ratio, we measured out amounts of each ingredient. After the ingredients were mixed thoroughly, 3.5 mL of H_2O were added to transform the mixture into a suspension. The water was added because our ingredients were dry powders whereas many of the actual active components are wet to improve safety during handling. We tested three cases with this mixture:

- No binder solution added
- Regular amount of binder solution added (1X)
- Doubled amount of binder solution added (2X)

After the creation of the final suspension, it was spread across the casting plate. A squeegee was used to push the primer into the holes of the casting plate and force it to take the form of a pellet. The excess primer suspension was scraped off using the silk screen squeegee. After the 1-min waiting period, the pellets were dispensed into a holding container by ejection using the push rod. The holding container was then set in a fume hood to allow the pellets to air-dry for testing. Commercially, the pellets at this point are placed in primer cases before being stored to dry. After drying, these commercial primer capsules are subjected to mechanical vibrations to line them up for inserting into the bullets. Having an intact pellet after drying is critical for making a bullet that is safe to fire.

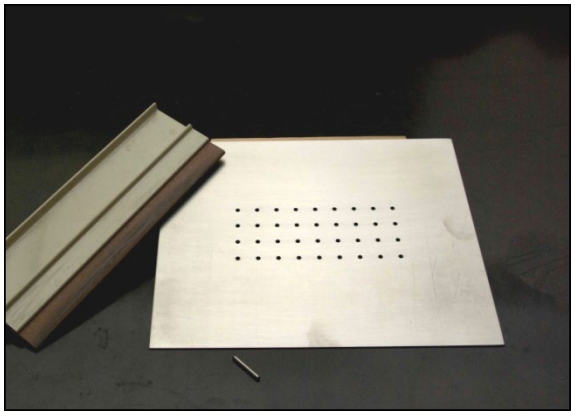

Figure 5-1. Equipment used for manufacture of inert primer pellets.

Integrity Testing

Integrity testing consists of some form of mechanical action on the pellets followed by some measure of the resulting damage. An easy, effective, and widely used measure of damage is weight loss. Choosing a suitable mechanical action is not as obvious. The experience at the Lake City plant is that defective primers are associated with the occurrence of primer dust. This suggests that some form of agitation—shaking, vibration, low force impact—would model the plant experience.

We looked for apparatuses in the laboratory that might be appropriate for providing the desired agitation. Sieve shakers were found to be too violent and thus did not differentiate between pellets with and without binder. An examination of the pharmaceutical literature showed that it is common to test the integrity of tablets with a tumbling test, which measures the weight loss experienced after tumbling for an amount of time in a defined apparatus. We found a piece of equipment in our laboratory that would simulate a tumbling test. We observed that the tumbling test successfully differentiated between different binders and provided good reproducibility of results.

Two additional tests, suggested by ATK, were examined—a radial crush test and mechanical vibration. The radial crush test (discussed later in this chapter) gave results that overall paralleled the results from the tumbling test. However, we did not experience good differentiation between the best binder candidates. The vibration test produced results that appeared to be equivalent to the tumbling test.

Tumbling Test

After air-drying, three pellets were weighed before being subjected to tumbling in a tumbling box (Fig. 5-2). This is a piece of equipment that we already had in our lab. It provided a means for tumbling the primer pellets similar to what the pharmaceutical industry uses to test the integrity of pills. The inert primer pellets were confined to plastic Petri dishes during the tumbling as shown in Figure 5-3.

The tumbling box was consistently set at 26 revolutions per minute with each tumbling session lasting 5 min. After tumbling, the three pellets were dispensed from the plastic Petri dishes onto a 40-mesh screen (0.420-mm openings) to eliminate the material broken from the pellets. Finally, the resulting pellets were reweighed.

We used this test on inert formulations made with the three GA samples tested in Phase One. The results shown in Table 5-2 appeared to be a reasonable measure of pellet friability at the normal binder concentration (1X) and twice the normal concentration (2X), although we had no target to judge performance. The standard deviations in parentheses after the weight loss number showed good reproducibility. There was sufficient sensitivity to differentiate among both the different GAs and the pellets made without binder. Notably, the pellets without binder suffered the greatest loss of material, which showed the necessity of a binder. Clearly, the GA drastically improved pellet integrity, and the improvement to the integrity was greater with the Hummel GA than with the other two GA. As shown by the following tumbling data, the pellet integrity improved in each round; thus, values should be compared within a series and not between series.

Having demonstrated that primer pellets could be manufactured using our formulation and method and that we had a reasonably sensitive method for testing their mechanical integrity, we proceeded to make a series of primer pellets using each of the candidate synthetic binders along with the GA controls at the same concentrations. To provide some redundancy, we examined each candidate binder at two concentration levels (normal and double). The preparation of pellets was made easier and better comparison was achieved by mixing a large batch of the dried components of the inert primer to be used with all the different binders. This large batch of material was mixed and ground in a ball mill to create a uniform mixture with a small and uniform particle size. Then it was only necessary to weigh a portion of the dried materials, add the appropriate amount of binder (1X or 2X), and then add water to make the pellets. The reason for the two levels was to gain an understanding of concentration because we did not know the effectiveness of alternative binders. The resulting inert primer pellets were then subjected to the tumbling test (Table 5-2).

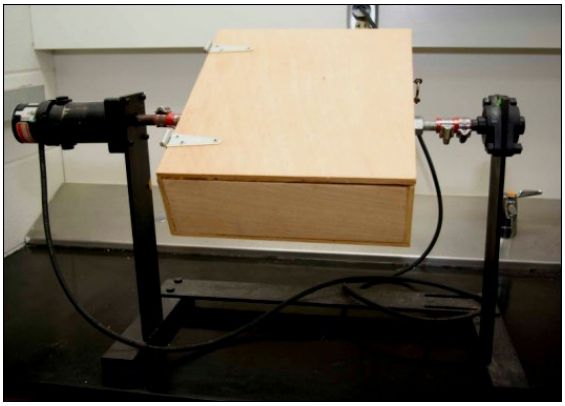

Figure 5-2. Tumbling box rotating about the central axis.

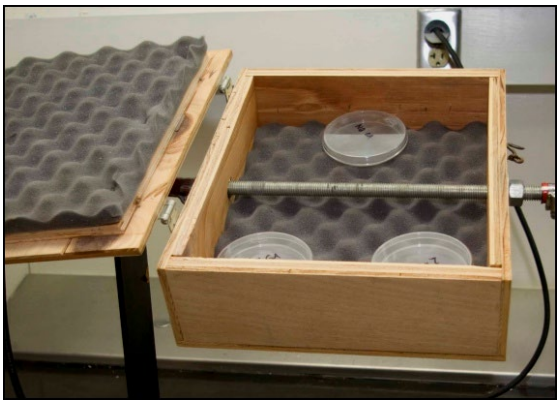

Figure 5-3. Petri dishes inside tumbling box.

In Series II, pellets made with the different GA samples were included along with some pellets prepared without binder. In all series, the order in which binders were used was randomly selected to provide some reference between series. We noted similar ranking among the pellets made with GA binders versus without binder, but there was substantially less material loss for Series II compared with Series I. This was attributed to greater experience in pellet manufacture and the effect of more uniform particle size from ball milling the dry components.

Table 5-3 shows a wide range of mechanical integrity. Some synthetic binders provided better integrity than the GAs,

Table 5-2—Friability test, material loss measured by tumbling test for Series I gum arabic in two concentration levels (1X and 2X)

	Weight loss (%)	
Binder	1X	2X
Hummel	9.0 (1.6)[a]	4.1 (2.7)
Colony	13 (4.0)	5.6 (1.0)
Quadra	39 (3.6)	12 (2.4)
No binder	72 (2.0)	—

[a]Numbers in parentheses are standard deviation.

Table 5-3—Material loss measured by tumbling test for Series II (second batch) pellets[a] made with normal concentration (1X) and double concentration (2X)

	Average material loss (%)	
Binder[b]	1X	2X
Hummel	1.14 (0.29)[c]	1.22 (0.71)
Quadra	4.24 (2.03)	2.50 (1.24)
Colony	4.43 (2.55)	3.65 (1.76)
No binder	17.00 (2.95)	N/A (N/A)
Dextrin D200	0.61 (0.33)	0.14 (0.12)
Duracet 12 DB	1.07 (0.54)	1.71 (1.69)
Cargill PI 08505	3.81 (1.77)	0.64 (0.54)
Acronal Opt. 120	4.77 (2.78)	2.40 (1.25)
Acronal 296 D na	5.21 (2.56)	5.21 (3.17)
PV A B-25	5.61 (5.71)	27.00 (14.93)
Glucidex 9	5.93 (2.99)	5.71 (3.41)
Butanal NS 198	6.20 (0.83)	3.54 (1.79)
Rhoplex MC 1834P	7.88 (1.47)	1.76 (0.91)
Acrodur 950L	9.94 (1.35)	23.37 (11.58)
Polyacr. 434949	16.02 (4.08)	1.94 (1.49)
PV P K15	19.69 (9.15)	2.55 (2.45)
Robond PS-2020	26.85 (8.83)	3.41 (1.71)
Sancure 20025	29.97 (11.96)	28.57 (15.31)
PV P/V A S-630	32.88 (12.99)	2.15 (2.16)
Butonal NX 1129	35.10 (6.90)	16.77 (11.28)

[a]For suppliers of materials, see Chapter 4.
[b]Entries with green shading were top-performing binders.
[c]Values in parentheses are standard deviation.

whereas some performed poorer than no binder. It is not difficult to identify the top performing binders from these results. The following binders were recommended (green shading in Table 5-3): Dextrin D200 (Cargill, Wayzata, Minnesota, USA), Duracet 12 DB (Franklin, Columbus, Ohio, USA), Rhoplex MC 1834P (Dow, Midland, Michigan, USA), Acronal Opt 120 (BASF, Freeport, Texas, USA), and Butanal NS 198 (BASF, Freeport, Texas, USA) with the latter two being more effective at the higher concentration. The Cargill Pl 08505 and Acronal 296 D were not selected because we were interested in examining different classes of binders and did not wish to choose more than one example of each class.

The selected binder candidates were examined again at the normal binder concentration (1X) and twice the normal concentration (2X) in Series III, which used a new ball mill ground mixture of the dry inert components. Series III, shown in Table 5-4, provided an opportunity to confirm the previous results.

The results of the Series III test confirmed our choice of binders as favored candidates for replacing GA. It should be noted that the controls Colony and No Binder pellets (red

Table 5-4—Material loss measured by tumbling test for Series III pellets at two concentration levels (1X and 2X) with Colony and No binder as controls (shaded in red)

	Average material loss (%)	
Binder	1X	2X
Duracet 12 DB	1.04 (0.44)[a]	1.85 (0.43)
Colony	1.04 (0.73)	—
Dextrin D200	1.09 (0.57)	0.71 (0.35)
Acronal Opt. 120	1.22 (0.57)	1.84 (0.54)
Rhoplex MC 1834P	1.30 (0.44)	1.32 (0.52)
Butanal NS 198	2.50 (1.19)	1.88 (0.44)
No binder	3.50 (1.40)	—

[a]Values in parentheses are standard deviation.

shading in Table 5-4) were prepared using the same batch of ball-milled dry ingredients but were made a week later. The material losses experienced in Series III were generally lower than those observed in Series II for the same binders, with the ranking of the candidates being similar. This lower weight loss was again attributed to improvements in the pellet making techniques compared with the previous series.

On August 4, 2009, there was a meeting of all the partners in the GA project at FPL. At the meeting, the progress of the binder selection was reviewed and plans for testing the selected binder candidates with FA-956 materials were formulated. Some new binder candidates were proposed for evaluation. Our partners pointed out that the poly(vinyl acrylate) latexes Robond and Rhoplex were used in combination in another primer formulation. We agreed to evaluate them in combination. ATK observed that Acronal Opt. 120 contained an alleged carcinogen, which the manufacturer did not identify. Without knowing the identity of the carcinogen there was no way to monitor for health and safety; therefore, it was removed from consideration as a binder candidate.

The new candidates, other selected GA replacements, and controls were evaluated in Series IV testing. The results are displayed in Table 5-5 for the normal binder concentration (1X) and twice the normal concentration (2X).

In Series IV, a different dextrin binder, Cargill Plus 08702, was evaluated to replace Dextrin D200. Dextrin D200 was purchased from Sigma-Aldrich (St. Louis, Missouri, USA), but we were not able to identify the original manufacturer. Cargill Plus 08702 was considered an appropriate choice because it is a refined dextrin available from a major supplier. The Celvols are poly(vinyl alcohol) polymers of different molecular weight. These were added because other primer formulations had included them as binders. Poly(vinyl alcohol) had not been included in the original selection list because its low solubility did not meet the

Table 5-5—Material loss measured by tumbling test for Series IV pellets at two concentration levels (1X and 2X) with Colony and No binder as controls (shaded in red)

	Average material loss (%)		
Binder	1X	2X	Comments
Ashland Flowstrength	0.05 (0.06)[a]	0.6 (0.8)	easy to use
Cargill Plus 08702	0.3 (0.2)	0.3 (0.4)	like Colony
Acrygen D 471	0.4 (0.3)	0.6 (0.4)	easy to use
Rhoplex/Robond	0.5 (0.3)	0.3 (0.3)	easy to use
Colony	0.6 (0.5)	0.4 (0.3)	jelly-like
Celvol 502	0.9 (0.5)	1.7 (1.3)	very sticky, difficult
Celvol 24203	1.2 (0.4)	1.6 (1.2)	very sticky, difficult
No binder	1.4 (0.8)	—	—
Ashland K11LL	3.8 (0.6)	3.4 (1.6)	very difficult
Ashland K110FL	4.4 (0.6)	1.7 (1.1)	very difficult

[a]Values in parentheses are standard deviation.

initial selection criteria. The Ashland materials were some new binders that we had received.

In addition to the material loss reported in Table 5-5, the observations noted by technician Jae Ahn of FPL during the manufacture of the pellets on the characteristics of the inert mixtures are given here:

No binder

- Cement-like texture
- Dried fairly quickly (about 30 seconds before extracting pellets)

Colony

- Jelly-like texture
- Dried fairly quickly (about 30 to 60 seconds before extracting pellets)

Robond/Rhoplex

- Glossy and smooth texture
- Dried fairly quickly (about 30 to 60 seconds before extracting pellets)

Celvol 502

- Very sticky, difficult to manage (could not make a consolidated pellet easily)
- Moderate drying time (between 60 and 90 seconds)
- Became more difficult to manage at 2X binder

Celvol V24203

- Very sticky, difficult to manage (cannot make a consolidated pellet easily)
- Moderate drying time (between 60 and 90 seconds)

Ashland Flostrength

- Smooth paste-like texture (easy to conform into a solid pellet)
- Dried fairly quickly (about 30 to 60 seconds before extracting pellets)
- Same observations for both 1X and 2X binder
- This seemed very promising

Ashland K110FL

- Very difficult to manage
- Needed to add more than standard amount of water to soften it up in order to allow proper mixing, however, the more water added the stickier (like a spider web) it became
- Very long drying time (between 8 and 10 min before extraction)

Ashland K11LL

- Very difficult to manage
- Needed to add more than standard amount of water to soften it up in order to allow proper mixing, however, the more water added the stickier (like a spider web) it became
- Very long drying time (between 8 and 10 min before extraction)
- Became more difficult to manage at 2X binder

AcryGen D471

- Similar to Flostrength (smooth, paste-like texture)
- Dried fairly quickly (about 30 to 60 seconds before extracting pellets)
- Same observations for both 1X and 2X

Cargill Plus 08702

- Similar to Colony (jelly-like texture)
- Dried at approximately 1 min
- Same observation for both 1X and 2X

Once again, the material losses observed in Series IV appeared to be appreciably lower than those observed in previous series. Part of this could be attributed to increased experience in pellet manufacture, but this may not be an important factor since this is a relative comparison of a GA binder with the inert binder formulation in each series.

Another factor was a different barium chloride. The fact that Series IV pellets showed lower weight loss after tumbling than did Series III pellets is believed to be due to the use of

a different lot of barium chloride. This new lot of barium chloride had a very small particle size; it was even finer than the particle size we created by ball milling. Because of the smaller particle size, the barium chloride dissolved more readily in our procedure. The dissolved barium chloride could have acted as another binder when it recrystallized during drying. Table 5-6 illustrates the effect of barium chloride particle size on the integrity of pellets prepared without binder. This is where the effect is most evident.

We had anticipated that barium chloride might act as a binder from the observation that smaller particle size barium chloride produces stronger control pellets, emphasizing the need in each series to include some pellets made without added binder. Barium nitrate, which is used in the live formulation, should act the same way (which is why a soluble barium salt was selected for the inert mixture). This particle size effect may not be noticed at ATK Lake City Plant because there is a longer time between preparing mixtures and casting pellets. However, the recrystallization of barium nitrate should contribute to the pellet integrity.

Recommendation

Based on specifications, physical properties, and performance of "inert formulations" in tumbling tests, we recommend five binders from different polymer classes for consideration as primer binders to replace GA. Each of the recommended binders performed as well as, or better than, Colony GA as a binder in our inert model pellets.

The recommended binders are the following:

- FlowStrength WSB40, Ashland Chemical, poly(acrylamide), solution
- Duracet 12 DB, Franklin, poly(vinyl acetate), latex
- Cargill Plus 08702, Cargill, dextrin, solid
- AcryGen D 471, Omnova Solutions, poly(styrene-acrylate), latex
- Rhoplex/Robond, Rohm & Haas, poly(vinyl acrylate), latex

These binders are each intended to represent different classes of synthetic polymeric adhesives. There are numerous commercially available polymers in each class that might perform quite well, and there are similar polymers offered by other manufacturers, which means that there are alternative potential suppliers. This is an important consideration in the selection of a binder.

Table 5-6—Percentage weight loss after tumbling test in pellets without binder

Series	Weight loss (%)	Attrition
I	76	Hand grinding
II	17	Ball milling
III	2.6	Better ball milling
IV	1.4	Very fine powder

Radial Crush Test

During a telephone conference with our partners, it was suggested that we use a radial crush test as a means of assessing the integrity of the pellets we manufactured. This type of test was used by ATK Launch Systems Division to evaluate similar pellets in the past. It involves applying an increasing compressive force across the plane of the pellet and recording failure events.

The FPL Engineering Mechanics Laboratory made measurements of the radial crush strength for Series II pellets. The apparatus that they used for this test is shown in Figure 5-4. They used a 5-lb (2.3-kg) load cell, the smallest available, to record the radial force (Fig. 5-5). Four pellets of each type were examined, and the detailed results are reported in Appendix C.

A representative load-deflection plot from a radial crush test is shown in Figure 5-5. No force is experienced at the load cell until the ram makes contact with the pellet. After contact, the force rises until some failure occurs, and if there is any irregularity at the edge of the pellet, that may break off before the pellet fails. After a small initial failure, the ram reconnects with the pellet and several more failure cycles occur. It is not clear which parameters are the most useful as a measure of pellet integrity. We considered four different parameters: (1) the ram displacement between initial contact and maximum force ($d@P_{max}$, in.), (2) the load value at maximum force (P_{max}, lb), (3) the area under the load-displacement plot up to maximum load (area under the curve to P_m), and (4) the total area under the load-displacement plot (total area under the curve).

The set of primer pellets made with the initial candidate binders, Series II, were subjected to the radial crush test. Data from this test showed considerable scatter, i.e., the standard deviation was rather large. Correlation plots were made comparing various parameters extracted from the crush tests with the results of the tumbling test (Fig. 5-6). In general, there was some correlation between the crush test data and the tumbling test results. The maximum force and the total area under the force-displacement curve are the parameters that best predicted friability loss; however, at very low friability loss (high pellet integrity), there was the largest scatter in the correlation plot. This means that the radial crush test data were not helpful in identifying the best binders.

The radial crush test is generally a good means of measuring pellet integrity, but the smallest transducer we had was not sufficiently sensitive for these small pellets. However, the overall correlation between the crush test and the tumbling test does add confidence to the friability results from the tumbling test. In speaking with Dr. Reed Blau, ATK Launch

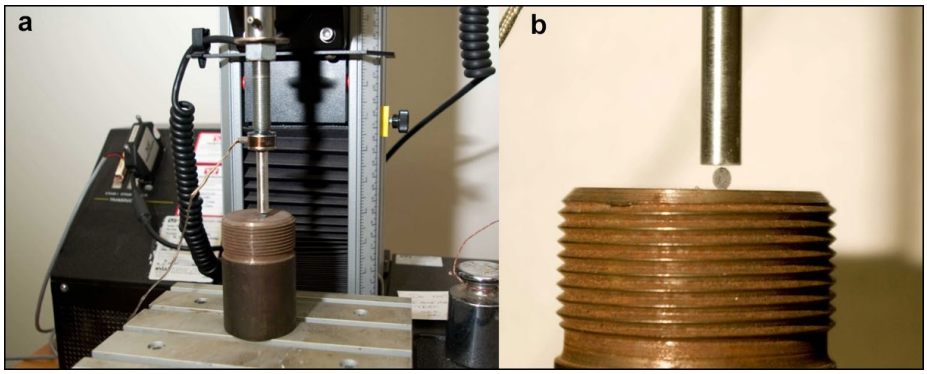

Figure 5-4. Apparatus used to measure radial crush strength: (a) image of pellet under compression ram; (b) close-up of pellet on stage.

Systems Division, he said that they measured about 25 pellets for each condition when using the radial crush test.

Vibrating Table Method

To help identify the best synthetic binders to replace GA in primer pellet formulations, we used a tumbling test that simulated material loss due to handling and was similar to tests used by the pharmaceutical industry to evaluate tablet integrity. We also tested material loss from some of the same primer pellets using a vibrating table (Model J-1-B, Syntron, Saltillo, Mississippi, USA), which was loaned to us by ATK Lake City. Part of our concern was to identify and define the optimum conditions for using the vibrating table as a pellet integrity test.

Previous measurements at ATK-LSG reported the pellet weight loss experienced after both 1- and 5-min exposure to the vibrating table set at the maximum amplitude. We observed that when the aforementioned model of vibrating table was set at the maximum setting, the sieve-cup assembly could not be confined to the vibrating table. The amplitude of vibration appeared to be too severe.

We learned from the instructions that there was an adjustment (air gap) that controlled the vibration amplitude. Furthermore, the instructions provided guidance on setting the amplitude while monitoring the current drawn by the table.

By placing the stainless steel sieve cup on the vibrating table with a small amount of powder in the bottom of the cup, it was easy to determine that the amplitude of displacement of the powder varied dramatically with location on the table.

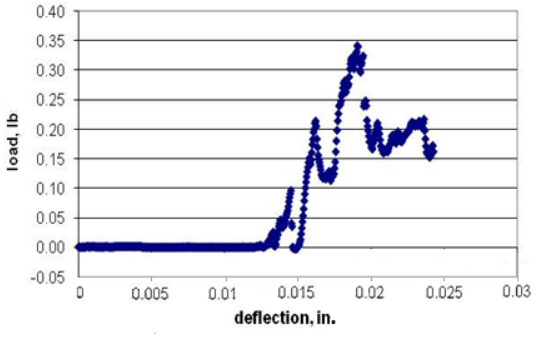

Figure 5-5. Load-deflection plot from a typical radial crush test.

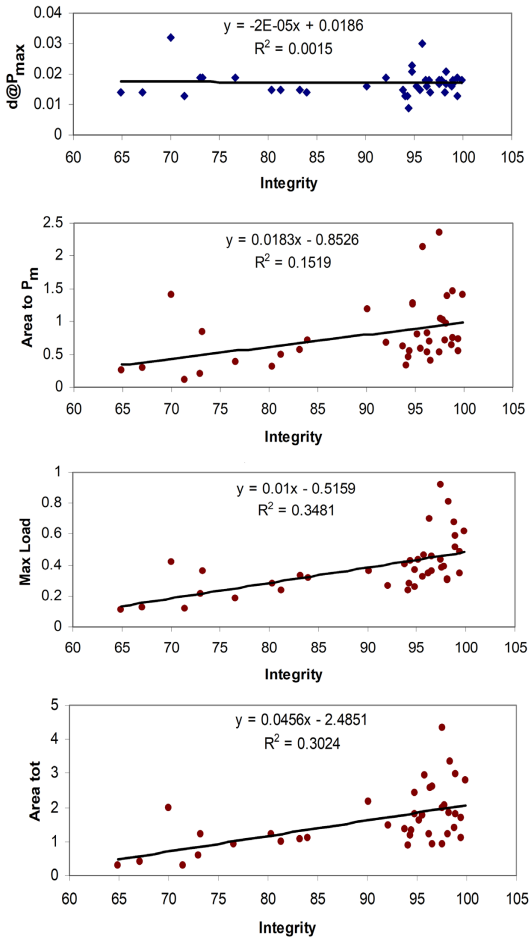

Figure 5-6. Correlation plots comparing radial crush test parameters with integrity (% material retained) measured by tumbling test.

Furthermore, the displacement amplitude was strongly dependent on good mechanical coupling of the cup to the table.

We were concerned about achieving reproducible results and sought to control the variables of cup location and coupling. In addition, we sought to identify a means for determining a table vibration amplitude appropriate for measuring the pellet integrity. To accomplish this, our machine shop fastened the sieve cup to the top of the vibrating table with a machine screw, so that it would always be in the same location.

The optimum vibration amplitude was determined by the weight loss experienced by certain pellets at different amplitude settings. The strategy we used to determine the optimum amplitude was to use pellets that exhibited the lowest integrity on the tumbling test (no binder, Series II) and pellets that showed high integrity (dextrin, Series IV). The optimum setting was chosen to include the entire range of weight loss observed with the friable pellets in the tumbling test and provide the best differentiation of integrity. The electrical current drawn by the vibrating table at this setting can be used to reproduce the favored condition.

Procedure

The following procedure was used to measure the integrity of pellets with the vibrating table:

- The amplitude for the vibrating table was set to 70. The vibrating table draws 0.58 amperes (0.34 amperes × 1.70) when operating at this setting.
- Pellet was weighed.
- Pellet was transferred to the cup on the vibrating table and the table was operated for 5 min.
- Contents of the cup were transferred into a 40-mesh sieve (0.420-mm openings).
- Pellet recovered from the sieve was weighed.

Results

In general, the vibrating table (when set to the above conditions) produced material losses similar to those experienced by the tumbling test. Tables 5-7, 5-8, and 5-9 give the results for three of the series of friability tests using the vibrating table and compare them with the results obtained using the tumbling test. Figures 5-7 through 5-12 are correlation plots that show a reasonable linear relationship between the friability results obtained by the two methods. The results cannot be expected to be exactly the same because material loss is a random process.

Furthermore, a smaller number of pellets were tested using the vibrating table, and thus, the standard deviation would be expected to be generally larger. When the losses are small, such as for the recommended binders, a small difference has a large effect. However, we found that the ranking of binders is about the same as that from the tumbling test, and the correlation between values determined by the tumbling test and vibrating table test are large and positive.

As was observed previously, the Series IV pellets showed lower weight loss after tumbling than did Series II and III pellets. Again, this is believed to be due to the use of a different lot of barium chloride as well as a gradual improvement in the quality of manufacturing the pellets achieved through experience. As noted previously, the particle size of the barium chloride played an important role due to its ease of dissolution with our short mixing time, and this may not play a role in the long times used for the commercial process.

For this reason, it is not advisable to compare results from one series with results from another series. However, the ranking of results (i.e., which was first, second, etc.) should be consistent within each series. We found that the results from tumbling tests and from vibrating table tests resulted in very similar ranking of binders.

Summary

After establishing a nonexplosive primer formulation, we tested the effect of different GA and synthetic binders. In summary, the three methods (tumbling, vibrating table, and radial crush tests) for determining pellet integrity showed relatively similar results. Because the three tests involved different forces on the pellets and the data sets were small, some variation in performance was expected. In general, the ranking of the binders appeared to show that barium nitrate provided some primer integrity. The tests showed that a binder was necessary to hold the pellets together. Some synthetic binders negatively affected pellet stability.

The data from the different series of tests cannot be combined because we improved the quality of the pellets with each subsequent series. The Hummel GA showed the best results, whereas on average the Quadra was the poorest. Of the synthetic binders, Ashland Chemical FlowStrength WSB40 poly (acrylamide) solution, Omnova Solutions AcryGen D 471 poly (styrene-acrylate) latex, Cargill Plus 08702 dextrin solid, and Franklin Duracet 12 DB poly (vinyl acetate) latex showed the best performances.

Table 5-7—Series IV percentage material loss from friability tests

	Vibrating table			Tumbling test		
Binder	Average material loss (%)	Standard deviation	No. of samples	Average material loss (%)	Standard deviation	No. of samples
Colony (1X)	1.18	0.62	2	0.6	0.5	12
Colony (2X)	0.65	N/A	1	0.4	0.3	12
Robond/Rho (1X)	0.70	0.64	2	0.5	0.3	12
Robond/Rho (2X)	0.78	0.35	3	0.3	0.3	12
PVOH 502 (1X)	2.13	0.69	3	0.9	0.5	12
PVOH 502 (2X)	2.96	1.30	3	1.7	1.3	12
Flostrength (1X)	0.71	0.18	3	0.05	0.06	12
Flostrength (2X)	1.18	0.57	3	0.6	0.8	12
Ashland K110 (1X)	6.95	0.60	3	4.4	0.6	12
Ashland K110 (2X)	3.59	1.05	3	1.7	1.1	12
AcryGen (1X)	1.85	0.70	3	0.4	0.3	12
AcryGen (2X)	2.43	1.11	3	0.6	0.4	12
Cargill Dextrin (1X)	0.73	0.12	3	0.3	0.2	12
Cargill Dextrin (2X)	0.62	0.32	3	0.3	0.4	12
No binder	1.40	0.29	2	1.4	0.8	12
Ashland K11L (1X)	4.12	0.13	3	3.8	0.6	12
Ashland K11L (2X)	3.28	0.29	3	3.4	1.6	12

Table 5-8—Series II percentage material loss from friability test

	Vibrating table			Tumbling test		
Binder	Average material loss (%)	Standard deviation	No. of samples	Average material loss (%)	Standard deviation	No. of samples
Acrodur 1X	9.90	0.94	3	9.9	1.35	12
Acrodur 2X	20.04	6.17	3	23.4	11.58	12
Dextrin 1X	3.82	2.66	3	0.6	0.33	12
Dextrin 2X	0.79	0.78	3	0.1	0.12	12
Pva B-25 1X	5.04	2.06	3	5.6	5.71	12
Pva B-25 2X	12.71	8.68	3	27	14.93	12
Colony 1X	4.02	1.57	3	4.4	2.55	12
Colony 2X	2.42	0.42	3	3.7	1.76	12
Duracet 1X	0.97	0.33	3	1.1	0.54	12
Duracet 2X	0.66	0.22	3	1.7	1.69	12
ButonalNX 1X	25.59	3.19	3	35.1	6.9	12
ButonalNX 2X	8.09	0.57	3	16.8	11.28	12
Polyacryl 1X	13.16	3.57	3	16	4.08	12
Polyacryl 2X	16.10	10.16	3	1.9	1.49	12
Hummel 1X	3.40	1.79	3	1.1	0.29	12
Hummel 2X	0.78	0.52	3	1.2	0.71	12
Cargill+ 1X	4.89	1.60	3	3.8	1.77	12
Cargill+ 2X	0.79	0.45	3	0.6	0.54	12
Glucidex 1X	5.17	4.18	3	5.9	2.99	12
Glucidex 2X	6.15	4.43	3	5.7	3.41	12
Quadra 1X	3.95	1.76	3	4.2	2.03	12
Quadra 2X	1.93	0.51	3	2.5	1.24	12
No binder	12.33	2.26	6	16.2	2.95	12

Table 5-9—Series III percentage material loss from friability test

	Vibrating table			Tumbling test		
Binder	Average material loss (%)	Standard deviation	No. of samples	Average material loss (%)	Standard deviation	No. of samples
Dextrin D (1X)	1.49	0.37	3	1.09	0.57	12
Dextrin D (2X)	1.11	1.12	3	0.71	0.35	12
Duracet (1X)	1.06	0.70	3	1.04	0.44	12
Duracet (2X)	2.00	1.29	3	1.85	0.43	12
Acronal (1X)	0.69	0.03	3	1.22	0.57	12
Acronal (2X)	1.84	0.65	3	1.84	0.54	12
Butanal (1X)	2.06	1.01	3	2.5	1.19	12
Butanal (2X)	1.68	0.39	3	1.88	0.44	12

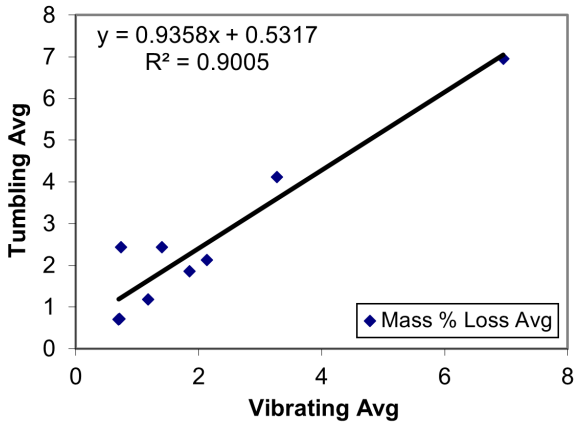

Figure 5-7. Correlation plot comparing Series IV loss on tumbling test to loss on vibrating table test for 1X concentration.

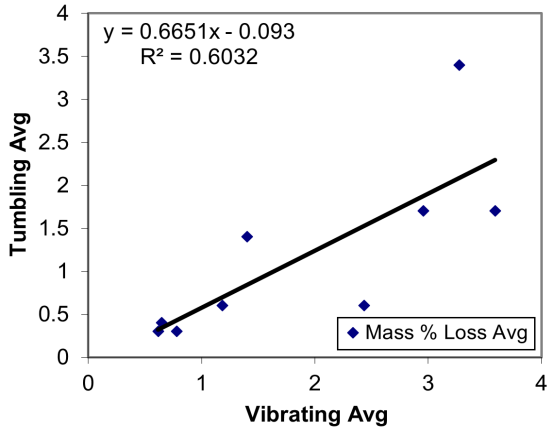

Figure 5-8. Correlation plot comparing Series IV loss on tumbling test to loss on vibrating table test for 2X concentration.

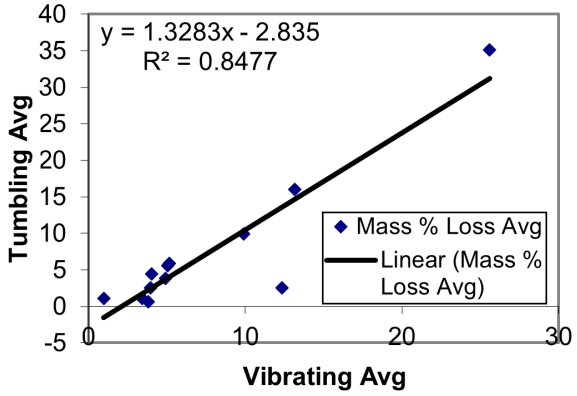

Figure 5-9. Correlation plot comparing Series II loss on tumbling test to loss on vibrating table test for 1X concentration.

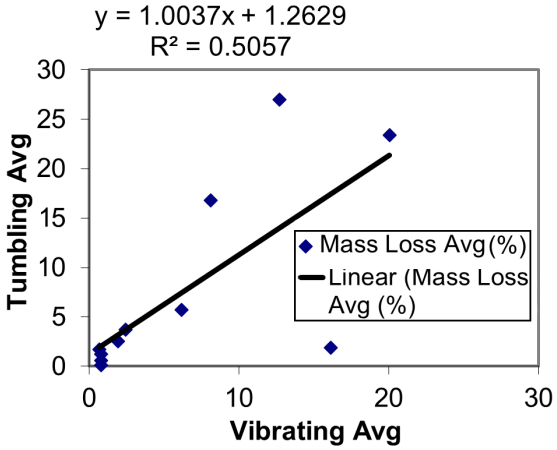

Figure 5-10. Correlation plot comparing Series II loss on tumbling test to loss on vibrating table test for 2X concentration.

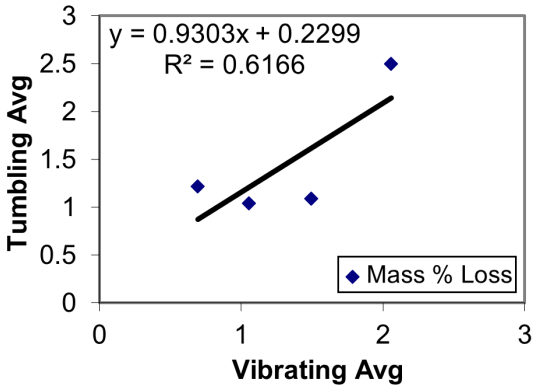

Figure 5-11. Correlation plot comparing Series III loss on tumbling test to loss on vibrating table test for 1X concentration.

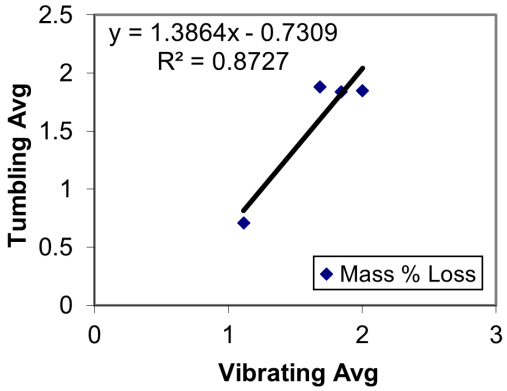

Figure 5-12. Correlation plot comparing Series III loss on tumbling test to loss on vibrating table test for 2X concentration.

Chapter Six
Recommendations

As part of the joint program to establish improved specifications for gum arabic (GA), the USDA Forest Service, Forest Products Laboratory (FPL), successfully developed methods for differentiating among GA samples and determining binder pellet integrity using an inert binder formulation. Unfortunately, the champion of this program at U.S. Army Joint Munitions Command (JMC) was assigned to other tasks, which became a higher priority. Thus, no evaluation of the synthetic primers was done at U.S. Army Armament Research Development and Engineering Center (ARDEC) at Picatinny Arsenal in New Jersey, JMC at Rock Island, Illinois, nor the Lake City Army Ammunition Plant (LCAAP) of Alliant Techsystems Inc. (ATK) at Independence, Missouri.

Overall Perspective

This chapter provides a summary of all portions of the FPL GA program on primer binder for small caliber ammunition. Phase One looked for better specifications for GA to prevent pellet fracture, which could lead to misfiring and potentially cause injury. Phase Two addressed the finding of a synthetic alternative to GA to avoid having to obtain the binder from the politically unstable region of sub-Saharan Africa. The work was successful in our laboratory, especially in developing a screening test that could be used as a quality control test for GA lots. However, the recommendations could not be verified in actual primer manufacture due to the program's loss of priority.

Phases One and Two

When we were challenged to evaluate different commercial GA samples, we wanted to understand what was known about the properties of GA that distinguish it from the other gums and other natural binders. The most unusual aspect is that, with GA, it is possible to make high-solids aqueous solutions that are low in viscosity. Other gums are often used as thickeners because a small percentage gives a large viscosity increase. Conversely, most gums at low percentage solids are used as thickeners in aqueous consumer and industrial products. As described in Chapter One, this is not due to the monomers in the GA polymers but instead to the morphology of the polymers. The carbohydrates in GA possess bushy side chains off the main protein or carbohydrate backbone giving the proteins a globular structure rather than a linear structure. These properties provide a very compact and stable structure for GA. The largely hydrophobic protein portion, which is attached to the very hydrophilic carbohydrate, appears to act as a macromolecular surfactant. Either a higher molecular weight or increased amount of protein, or both, could lead to improved binder performance. Although the literature shows that many methods have been used to characterize the GA structures, none of these seemed useful in a low sophistication plant nor were relatable directly to GA use as a binder. Molecular weight determination and a better rheology measurement would be useful. Further evaluation may find that some other materials may be suitable for improved performance. These include mesquite gum, which is produced in North America, and Acacia (sen) SUPER GUM™ (San-Ei Gen F.F.I., Inc., Osaka, Japan), which has more high molecular weight components.

In Chapter Two, we covered 16 methods used to compare GAs from three vendors. For two of the three GA vendors, we received samples from two different lots, whereas the samples from the third vendor were differently named samples of the same type. Before testing, we knew that both the Colony and Hummel were from Chad (*Acacia senegal* (L.) Willdenow), while the Brenntag (Quadra) gum was from Eritrea (*Acacia seyal*). Thus, six GA samples were tested in a blind fashion. All GAs passed the current product specifications, as well as some typical characterizations of GAs done by the military laboratories.

For most of these analyses, the Colony and Hummel products were very similar. However, there were differences in the apparent viscosity measurements, dry particle sizes, and dissolution rates. The physical property that distinguishes the Hummel GA most from the others is the greater amount of arabinogalactan-protein (AGP) fraction. This accounts for its high viscosity at low shear rate and shear thinning rheology. The presence of this AGP fraction could also be responsible for the better binder performance seen in Chapter Five. The food and beverage industry values the AGP component of GA for colloid stabilization.

It was instructive to revisit these measurements after evaluating these GA samples as adhesives in the later-developed inert formulations. We found that the Hummel GA was a superior binder to the other two. Thus, a measure of protein content and molecular weight might be important to binder performance.

Additional structure and rheology determinations were made in Chapter Three to better comprehend the role of GA as an effective binder using additional structural tests. The literature and test data supported the concept that the Hummel GA, with its greater content of high molecular weight components, generated the largest particle sizes from the GA solution.

In summary, the specifications for GA can be enhanced by incorporating the following measurements which were most effective in distinguishing the differences among the three GA samples. Gel permeation chromatography (GPC) successfully isolated and quantified the GA components. Brookfield and rotational viscosity were effective in demonstrating the presence of high molecular weight species by their effect on rheology. The shear force and peel force measurements directly demonstrated the difference in adhesion strength for the various GAs. Based on the research in Chapter Five, the inert binder formulation with the tumble test may be the most important specification because it tests the actual binder performance.

In Phase Two, we moved from evaluating the current GA binder to seeking other synthetic binders that could be made in the United States, thus removing the concern about obtaining a key ingredient from the politically volatile region of sub-Saharan Africa. The first task, covered in Chapter Four, was to create a list of all the reasonable adhesives and binders that we could think of for this application and then to remove those that did not fit the general criteria of high solids with low viscosity. This was in addition to the criteria that had been developed by the other members of the team. From the list of 35 polymer classes, 14 were selected for further evaluation.

The research in Chapter Five further decreased the number of recommended non-GA binders from specific products and selected the best alternative binders. Because these alternative binders had a variety of compositions, functional groups, and molecular weights and structures and no similarity to the GA, the only suitable route was to make up primer formulations using the binder candidates and test their performance. However, it was not feasible for us to safely test the active primer formulation; thus, an inert formulation was developed using the best nonexplosive substitutes for the reactive ingredients. After this was done, we were able to make primer pellets that were similar to those made with the commercial process. After looking at four test methods, including two that had been done by our partners with live primer formulations, a test method similar to that used for pharmaceutical pellets was adopted. The inert primer formulations were used to make pellets whose physical integrity could be determined by a simple tumbling test. This process was used to reduce the number of recommended replacement binders to five commercial products. Of these, dextrin was found to be the most similar to GA and is likely to be the most economically attractive. In addition, the tests showed that the finer particle size of barium chloride used to replace barium nitrate made less friable pellets, making the particle size of barium nitrate a possible commercial variable. Although this program was technically successful in all of its objectives, there was no commercial follow-up because the military support was cancelled. However, this report details all the work that was done, thereby clearly laying out the next steps to commercial reality if there is future interest.

Appendix A
Specification Testing of Three Gum Arabic (Acacia) Samples

To be certain that the gum arabics that FPL examined met the in-place specifications, Edward Hochberg and Richard Squillace of the Energetic Materials Analysis Laboratory (EMAL) were charged with performing the standard analysis methods on these samples. They performed specification tests on three samples of gum arabic. Two of the samples arrived at the same time and were logged in simultaneously. The third sample arrived later. The samples were all finely powdered and required no further grinding. The sample designations used are those that were written on the bags. These are listed below along with the EMAL login numbers:

Sample designation	EMAL login number
Hummel	07-239-1a
Colony	07-239-1b
Brenntag	07-260-1

The specification used was Federal Specification JJJ-A-20. The specification tests and requirements from section 3 are listed in the following display:

Requirement number	Test name	Specification requirement
3.2	Insoluble residue	No more than 1.0 percent by weight when tested as specified in 4.3.1
3.3	Total ash	No more than 4.0 percent by weight when tested as specified in 4.3.2
3.4	Acid-insoluble salt	No more than 0.5 percent by weight when tested as specified in 4.3.3
3.5	Moisture	No more than 15.0 percent by weight when tested as specified in 4.3.4
3.6	Tannin-bearing gums	None when tested as specified in 4.3.5
3.7	Starch and dextrin	None when tested as specified in 4.3.6
3.8	Identification	A flocculent or curdy white precipitate immediately formed when tested as specified in 4.3.7
3.9	Solubility	A free-flowing liquid, uniform in appearance and without any indication of ropiness when tested as specified in 4.3.8
3.10	Reduction of Fehling's solution	Not more than a trace of cuprous oxide shall be formed when tested as specified in 4.3.9
3.11	Acidity	
3.11.1	Inorganic acidity	The acacia shall have no inorganic acidity when tested as specified in 4.3.10.1
3.11.2	Organic acidity	No more than 0.4 percent as acetic acid when tested as specified in 4.3.10.2

EMAL was asked to test for all the above except identification.

The procedures used for each test are derived from the specification. Originally, the tests were run a single time for familiarization with the method, and then those tests with numerical results were run in duplicate. The procedures are described individually in the following sections.

Test 4.3.1 – Insoluble Residue

Five grams of sample were weighed and put into a 250-mL Erlenmeyer flask, and 100 mL of de-ionized water were added. Samples were dissolved with the use of a multi-pulse vortexer (Glas-Col, Terre Haute, Indiana, USA). This device continuously swirls the flask and its contents. After the samples were dissolved, 10 mL of 10% hydrochloric acid were added and the flasks were boiled gently for 15 min. While the samples were hot, filtering by suction was performed using a weighed Gooch crucible. The crucibles used for these analyses were perforated crucibles with removable fritted filter pads. The pads were Whatman Grade 934-AH porosity. The residues retained in the crucibles were washed with hot de-ionized water. The crucibles were dried at 100 °C, cooled in a desiccator, and weighed. The Colony sample had more residue than the other samples and the filtering was difficult. The duplicate tests for Colony were run using 1.5-g samples. The insoluble residue was calculated as follows:

$$IR = [(A - B)/C] \times 100$$

Where IR is weight percent of insoluble residue, A is weight of crucible and residue, B is weight of crucible, and C is weight of sample.

Test 4.3.2 – Total Ash

For this test, 2 to 4 g of sample were weighed into a preweighed crucible. The procedure says to incinerate (at not to exceed very dull redness) until the sample is free from carbon. The specification does not indicate the source of heat. Possibly a flame could be used. For these tests, a muffle furnace was used. It was found necessary to go to about 825 °C to make sure all carbon appeared gone. Even at those temperatures, the Colony sample was slightly darker than the others indicating possible carbon content. The spec method gives procedures for getting rid of the leftover carbon. Hot water is added to the charred mash, the mash collects on ashless filter paper, the residue and filter paper are incinerated until the ash is white, and then everything is reheated. This involves several transfers of material, which may cause further errors. Since the amount of ash is well below the threshold amount, these procedures were not used.

The crucibles were cooled in a desiccator and weighed. The total ash was calculated as follows:

$$TA = [(A - B)/C] \times 100$$

Where TA is weight percent of total ash, A is weight of crucible and residue, B is weight of crucible, and C is weight of sample.

Test 4.3.3 - Acid-Insoluble Ash

The ash from procedure 4.3.2 was transferred to a beaker. Then, 25 mL of 10% hydrochloric acid were added, and the contents of the beaker were boiled for 5 min. The contents of the beaker were filtered through a preweighed crucible, washed with hot de-ionized water, and reheated in the muffle furnace to about 825 °C.

The crucibles were cooled in a desiccator and weighed. In all three cases, the ash appeared to have been completely dissolved. The test was repeated in duplicate, but this time instead of incinerating a second time, the contents of the crucibles were filtered through Gooch crucibles with 9234-AH fritted filters and dried. The carbon content of the Colony sample was more apparent this way.

Test 4.3.4 – Moisture

Approximately 10 g of sample was weighed into a preweighed porcelain dish and dried at 100 to 105 °C for 5 h. The dish was cooled in a desiccator and reweighed. The dish was heated for another hour, cooled, and weighed to see if there was any further weight loss. In all three cases, there was no significant change after the first weighing. The moisture was calculated as follows:

$$M = [(A - B)/C] \times 100$$

M is weight percent moisture, A is weight of dish and sample before heating, B is weight of dish and sample after heating, and C is weight of sample.

Test 4.3.5 – Tannin-Bearing Gums

For this test, 2% solutions of the gums were prepared. Then, 0.1 mL of 0.3 N ferric chloride solution was added to a 10-mL aliquot. A 10% ferric chloride solution that approximates this concentration is available from Fisher Scientific (Waltham, Massachusetts, USA). Formation of a blackish coloration or blackish precipitate was taken as an indication of the presence of tannin-bearing gums.

Test 4.3.6 – Starch and Dextrin

For this test, 2% solutions of the gums were prepared. The solutions were boiled for several minutes and then allowed to cool. Three drops of a 0.10 N iodine solution were added. Formation of a bluish or reddish coloration was taken as an indication of starch or dextrin.

Test 4.3.8 – Solubility

Approximately 35 mL of sample were added to a 250-mL Erlenmeyer flask. Then, 100 mL of de-ionized water were added. The flask was stoppered and placed in the Glas-Col multi-pulse vortexer overnight. In the morning, the sample solution was poured into a beaker. It was inspected for uniformity in appearance, free flow, and absence of ropiness.

Test 4.3.9 – Reduction of Fehling's Solution

Fehling's reagent is a mixture of two solutions: copper sulfate and alkaline sodium tartrate. These solutions are mixed just before use. These solutions are available from Fisher Scientific. For this test, 2% solutions of the samples were prepared. Then 25 to 50 mL of the sample solutions were mixed with equal volumes of the mixed Fehling's solution, were brought to a boil, and were heated at boiling for 2 min. Samples were examined for the presence of cuprous oxide. This may be shown by a lessening of the blue color of the solution or formation of insoluble precipitate.

Test 4.3.10.1 – Inorganic Acidity

For this test, 1 g of sample was dissolved in 100 mL of de-ionized water until equally dispersed. Then, 1 mL of a 0.1 methyl orange solution was added. If inorganic acidity was absent, the color remained orange-yellow, whereas strong acidity turned the sample red.

Test 4.3.10.2- Organic Acidity

For this test, 1 g of sample was dissolved in 100 mL of de-ionized water until equally dispersed. Then, 0.1 mL of phenolphthalein indicator solution was added. The solution was titrated with 0.1 N sodium hydroxide solution until a permanent pink color was obtained. The organic acidity to acetic acid was calculated as follows:

$$AA = 6.0VN/W$$

Where AA is percent acidity as acetic acid, V is milliliters of sodium hydroxide solution used, N is normality of the sodium hydroxide solution, and W is weight of the sample.

Results

The following display gives the results of the duplicate analyses:

Property	Specification value	Hummel	Colony	Brenntag
Insoluble residue	1.0% max	0.05 0.05	0.21 0.22	0.09 0.09
Total ash	4.0% max	2.7 2.6	3.0 3.0	3.2 3.5
Acid-insoluble ash	0.5% max	0.06 0.04	0.12 0.10	0.00 0.00
Moisture	15.0% max	9.5 9.6	12.8 12.8	5.2 5.1
Tannin-bearing gums	None	None	None	None
Starch and dextrin	None	None	None	None
Solubility	Free-flowing liquid Uniform in appearance No ropiness	Pass	Pass	Pass
Reduction of Fehling's solution	Trace of cuprous oxide	Pass	Pass	Pass
Inorganic acidity	None	None	None	None
Organic acidity	0.4% max	0.26 0.27	0.34 0.35	0.31 0.31

Discussion

All three samples passed all the tests. The Hummel and Brenntag samples appeared cleaner. The Colony sample had more insoluble residue. Smaller aliquots of sample were needed to allow a reasonable rate of filtration. It also had more carbonaceous matter that resisted burning off in the total ash test. The amount was still so low that attempting to burn it all off by transferring it to another beaker, filtering into filter paper, and incinerating the filter paper could have caused further significant errors to accumulate. It also had slightly greater values of organic acidity and moisture.

Appendix B
Other Properties: Material Analysis on Three Gum Arabic Samples

The objective of this testing was to analyze three samples of gum arabic (GA) with instruments available at the Pyrotechnic Research & Technology Branch of the U.S. Army, Armament Research, Development and Engineering Center (ARDEC), Picatinny Arsenal, New Jersey, USA. The GA samples were subjected to the following tests: simultaneous differential thermal (SDT) analysis/thermogravimetric analysis, dispersion particle size analysis, surface area analysis, and scanning electron microscopy (SEM).

Samples

Sample A

Manufacturer: Colony

Sample Name: Gum Arabic

Lot #: 07/03286

Appearance: White to off white

Sample B

Manufacturer: Hummel

Sample Name: Gum Arabic

Lot #: GA-04-271

Appearance: White to off white

Sample C

Manufacturer: Quadra

Sample Name: Gum Arabic

Lot #: unknown

Appearance: White to off white

Procedure

Each sample of GA was tested according to the following procedures.

Simultaneous Differential Thermal Analysis/Thermogravimetric Analysis

The thermal analysis was performed on a TA Instruments (New Castle, Delaware, USA) SDT Q600. The analysis was performed in a dry, inert gas environment (99% pure argon) at a flow rate of 25 to 100 mL/min. The sample was run from ambient to 400 °C at a rate of 10 ± 0.1 °C/min.

The reaction temperature and the weight loss of the sample were collected and plotted with temperature (Figs. B-1 to B-3). Transitions were marked with a peak when the specimen absorbed (endothermic) or released (exothermic)

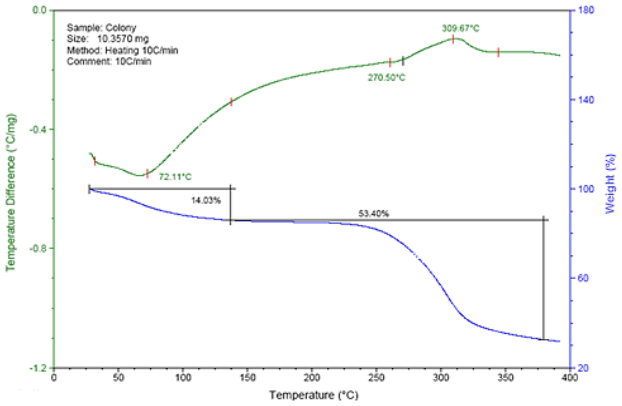

Figure B-1. Simultaneous differential thermal analysis/thermogravimetric analysis summary for Colony sample.

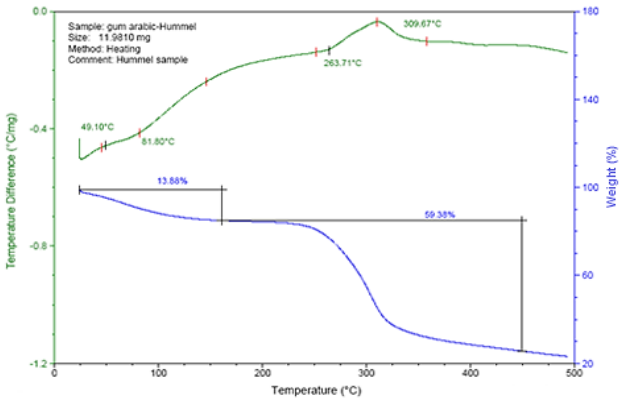

Figure B-2. Simultaneous differential thermal analysis/thermogravimetric analysis summary for Hummel sample.

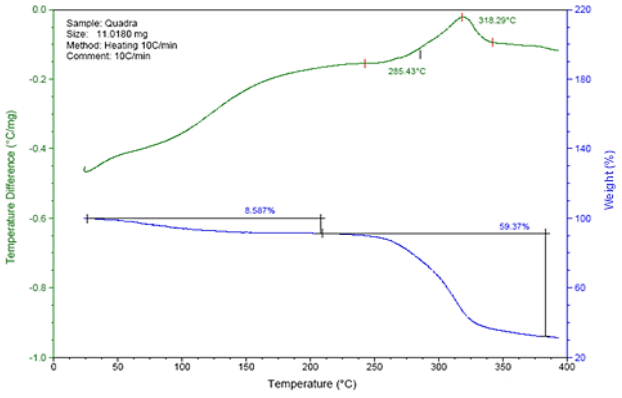

Figure B-3. Simultaneous differential thermal analysis/thermogravimetric analysis summary for Quadra sample.

energy. The analysis was conducted on all three GA samples from the same lots used in FPL analyses (Table B-1).

Dispersion Particle Size Analysis

Particle size analysis was performed on a Microtrac (Montgomeryville, Pennsylvania, USA) S3500 in accordance with ISO 13320-1. A small amount of each GA sample was then transferred to the particle size analyzer.

The flow rate of the instrument was set to 35% (measured vs. full power) for samples A, B, and C. Each sample was sonicated for 60 s at 25 W prior to measuring the particle size. The refractive index of the titanium dioxide was set to 1.476. Each sample was run three times, and the results are the average of three measurements (Table B-2).

Solid Surface Area Analysis

The surface area of the samples was measured with a Micromeritics (Norcross, Georgia, USA) TriStar surface area analyzer using the process of physical adsorption. A clean, dry sample of GA was placed into a sample tube, and the sample was evacuated. The sample was cooled to cryogenic temperature and dosed with the adsorbate gas (N_2). The adsorbed gas, saturation pressure, absolute pressure, and sample mass were used to calculate the adsorption and surface area of the sample.

Prior to testing surface area, the GA samples were heated to 50 °C for 4 h under nitrogen purge to remove any adsorbed gases or moisture.

Scanning Electron Microscopy

The GA samples were placed on brass analysis stubs and placed into a JEOL (Tokyo, Japan) JSM-6380LV scanning electron microscope. The samples were run as received without any coating or processing. The microscopy power was kept low (to prevent imaging problems), and images were taken at varying magnifications under vacuum.

Table B-1—Thermal analysis summary

Sample	Peak 1 (°C)	Peak 1 weight loss (%)	Peak 2 (°C)	Peak 2 weight loss (%)
A, Colony	72.11	14.03	309.67	53.40
B, Hummel	81.80	13.88	309.67	59.38
C, Quadra	—	—	318.29	59.37

Table B-2—Particle size analysis summary, values in micrometers (μm)

Sample	10%	50%	90%	MV[a]
A, Colony	15.45	46.34	86.15	49.16
B, Hummel	27.64	79.38	181.3	97.81
C, Quadra	23.14	57.79	133.3	76.37

[a]MV, mean diameter of the volume distribution.

Results

The results of each test are presented below. A discussion of each test follows the results.

Simultaneous Differential Thermal Analysis/Thermogravimetric Analysis

FPL analysis of the data is that the first transition is too broad for a decent comparison of the glass transition temperatures for the three samples and the second indicates decomposition of the materials (Figs. B-1 to B-3 and Table B-1).

Dispersion Particle Size Analysis

All GA samples exhibited a single distribution, as seen in Figure B-4. The samples appeared to have a maximum between 10 and 100 microns. The Colony sample had a tighter distribution than both the Hummel and Quadra samples. The Quadra and Hummel samples were both similar in size whereas the Colony exhibited a smaller size.

Solid Surface Area Analysis

All samples had the same appearance of a fine white to off white powder with a surface area 0.55 m^2/g or less. The order of increasing surface area (smallest to highest) was Colony, Hummel, and Quadra (Table B-3).

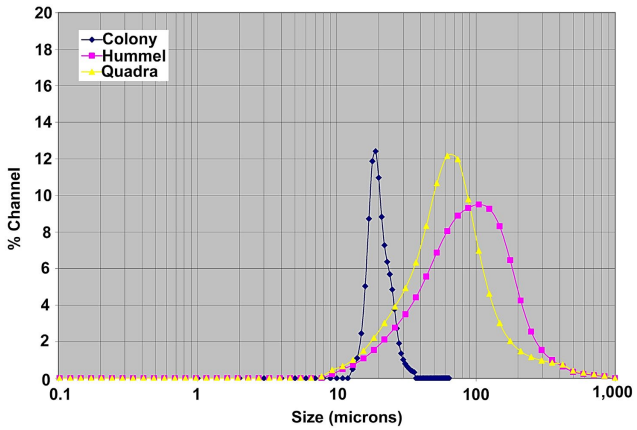

Figure B-4. Particle size analysis summary for gum arabic samples.

Table B-3—Surface area analysis results

Sample	Manufacturer	Surface area (m^2/g)
A	Colony	0.380
B	Hummel	0.443
C	Quadra	0.551

Scanning Electron Microscopy

The results of the SEM analysis are shown in Figures B-5 through B-7. FPL evaluation resulted in the opinion that the Colony seemed to be ground whereas the Quadra and Hummel were probably spray-dried due to the spherical shape.

Conclusions

The results of the tests performed on the GA samples indicate that macroscopically they all appeared very similar. All the samples exhibited similar thermal profiles after SDT analysis.

Scanning electron microscopy showed that the Quadra and Hummel were similar in size and that both exhibited round structures. The distribution displayed for particle size of both Quadra and Hummel were similar (between 70 and 90 um). Not only did Quadra and Hummel have larger particle size, they also exhibited larger surface area compared with Colony. The samples decreased in surface area (largest to smallest) in the following order: Quadra, Hummel, and Colony. The distribution of Colony was tighter with a smaller particle size of 49 microns, which was also seen in the SEM images. Colony showed a flaky structure, which was different than the round structure of the other two samples.

Although all samples exhibited a similar thermal profile, Quadra and Hummel were distinctively similar in both size and structure, whereas Colony displayed differences in these areas.

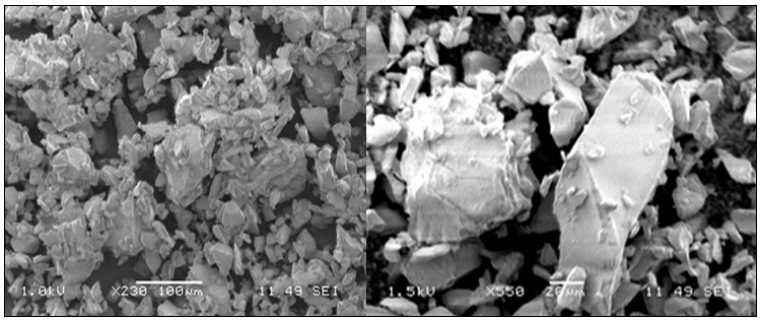

Figure B-5. SEM images of Colony gum arabic at 230× (left) and 550× (right) magnification.

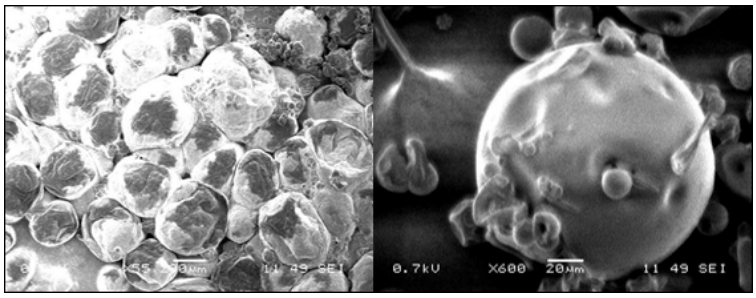

Figure B-6. SEM images of Hummel gum arabic at 55× (left) and 600× (right) magnification.

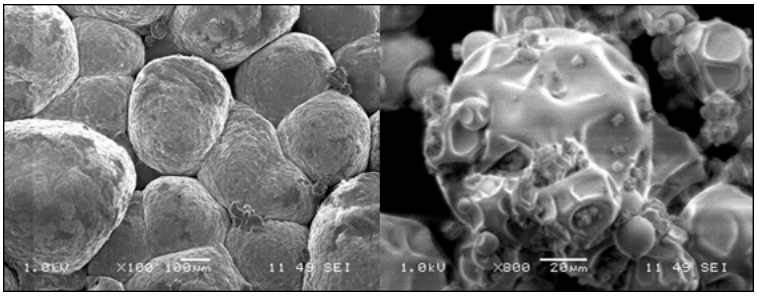

Figure B-7. SEM images of Quadra gum arabic at 100× (left) and 800× (right) magnification.

Appendix C
Radial Crush Strength Data

Binder name	Max load	$d@P_{max}$	Area to P_m	Area total	Note
Butanal NS 198 (1X)					
1st	0.291	0.0145	0.000276	0.000676	
2nd	0.264	0.0171	0.000164	0.000297	
3rd	0.484	0.0098	0.000371	0.001857	
4th	0.567	0.0199	0.001702	0.002594	
average	0.402	0.015	0.628	1.356	
standard deviation	0.147	0.004	0.721	1.059	
Butanal NS 198 (2X)					
1st	0.413	0.0154	0.000708	0.003962	
2nd	0.565	0.0162	0.001121	0.002373	
3rd	0.373	0.0239	0.000684	0.001943	
4th	0.471	0.0159	0.000245	0.002147	
average	0.455	0.018	0.689	2.606	
standard deviation	0.084	0.004	0.358	0.921	
Acrodur 950L (1X)					
1st	0.310	0.0119	0.000605	0.001175	
2nd	0.343	0.0264	0.003359	0.004259	
3rd	0.414	0.0108	0.000329	0.001793	
4th	0.383	0.0137	0.000454	0.001388	
average	0.363	0.016	1.187	2.154	
standard deviation	0.045	0.007	1.452	1.427	
Acrodur 950L (2X)					
1st	0.275	0.0150	0.000724	0.002071	
2nd	0.169	0.0141	0.000344	0.000835	
3rd	0.087	0.0290	0.000178	0.000245	
4th	0.202	0.0169	0.000291	0.000549	
average	0.183	0.019	0.384	0.925	
standard deviation	0.078	0.007	0.237	0.801	
Dextrin D200 (1X)					
1st	0.536	0.0132	0.000534	0.001379	
2nd	0.338	0.0130	0.000230	0.001587	
3rd	0.372	0.0119	0.000561	0.001851	
4th	0.692	0.0121	0.000864	0.001962	
average	0.485	0.013	0.547	1.695	
standard deviation	0.163	0.001	0.259	0.263	
Dextrin D200 (2X)					
1st	0.449	0.0174	0.001334	0.003774	
2nd	0.803	0.0224	0.003470	0.003847	
3rd	0.676	0.0147	0.000512	0.001341	
4th	0.530	0.0161	0.000328	0.002167	
average	0.614	0.018	1.411	2.782	
standard deviation	0.157	0.003	1.441	1.235	

Binder name	Max load	$d@P_{max}$	Area to P_m	Area total	Note
PVA B-25 (1X)					
1st	0.462	0.0094	0.000474	0.001771	
2nd	0.622	0.0109	0.001109	0.002007	
3rd	0.192	0.0080	0.000061	0.000149	Had crack when started
4th	—	—	—	—	Only three in jar
average	0.425	0.009	0.548	1.309	
standard deviation	0.217	0.001	0.528	1.012	
PVA B-25 (2X)					
1st	0.283	0.0140	0.000230	0.000996	
2nd	0.193	0.0162	0.000133	0.000622	
3rd	0.077	0.0144	0.000107	0.000230	
4th	0.249	0.0305	0.000356	0.000475	Not round, missing chunk
average	0.201	0.019	0.207	0.581	
standard deviation	0.090	0.008	0.113	0.321	
Duracet 12 DB (1X)					
1st	0.645	0.0167	0.001339	0.003276	
2nd	0.431	0.0144	0.000473	0.001824	
3rd	0.531	0.0241	0.003576	0.004982	
4th	0.464	0.0132	0.000475	0.001896	
average	0.518	0.017	1.466	2.995	
standard deviation	0.094	0.005	1.465	1.484	
Duracet 12 DB (2X)					
1st	0.753	0.0178	0.001917	0.004507	
2nd	0.943	0.0178	0.001572	0.002959	
3rd	0.628	0.0153	0.000486	0.002748	
4th	0.913	0.0180	0.001556	0.003114	
average	0.809	0.017	1.383	3.332	
standard deviation	0.147	0.001	0.621	0.797	
Butonal NX 1129 (1X)					
1st	0.063	0.0135	0.000038	0.000049	
2nd	0.152	0.0188	0.000188	0.000318	
3rd	0.168	0.0161	0.000682	0.000767	
4th	0.067	0.0074	0.000120	0.000097	
average	0.113	0.014	0.257	0.308	
standard deviation	0.055	0.005	0.290	0.328	
Butonal NX 1129 (2X)					
1st	0.282	0.0127	0.000600	0.000805	
2nd	0.471	0.0167	0.000693	0.002025	
3rd	0.347	0.0151	0.000557	0.001096	
4th	0.231	0.0169	0.000381	0.000389	
average	0.333	0.015	0.558	1.079	
standard deviation	0.104	0.002	0.131	0.694	
Acronal Opt. 120 (1X)					
1st	0.561	0.0173	0.000892	0.001996	
2nd	0.254	0.0144	0.000389	0.000813	
3rd	0.395	0.0170	0.001175	0.001577	
4th	0.538	0.0167	0.000762	0.002115	
average	0.437	0.016	0.805	1.625	
standard deviation	0.142	0.001	0.326	0.589	

Binder name	Max load	$d@P_{max}$	Area to P_m	Area total	Note
Acronal Opt. 120 (2X)					
1st	0.457	0.0161	0.001222	0.001962	
2nd	0.298	0.0180	0.000286	0.001893	
3rd	0.439	0.0189	0.001326	0.002045	
4th	0.351	0.0186	0.001357	0.002041	
average	0.386	0.018	1.048	1.985	
standard deviation	0.075	0.001	0.511	0.073	
Polyacr. 434949 (1X)					
1st	0.212	0.0136	0.000667	0.000855	
2nd	0.262	0.0126	0.000411	0.001083	
3rd	0.330	0.0143	0.001048	0.001387	
4th	0.450	0.0154	0.000705	0.001126	
average	0.313	0.014	0.708	1.113	
standard deviation	0.103	0.001	0.262	0.218	
Polyacr. 434949 (2X)					
1st	0.247	0.0142	0.000458	0.001258	
2nd	0.225	0.0142	0.000544	0.000997	
3rd	0.281	0.0140	0.001015	0.001192	
4th	0.468	0.0138	0.000834	0.001401	
average	0.305	0.014	0.713	1.212	
standard deviation	0.111	0.000	0.258	0.168	
Cargill Pl. 08505 (1X)					
1st	0.274	0.0173	0.000475	0.000749	
2nd	0.299	0.0206	0.000892	0.001315	
3rd	0.394	0.0161	0.000493	0.001837	
4th	0.429	0.0163	0.000277	0.000979	
average	0.349	0.018	0.534	1.220	
standard deviation	0.074	0.002	0.258	0.472	
Cargill Pl. 08505 (2X)					
1st	0.508	0.0163	0.000748	0.001606	
2nd	0.407	0.0153	0.000369	0.000812	
3rd	0.483	0.0158	0.001071	0.001442	
4th	0.248	0.0162	0.000713	0.001172	
average	0.347	0.019	0.727	1.110	
standard deviation	0.117	0.006	0.287	0.265	
Robond PS-2020 (1X)					
1st	0.251	0.0276	0.000756	0.001016	
2nd	0.200	0.0143	0.000107	0.000493	
3rd	0.534	0.0197	0.001790	0.002029	
4th	0.451	0.0162	0.000682	0.001293	
average	0.359	0.019	0.834	1.208	
standard deviation	0.159	0.006	0.700	0.640	
Robond PS-2020 (2X)					
1st	0.497	0.0148	0.000353	0.001004	
2nd	0.184	0.0134	0.000146	0.000749	Front fell off, split
3rd	0.474	0.0141	0.000782	0.000994	
4th	0.275	0.0145	0.000343	0.000904	
average	0.358	0.014	0.406	0.913	
standard deviation	0.153	0.001	0.268	0.118	

Binder name	Max load	$d@P_{max}$	Area to P_m	Area total	Note
PVP K15 (1X)					
1st	0.209	0.0137	0.000190	0.001460	
2nd	0.224	0.0149	0.000350	0.000613	
3rd	0.280	0.0165	0.000258	0.001004	
4th	0.394	0.0140	0.000472	0.001798	
average	0.277	0.015	0.317	1.219	
standard deviation	0.084	0.001	0.122	0.518	
PVP K15 (2X)					
1st	0.659	0.0198	0.001003	0.001519	
2nd	0.567	0.0157	0.000572	0.000942	
3rd	0.289	0.0152	0.000165	0.000732	
4th	0.216	0.0162	0.000345	0.000505	Crumbled
average	0.433	0.017	0.521	0.925	
standard deviation	0.214	0.002	0.362	0.435	
Rhoplex MC 1834P (1X)					
1st	0.336	0.0166	0.000732	0.001751	
2nd	0.210	0.0154	0.000225	0.000866	
3rd	0.256	0.0303	0.001402	0.002082	Odd-shaped piece
4th	0.265	0.0150	0.000343	0.001124	
average	0.267	0.019	0.676	1.456	
standard deviation	0.052	0.007	0.531	0.559	
Rhoplex MC 1834P (2X)					
1st	0.352	0.0244	0.001990	0.002705	
2nd	0.281	0.0221	0.000921	0.001588	
3rd	0.248	0.0153	0.000419	0.001274	
4th	0.351	0.0238	0.000574	0.001858	
average	0.308	0.021	0.976	1.856	
standard deviation	0.052	0.004	0.708	0.614	
Sancure 20025 (1X)					
1st	0.076	0.0193	0.000048	0.000260	Crumbled
2nd	1.393	0.0605	0.005147	0.006964	Crumbly/odd shape
3rd	0.127	0.0196	0.000267	0.000613	Crumbly/odd shape
4th	0.069	0.0300	0.000126	0.000070	
average	0.416	0.032	1.397	1.977	
standard deviation	0.652	0.019	2.502	3.332	
Sancure 20025 (2X)					
1st	0.078	0.0143	0.000085	0.000048	Crumbly
2nd	0.091	0.0118	0.000081	0.000090	Crumbly
3rd	0.184	0.0126	0.000170	0.000750	Crumbled during setup
4th	—	—	—	—	
average	0.118	0.013	0.112	0.296	
standard deviation	0.058	0.001	0.050	0.393	
Acronal 296 D na (1X)					
1st	0.434	0.0160	0.001097	0.002919	
2nd	0.331	0.0153	0.000587	0.002119	
3rd	0.320	0.0382	0.002920	0.003419	
4th	0.385	0.0143	0.000516	0.001184	
average	0.367	0.021	1.280	2.410	
standard deviation	0.053	0.012	1.124	0.977	

Binder name	Max load	$d@P_{max}$	Area to P_m	Area total	Note
Acronal 296 D na (2X)					
1st	0.316	0.0256	0.002261	0.002906	
2nd	0.276	0.0204	0.001061	0.001651	
3rd	0.182	0.0224	0.000436	0.000804	
4th	—	—	—	—	
average	0.258	0.023	1.253	1.787	
standard deviation	0.069	0.003	0.927	1.057	
PVP/VA S-630 (1X)					
1st	0.070	0.0144	0.000071	0.000219	
2nd	0.100	0.0101	0.000209	0.000289	
3rd	0.084	0.0142	0.000101	0.000030	
4th	0.238	0.0160	0.000768	0.001108	
average	0.123	0.014	0.287	0.411	
standard deviation	0.078	0.003	0.326	0.477	
PVP/VA S-630 (2X)					
1st	0.551	0.0207	0.003199	0.003886	
2nd	0.179	0.0226	0.000297	0.001466	
3rd	0.395	0.0113	0.000241	0.001231	
4th	0.426	0.0182	0.000314	0.001696	
average	0.388	0.018	1.013	2.070	
standard deviation	0.155	0.005	1.458	1.225	
Glucidex 9 (1X)					
1st	0.202	0.0145	0.000343	0.000618	
2nd	0.177	0.0151	0.000414	0.001178	
3rd	0.242	0.0128	0.000199	0.000933	
4th	0.306	0.0100	0.000330	0.000827	
average	0.232	0.013	0.321	0.889	
standard deviation	0.056	0.002	0.089	0.233	
Glucidex 9 (2X)					
1st	0.389	0.0169	0.001046	0.002027	
2nd	0.090	0.0095	0.000222	0.000266	
3rd	0.232	0.0115	0.000168	0.000982	
4th	0.393	0.0156	0.000387	0.001397	
average	0.276	0.013	0.456	1.168	
standard deviation	0.145	0.003	0.404	0.739	
Colony (1X)					
1st	0.281	0.0142	0.000230	0.000559	
2nd	0.389	0.0152	0.000627	0.002610	
3rd	0.366	0.0162	0.001098	0.002642	
4th	0.259	0.0128	0.000367	0.001279	
average	0.324	0.015	0.581	1.772	
standard deviation	0.063	0.001	0.382	1.029	
Colony (2X)					
1st	0.794	0.0169	0.000993	0.002894	
2nd	0.671	0.0158	0.000815	0.001866	
3rd	0.641	0.0139	0.000656	0.001966	
4th	0.703	0.0154	0.000801	0.003556	
average	0.702	0.016	0.816	2.571	
standard deviation	0.066	0.001	0.138	0.803	

Binder name	Max load	$d@P_{max}$	Area to P_m	Area total	Note
Hummel (1X)					
1st	0.579	0.0187	0.000586	0.001397	
2nd	1.033	0.0187	0.001426	0.002737	
3rd	0.490	0.0170	0.000788	0.002195	
4th	0.258	0.0169	0.000229	0.000882	
average	0.590	0.018	0.757	1.803	
standard deviation	0.325	0.001	0.502	0.824	
Hummel (2X)					
1st	0.443	0.0170	0.000931	0.001377	
2nd	0.412	0.0160	0.000325	0.000585	
3rd	0.994	0.0153	0.000746	0.001741	
4th	0.871	0.0149	0.000544	0.001892	
average	0.680	0.016	0.636	1.399	
standard deviation	0.296	0.001	0.261	0.584	
Quadra (1X)					
1st	0.482	0.0421	0.000652	0.001747	Odd shape
2nd	0.232	0.0172	0.000357	0.001114	
3rd	0.491	0.0211	0.001646	0.002379	
4th	0.656	0.0377	0.005898	0.006561	Pieces crumbled off
average	0.465	0.030	2.139	2.950	
standard deviation	0.175	0.012	2.566	2.462	
Quadra (2X)					
1st	1.321	0.0181	0.003299	0.006246	
2nd	0.592	0.0182	0.001502	0.003351	
3rd	0.989	0.0159	0.001201	0.003150	Looked cracked to start
4th	0.784	0.0209	0.003441	0.004559	
average	0.922	0.018	2.361	4.326	
standard deviation	0.312	0.002	1.173	1.423	
No Binder					
1st	0.342	0.0191	0.000787	0.001825	
2nd	0.230	0.0148	0.000163	0.000126	
3rd	0.148	0.0145	0.000358	0.000808	
4th	0.209	0.0134	0.000669	0.001235	
average	0.232	0.015	0.494	0.998	
standard deviation	0.081	0.002	0.285	0.716	