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Analyzing the strength of different mixtures of prehistoric pine pitch glue.

by

Daniel M. Parker

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To the Graduate Faculty:

The members of the committee appointed to examine the thesis of Daniel Parker find it satisfactory and recommend that it be accepted.

Charles Speer, PhD
Major Advisor

Katherine Reedy, PhD
Committee Member

Leif Tapanila, PhD
Graduate Faculty Representative

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Analyzing the strength of different mixtures of prehistoric pine pitch glue.

Thesis Abstract – Idaho State University (2018)

Pine pitch glue has been a minimally studied artifact by archaeologists that has been used for thousands of years and still, very little is known about it. The concepts to be discussed in this thesis will be defining what pine pitch glue is and how it is made. Additionally, the many possible applications of pine pitch glue will be explored and compared to other glues and adhesives in prehistory. Several examples of pine pitch glue were created for experiments to test the potential strength for these glues in comparison to a base and two exemplars, in hide glue and modern wood glue. These experiments were designed with the aid of knowledge acquired through previous experiments exploring this topic for a senior research paper. This previous research will be discussed. These experiments required the development of a custom jig to accommodate the strength testing. A variety of samples determining strength provided data that would create a much-needed background on these glues and why they were or were not used in prehistory.

Key Words: Adhesive, Glue, Archaeology, Prehistoric, Pine Pitch

Introduction

Most archaeology scholars understand that prehistoric glues are a relatively simple compound of varying percentages of natural materials. However, the mechanical properties of these compounds are unknown. An experiment was conducted to examine these properties, and to find the strength behind these compounds. Samples of pine pitch glues were created, and their strength was tested to discover what type of force they could handle. The creation of typical pine pitch glue is a combination of pine pitch, ash, and a fibrous binder.

In order to avoid any ambiguity, several definitions are necessary. Pine pitch is a liquid from trees can be defined in many ways, and this is one of the main ingredients for this adhesive. Sap is defined as the fluid, chiefly water with dissolved sugars and mineral salts that circulate in the vascular system of a plant (Mitkidou, 2007). Pitch can best be described as several viscoelastic polymers (Mitkidou, 2007). Pitch can be natural or manufactured, derived from petroleum, coal tar or plants. Various forms of pitch may also be called tar or bitumen. Pitch produced from plants is also known as resin, a sticky flammable organic substance, insoluble in water, exuded by some trees and other plants. Tar is a dark, thick, and flammable liquid that is distilled from wood or coal (Mitkidou, 2007). Bitumen is a black viscous mixture of hydrocarbons obtained from natural petroleum distillation (Pfeiffer, 1940).

For this paper the main adhesive will be referred to as pine pitch glue. The base samples were a simple combination of pine pitch and ash mixtures. Additionally, for other samples various binders including dried leaf, bark, and bees wax were added to the base sample mixture. These binders were added to investigate if any variations in strength and holding ability existed between these samples. Each sample was tested several times until the glue strength peaked and the strength began to decline or fail. To further understand how these glues may have functioned in the past, it is best to identify what makes these glues operate most efficiently in terms of strength. This also provides help in asking the question why were some glues used at one time for one purpose and not used in other instances. Some primary examples will be compared to a birch bark tar that is mainly found in the European continent. Archaeological sites around the world will be also be discussed where glues and adhesives have been discovered.

This thesis is organized into several main sections including: Background, Methods, Results, Discussion, Applications, and Conclusions. Background will analyze where the trees are found and where the pitch could be available, as well as a brief history of prehistoric glue in general. Methods will describe how the experiment overall as planned out and how the tools were going to be used. Results will discuss how the experiment resulted and compare the pine pitch glues to each other. Discussion will tie everything back together and start to answer some questions. Applications will introduce some archaeology problems, experimental archaeology review, and how pine pitch glue could apply to different tool technology. Finally the conclusion will introduce some future research and bring in a final analysis of the glue results.

Background

Tree Ecology

Similar forms of glue have been used all over the world. For the North American continent, it is common to find a pine pitch based glue, where in Europe it was a birch tar base. When collecting the parts to make the glue, gathering pine sap is a simpler process, because when a pine tree is wounded it will leach sap out to cover itself up. Birch sap is a different process, to gather the sap from a birch tree the bark itself needs to be cooked to release the sap. When harvesting from a pine tree the tree will live for a long time if done properly. Harvesting from a birch tree will bring a completely different result. The bark must be removed in order to acquire the sap it holds. This in turn this will kill the tree because it does not have anything to protect itself with. Something to consider is what types of environments Douglas Fir and Birch trees grow in. The sap that was collected for this experiment came from a Pseudotsuga menziesii, also known as Douglas Fir.

The Douglas Fir tends to grow in a hardiness zone between 4-6, which takes up most of the Northern half of North America (Figure 1). These temperature ranges are negative 30 Fahrenheit and up. In Europe the overall area where the hardiness zone in which Douglas Fir can grow reliably is limited. Central and Eastern Europe have zones in which they could possibly thrive, but it is on the low end of the hardiness zone. Most of Europe has zones that are 7-9; these temperatures could hold the Douglas Fir trees but they do not seem to be nearly as common. The *Betula papyrifera*, or Birch tree can handle even colder climates so they can grow in more places than Douglas Fir. Birch trees have a hardiness rating of about 2-7, this allows them a larger range to grow and expand in about 90 percent of Europe and even towards Russia. The hardiness zones for the Birch trees are roughly negative 50 and up (Figure 2).

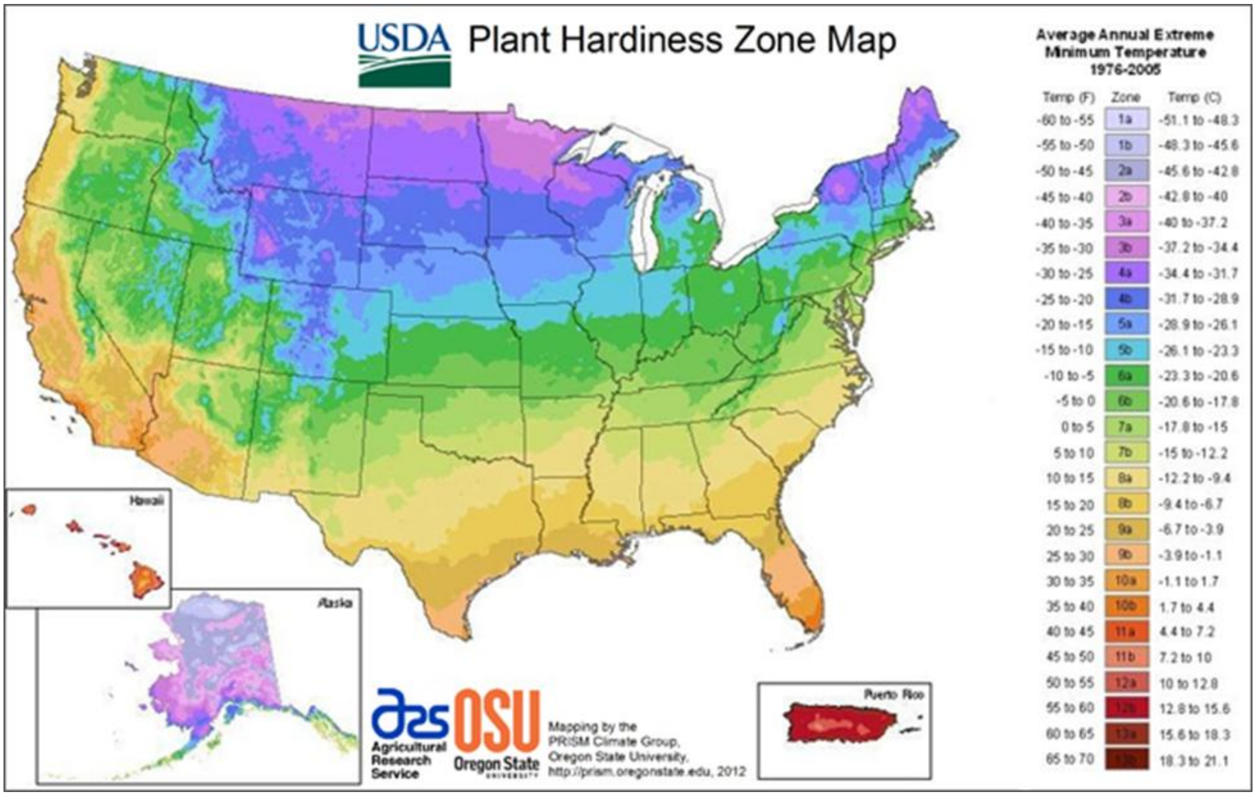


Figure 1 – This photo shows an approximate location of the hardiness zones within the United States.

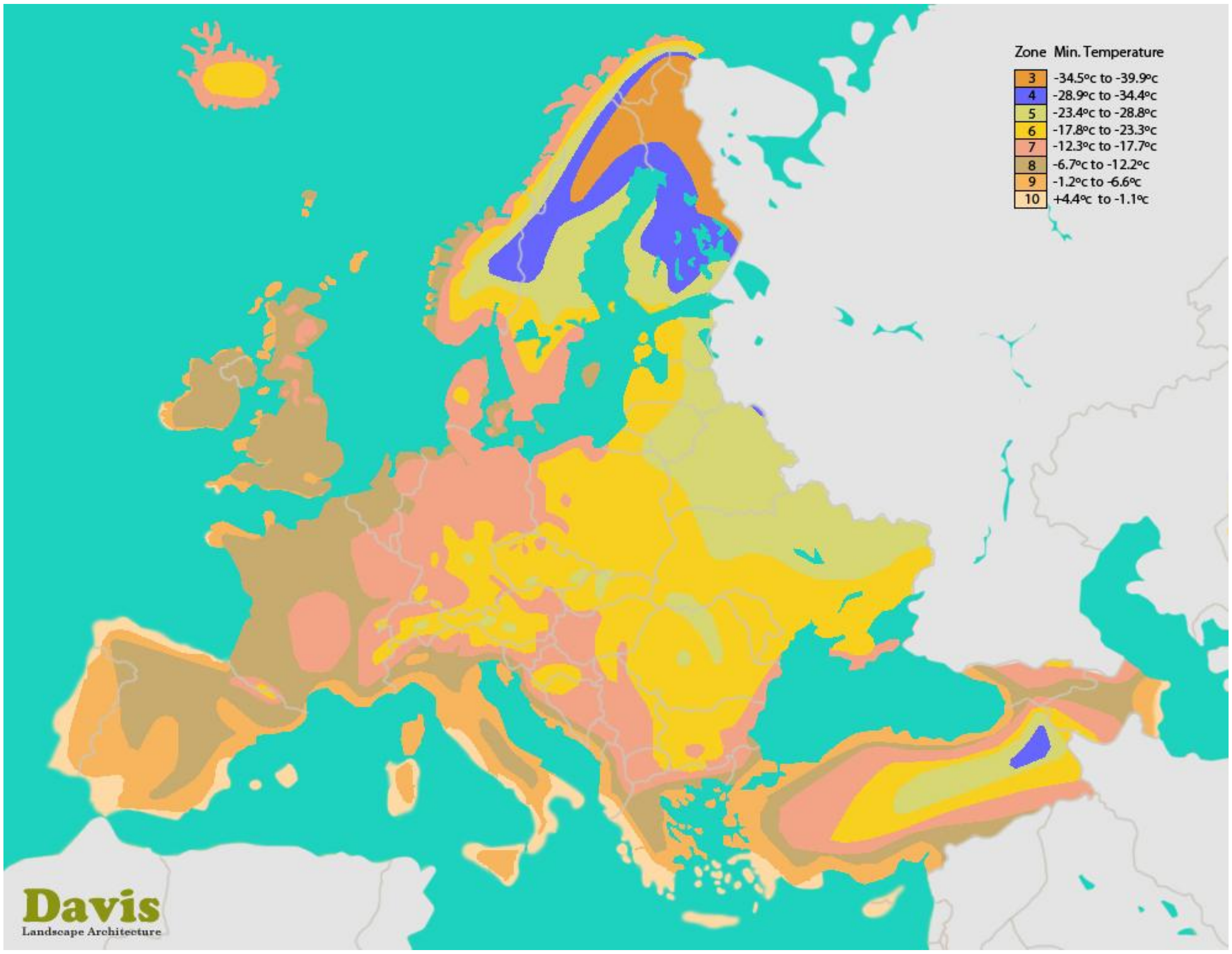


Figure 2 – This photo shows the approximate location of the hardiness zones in Europe.

Examples of Prehistoric Glues found at Archaeological Sites

There are several places that prehistoric glues have been found, two of which are within Italy and South Africa. A red and black organic material had been discovered in a cave system near Sibudu, South Africa (Wadley, 2009). Under further inspection it was discovered that it was a pitch and ochre compound used to haft stone tools. When analyzed with light microscopy the compound was dated to about 70,000 years old (Wadley, 2009). Like most points found as far back as these and more modern types they all seem to be hafted on the opposite side of the 'blade' edge (Wadley, 2010). This makes sense of course because what good would a sharp edge be if it were covered with adhesive and pointed towards the hafting

Other evidence has been found that was dated to be older. Dated to the Middle to Late Pleistocene some mammalian fossils were discovered in central Italy. Along with these fossils a small collection of stone tools were found. Black organic material was found at an excavation site near the Upper Valdarno Basin (Mazza, 2006). These were later analyzed using light microscopy and believed to be a form of adhesive. They appear to have been used to haft stone tools onto handles; in order add leverage to the tool (Lombard, 2008). Much like modern wrenches and tools it is hard to create a lot of power using a small tool. When the handle is lengthened it creates more torque and allows for more leverage. This allows the reach to be greater and more force can be applied to the tool.

Pine pitch and birch tar were not the only adhesive compounds used to adhere items together. Hide glue for instance, was produced by boiling animal hides until collagen released from the hide. When reduced it became a strong glue like that of modern wood glue. Hide glue is possibly a great adhesive to have available but it takes longer to refine and will spoil over time.

This is an organic animal byproduct, it needs water to become active and so that that the mixture isn’t too thick. A downfall for hide glue is that is it water soluble so this limits the overall uses of it.

There are many other forms of glues and adhesives that were used in prehistory that will not be analyzed within this experiment but are worth mentioning for showing the vast range of options available to hunter-gatherers depending on region. One such adhesive is known as bitumen sometimes also referred to as asphaltum. Bitumen was discovered at Gura Cheii-Râsnov Cave in Romania that was molded onto projectile points (Carciumaru, 2012). Bitumen is a viscoelastic compound which means at low temperatures it is brittle, at room temperatures it is flexible, and at higher temperatures it will flow. This substance is formed by thermal degradation of organic material incorporated and preserved in sediments (Carciumaru, 2012). It was not until several excavations had been conducted that this substance was found within the cave. Only small amounts remained on a few of the projectile points, this made it difficult for the researchers involved to collect proper samples. Dating of organic material that was found in association with these artifacts revealed an age of approximately 44,000 years old (Carciumaru, 2012: 1943).

There are even some cases that the ingredients for the glue were used for other things such as waterproofing baskets (Harper, 1970). Pine pitch glues would have greater effect waterproofing baskets than hide glue; as mentioned before hide glue can be dissolved with water and will weaken when wet for long periods. There were many uses for adhesives and glues in prehistory in addition to the typical binding of projectile points to darts or arrows. When the Tyrolean Iceman was discovered, he had a copper axe that had birch tar glue holding it onto the handle (Sauter, 2000).

It is important to understand the environmental setting where these glues were used in order to recreate them. To understand this there needs to evidence in the archaeological record of prehistoric glues. Any glue that has been found archaeologically would need to be analyzed to see what its chemical makeup is. Non-destructive analyses would be ideal for prehistoric glues because it is difficult to find. Along with the analyses process it not only would allow the user to see what it is made of, but the information could be used to start a database of prehistoric adhesives. Then that information could be compared to modern samples to identify which material creates which chemical signal.

Reverse engineering known adhesives would help greatly in discovering what people of the past may have used for this product. The difficult part is trying to reproduce these compounds the way they were made hundreds of years ago. The curiosity of people is what helps modern people try to understand the past with so little to help us in the end. There needs to be a want to help understand how and why things worked the way they did in the past. The overall outcomes may not actually tell how things were, but they will help by giving insight into how it could have been.

Scientists must find material culture before anything else may be conducted to analyze it. There are several known sites within Europe and Africa concerning glue and other adhesives. They all served different uses, and all held high importance on helping technology advance forward as it has. There are several other archaeological sites within Southern Africa that a resin-based glue has been found. These sites are Apollo 11, Diepkloff cave, Peers cave, Rose Cottage, and Umhlatuzana cave (CharriÃ©-Duhaut, 2012). All of these places have found bifaces or projectile points that have had black organic material that resembled pitch glue. The blades that were found all followed similar characteristics that the residue was opposite of what would have been the sharp edge. When the residue was discovered on the blades it was found on both sides of it, signifying that it was part of a hafting unit (CharriÃ©-Duhaut, 2012). Every blade displayed use wear and suggest they were used as potential scrapers or simple knives.

For most pitch based glues pine sap or birch tar are the main ingredients with either ochre or ash as the tempering agent. It seems that in Europe ochre is more popular within the adhesive mixtures compared to carbon based ingredients. At first it does not seem like it would work very well when adding it to an adhesive because it is more of a sand/stone material. When looking at these types of adhesives something needs to be added to the resin or tar so that it is less brittle and will withstand more force.

Within Italy there is another site that was found that it too contained an organic adhesive that was found along with mid-late Pleistocene fossils of mammalian remains. Among these fossils there were three lithic implements, one of which contained a black organic compound on it (Mazza, 2006). Not only were these lithic tools found with adhesive attached to them, but they were also one of the first tools found within the area that was being excavated. Two of the three tools were found mixed in with the fossil remains, and despite their cultural and chronological attribution, the stone tools hold high significance to the area and even more so since there is still adhesive on them. It was discovered that this adhesive was a birch tar base and it is not known to have been found in Early Palaeolithic levels. It is still not known if the stone tool technique lasted throughout Italy as time went on (Mazza, 2006).

France holds more information of how people of the past used adhesives. This time the adhesive was not used on projectile points, rather they were applied to burins, similar to modern cold chisels. It is associated that the adhesive used with these tools is that of birch tar. This is not surprising since most sites found in Europe involving some form of organic adhesive is based from the birch tar. It is one the oldest known synthetically produced materials and has been recognized as early as the Middle Palaeolithic (Dinnis, 2009). The production of birch tar entails that rolls of the bark are lit and placed into an oxygen free environment, so that the bark can sweat out the sticky liquid. This liquid could be used right away to haft items together or other things may be added to add strength to the adhesive. The addition of material all depended on the actual use of the adhesive.

North Germany also had some interesting information concerning prehistoric adhesives. Germany has been an interesting location for a significant portion of prehistoric artifacts. In this location there were several blades found and some of which had a black organic residue found on them. After making samples that were thought to be similar it was decided that the residue was a birch tar compound. These samples were based off experimental samples from Neolithic lake dwellings in Switzerland (Pawlik, 2011). Pawlik goes into more detail on how to extract the sap from birch trees. A process called dry distillation, meaning it needs an airtight container with a retort. The retort is filled with the bark and is heated up and turned into the liquid tar. It is thought that they used narrow pit in the ground with stones at the bottom to collect the tar (Pawlik, 2011). From what is known at this moment people this far back did not have large collections of pottery or other airtight tools. All of the artifacts found were described as projectile points or some form of working tools. Most of them had a black liquid smeared on them on which lead them to believe that they were hafted at some point in their life. During the excavations on the site, two samples of birch tar were found and there were clear fingerprints found that molded the shapes, so it is clear that these pieces were worked by humans (Pawlik, 2011). Europe and Africa are not the only places that hold prehistoric adhesives. In the Americas, there are examples of a different form than that of birch tar.

In both modern history and prehistoric times tar has been produced by using earth mounds as distillers (Kozowyk, 2017). It is not totally known how people in the past truly produced tar for adhesives, but it is being speculated that it was creating with some form of dry distillation. Ceramic containers are rare to find when going back so far in time, and when using and earth mound it would be easy to collapse and remake another one quickly. Kozowyk was trying to find a method in which they could produce large amounts of tar from birch trees without using excessive amounts of bark and extreme heat to extract the tar/sap. The best method found in the tests were using a raised structure so that the tar had an area to fall to (Kozowyk, 2017). This would save more of the tar so that it didn't get evaporated out of the mixture.

In Central Oregon at the Hoyt site, a black opaque Clovis point was found that exhibited scratches with a red hue to it (Tankersley, 1994). This substance was analyzed, and it included bitumen, animal proteins, and plant resins. During the analysis the organic resin, substance did not react like they originally thought when they applied the materials to solvents. This led them to believe that it was made of harder objects. It was then believed that the compound was an amber and charcoal mix. Amber is a fossilized version of resins and is normally a lot denser and harder material. Once charcoal/ash is added to the mixture it acts like a temper and gives the compound extra flex and strength. In this part of Oregon amber was an excellent resource because pitch bearing trees were far and few between (Tankersley, 1994). Typically, amber works excellent as an adhesive but it has not been known to survive long periods when it had been buried. The minerals and the moisture will tend to eat organic materials. With that organic material does not typically last when exposed to the elements or even buried. What makes them last longer is being in a dry climate and very little elemental contact. It has been common to find Clovis points that have abrading on them near the base. It is believed that having opposing abrading surfaces would aid in the adhesive attaching the two materials together. The adhesive would be able to attach to the groves and hold in a cross-stitch manner which adds more strength.

Further north into Northwest Canada projectile points were found from atlatl and arrows. It is thought that these tools were used from around 9,000 until about 1,200 years ago (Helwig, 2013). These artifacts were found within frozen ground, this made it so that the organic material and other artifacts were well preserved. From the samples collected the examinations were first done with the naked eye and then a microscope was used, all with the aid of an ultra-violate light source. Similar to most organic samples found all samples were done with careful planning and limited samples were used. Resin-based hafting was analyzed on approximately eleven samples (Helwig, 2013). When the sampling was conducted it was found that most of the resins were from spruce trees. These trees are typically found farther North than the Douglas Fir tree. Apart from just resin found there was even signs of fat and cholesterol found on the adhesives. The hardest part about finding them stuck to the adhesives is trying to find out if they were used to harvest animals or if those parts were used to help create the compound. Like other glues, it was discovered that ochre was an ingredient within these samples as well. So there has to be some correlation between prehistoric glues and the use of ochre in these adhesives. Ash/charcoal are a very common ingredient for prehistoric glue because of the tempering affect. Ochre at first does not seem to make much sense because it is normally a stone-based compound in of itself. It seems in most or all cases when ice patch artifacts are found the ingredients come back as spruce no matter the age or projectile type (Helwig, 2013). In these samples it seems that they animal fats found within were used as a tempering agent much like beeswax would be.

Methods

The objectives of this study were to 1) identify the peaks for varying glue types, 2) discover the strongest pine pitch glue, and 3) identify if there is a difference between the varying materials to create different strengths. There were several methods of focus to reach the results that were obtained. After a considerable thinking and research it was decided that a force gauge that would lock the peak number was needed. As well as a stand that would allow for a straight 90-degree angle when the samples were being tested. Figuring out the methods on how to conduct the experiment was the biggest challenge of this whole experiment. Creating the glue mixtures and the amounts was difficult but once a plan was made they were easy to create. Attempting to find an accurate way to measure the applied force was one of the more difficult things to discover.

Early Research Observations

In order to help answer the question of how these glues might have functioned in prehistory, several experiments were conducted. Working from a pilot experiment for a senior research thesis, this master's thesis is using similar methods but an expanded sample set to identify holding strength. For clarity, the basic outline of the pilot experiment is given first and is then followed by the current experiment. The methods for the pilot experiment are the same as those of the current study. The pilot experiment consisted of ten sample types of glue. The main purpose of the initial experiments was to analyze to see the strength of these glues through the level of tensile force each of the compounds could withstand. Tensile strength is a good indicator for glues of the holding strength of two materials together. It was hypothesized that different materials added to a pine pitch base would create varying amounts of tensile strength.

Each sample type was tested to identify any deviation in tensile strength. The previous experiment had every sample consistent with the exact same concentration of ingredients. Every ingredient was weighed out on a digital scale with 0.01 gram accuracy. Each sample was tested ten times to allow for enough data to compare between the ten sample types. Afterwards, the data was statistically compared to each other to see the difference between the ten sample types. This created a standard deviation between them and showed how much variation the same glue could produce. The experimental results are given below in Graph 1.

Graph 1. Experimental results of pilot experiment of glue strengths.

Samples in psi	Wood Glue	Plain Pine Pitch	Leaf Added	Beeswax Added	Leaf/Beeswax Added	Bark Added
Test 1	79	45	16	90	80	16
Test 2	80	52	23	73	60	30
Test 3	84	64	22	68	29	9
Test 4	78	12	42	60	81	23
Test 5	79	28	18	42	73	22
Test 6	75	10	25	48	52	20
Test 7	89	32	6	80	24	18
Test 8	78	23	12	28	24	5
Test 9	79	29	10	28	48	15
Test 10	77	8	26	18	20	25
Average	79.80	30.30	20.00	53.50	49.10	18.30
Max	89	64	42	90	81	30
Min	75	8	6	18	20	5
Standard Deviation	3.97	18.65	10.21	24.47	24.00	7.45

Current Study

For the current experiment, the plain pine pitch was the only sample type that did not change in concentration. All other compounds would range from a quarter gram up to two grams of binder additive. The hope for this was to allow enough range between samples to tell a difference but close enough that it shows how little amounts can alter the strength. It was hypothesized from observations in the previous study that when adding too much ash or dry compounds to the sap it could become too weak with no adhesive properties. While alternatively, if not enough was added it was hypothesized to act like a crystalline structure. This was thought to potentially be weak in strength but also brittle with tendency to cause cracking depending on the force applied. These observations were made visually during the mixing of various additives and collecting of materials.

Apparatus construction

In order to test the tensile strength of the various samples it was determined that the cheapest, simplest, and most accessible approach would be to create a custom apparatus. In order to build the apparatus to handle the force gauge and create a 90 degree angle for pulling on each of the samples in tension it was necessary to use a 2 inch x 6 inch x 36 inch oak board as the overall base. Two aluminum 2 inch x 2 inch square posts reaching approximately 48 inches high by 2 inches wide were used for the arms that would be the guides for the gauge. A small metal back board was placed behind the gauge in order to mount it onto a 2 inch x 4 inch with brackets to go around the aluminum posts (see Figure 3). In doing this it would allow the gauge to be slid up and down the posts with simple ease. At the top of the two posts a rod was placed to keep them evenly spaced apart and to keep them as close to 90 degrees as possible. Additionally, some lubrication for the posts and the brackets was used in order for them to move freely with minimal friction. This lubrication made applying force much smoother than the pilot study and allowed the gauge to be pulled in a more consistent and constant manner at a 90 degree angle.

The other half of the apparatus was the board structure that was built to apply the glue samples to for testing the tensile holding capability. Two pieces of red oak were used and attached together with screws. One board had 48 individual holes drilled into it with each at a diameter of 33 millimeter and the other was left alone. The holes were then perfectly suited to receive the plug that was removed during drilling with enough restriction laterally to control any

Figure 3 – From L-R: Apparatus used for pulling, close-up of board structure with plugs and hooks attached, board structure with plugs removed.

deviation. Therefore, the plug that was removed could now be glued to the underlying board and be set in place with no “wiggle” room to deviate when being pulled on in tension. It would also reduce the amount of possible excess glue being pushed out from under the plugs and allowed the glue to truly hold the plugs in place with consistent application.

All the plugs were outfitted with eye hooks to allow for easy detachment when they were being pulled on with the force gauge. They were also placed in the center of the plugs to allow for an even pull. This was to avoid pulling off center or pull at an angle because it would adjust the hold of the glue and alter the results. All the eye hooks were the same size to increase the amount of consistency in the experiment. At this moment of the experiment all the precautions taken were to make it so that there were as few differences between the equipment as possible. The only difference wanted was between the glues to make the test as reliable and consistent as possible.

Glue Creation

To make the glue, a scale was needed that could weigh items as low as 0.25 grams. This was accomplished using a RCBS 5-0-5 powder grain scale for this experiment. The idea was that this item could measure gun powder to reload ammunition precisely, it could measure ash, bark, and leaf precisely for glue. The only thing that needed to be done when weighing it all out was convert grains into grams, which is 1 grain to 0.064 grams. Weighing the pine sap for the experiment was a little simpler, a simple food scale could be used for that. Weighing out 10 grams of an item is less complicated than that of a low mass powder. Once everything was able to be weighed out it was simple to create the combinations to make up all of the samples needed for the experiment. The idea was for each plug to be pulled in a straight manner to reduce the amount of twisting and torqueing of materials. It was the glue that was the main focus for the experiment not the strength of the wood. Some of the samples turned out to be more of a grainy powder rather than that of a smooth liquid that could be molded to the wood plug.

The first time these samples were being made it was thought that 10 grams pine sap to 1 gram ash would be the original set up. Shortly after that when increasing the amounts by 1 gram each they mixture was just not possible and would fail every time. This was because of having a larger volume of dry ingredients to the wet ingredients. For this reason, the ash samples were started in small amounts. It also shows that with small amounts of resources there is a lot of possibilities that could happen with the glue. Creating these small samples also made it possible to create large amounts of sample types without having to collect more resources. One of the major issues for using pine sap as a base is that there is only a short time that it can be collected reliably and in any large amount.

Knowing this needed large amounts of resources, they were collected well in advance for this experiment. Early on, the estimate for a minimum of 424 grams of pine sap alone, it was determined this was a significant amount requiring extensive collecting. Finding large amounts of sap in one area where trees are healthy is difficult and time consuming. Collecting the other ingredients was not nearly as difficult: burning pine logs was all that was needed for collecting ash, pulling leaves off of trees and allowing them to dry, and removing pieces of loose pine bark to avoid harming trees. All of these were simple and did not take away from the plants that were healthy and thriving. A goal for this project was to not affect any healthy trees in a negative way through pine sap collection methods used in prehistory that included cutting grooves into the pine trees deeply to increase flow of sap (Campbell, 2009).

As previously mentioned it is near impossible to collect birch tar without removing the bark and reducing it down by cooking it. This process kills the tree by taking away its defense to insects and animals. As aforementioned for pine trees, it is possible to artificially increase sap production by creating channels for sap to travel and not kill the tree right away. If done properly it would simply become a scar on the tree and it would live afterwards. Only when the tree is scarred too much will it start to create a negative impact on the tree and start to kill it off.

Similar Experimental Methods Approach

In order to clarify the method used here in addition to the slow steady pull (tensile) force that was employed for each sample it is necessary to cite a recent similar study. While this study's experiment has used samples consisting of pine sap, ash, leaf, bark, and bees wax the recent paper by Kozowyk (2016) implemented experiments using ochre as its additional binder. Similar to the current study, as ash was involved as a tempering agent for this experiment, ochre was the tempering agent for the 2016 paper. Kozowyk did similar processes that have been explained above. He used a constant ingredient for his samples and altered some of the other ingredients. The largest difference between the experimental methods presented here was that a simple pull (tensile) force was used where Kozowyk's experiment involved sideway (shear) force. He explained that with high amounts of speed during a test the sample can hold more strain to the unit, but it becomes very brittle at the same time (Kozowyk, 2016). Where making it a slow constant pull it becomes more elastic and will handle longer periods of strain but will break at a lower force point.

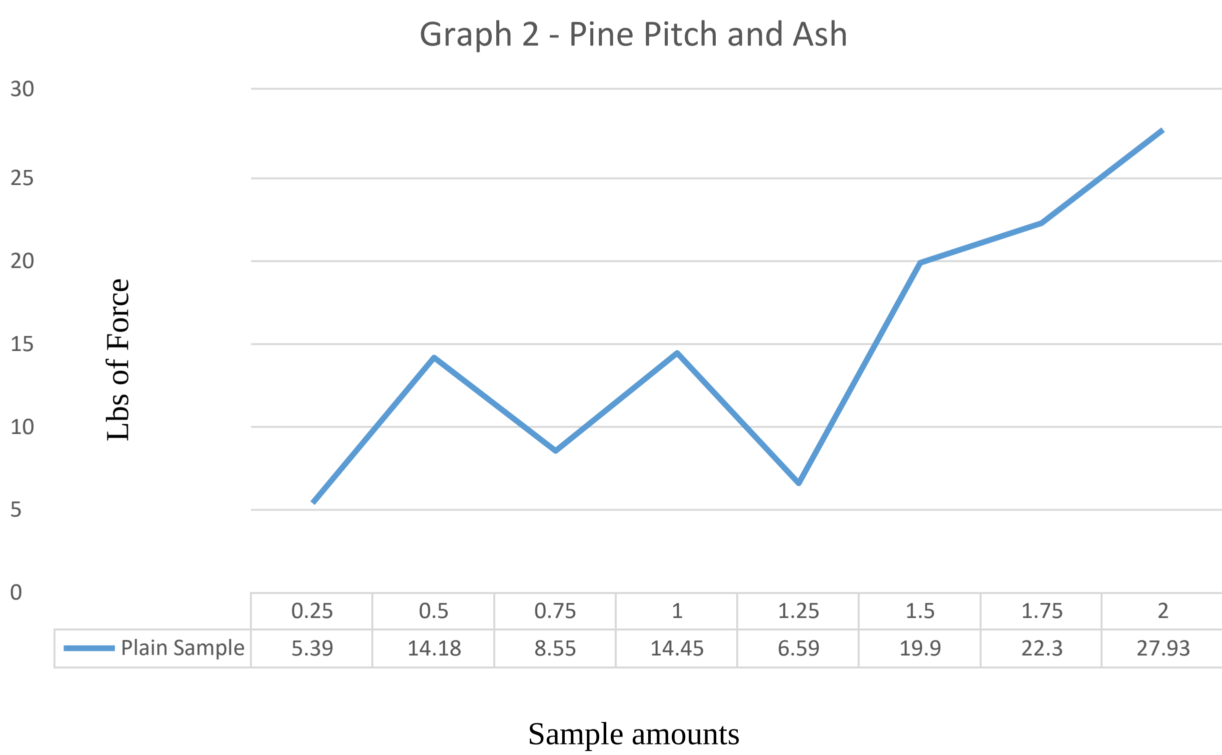
There are differences between the two experiments but there are many similarities between them too. As just mentioned Kozowyk's experiment was shear where this one is pull force. In the end it is just force but the difference is how the force is being applied. Shearing apart will act different than pulling two items apart. This is what makes these two tests different but at the same time tell different parts of the same story. It is needed for an experiment such as this. It allows for multiple views on how this prehistoric glue works and reacts to different types of stress. Most modern glues are tested in similar ways to make sure they will handle numerous scenarios of use. The key to testing them differently is to employ different amounts of the various compounds to create variety within the samples. This also allows for different ingredient samples that could show an ideal mixture for different scenarios.

Wood glue as mentioned above is the example test for this experiment to allow for some form of comparison. Hide glue will be analyzed to allow for a simple comparison to a different form of prehistoric glue. This will show how the pine sap glue compares to the others and explain a little more on the benefits to using both. Each type of glue will have a slightly different use to the other pieces and will have a different strength. As previously mentioned that is why this experiment is being conducted, in order to show why people would have possibly chose these glues to aid them in their lives. It will not be able to explain everything, but it will allow for some insight into the past.

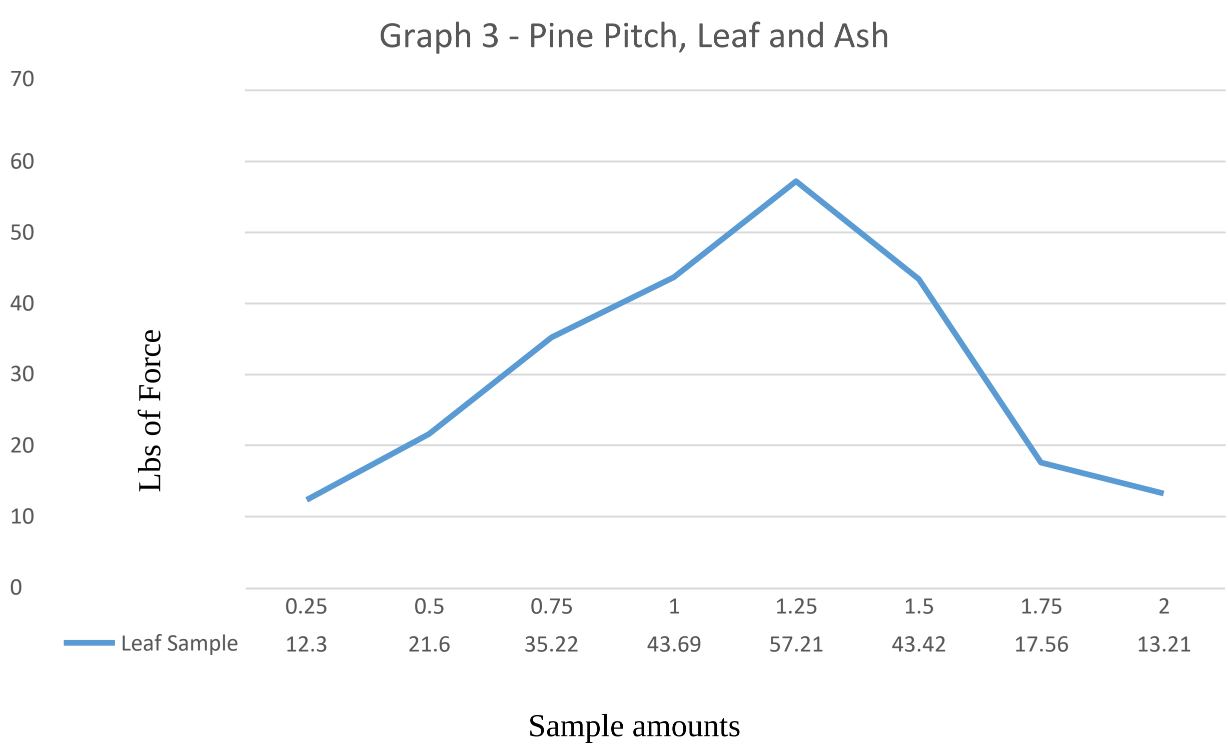
Results

For this experiment all of the graphs data points are referred to in pounds of force (F_{lb}). On the graphs listed below the numbers listed horizontally are the pine pitch glue amounts. The other set of numbers placed vertically are the amount of force in pounds the glue was able to withstand. Pine pitch and ash glue refers to just pine pitch and ash in the final adhesive. This was used as the control glue in order to have a general standing point.

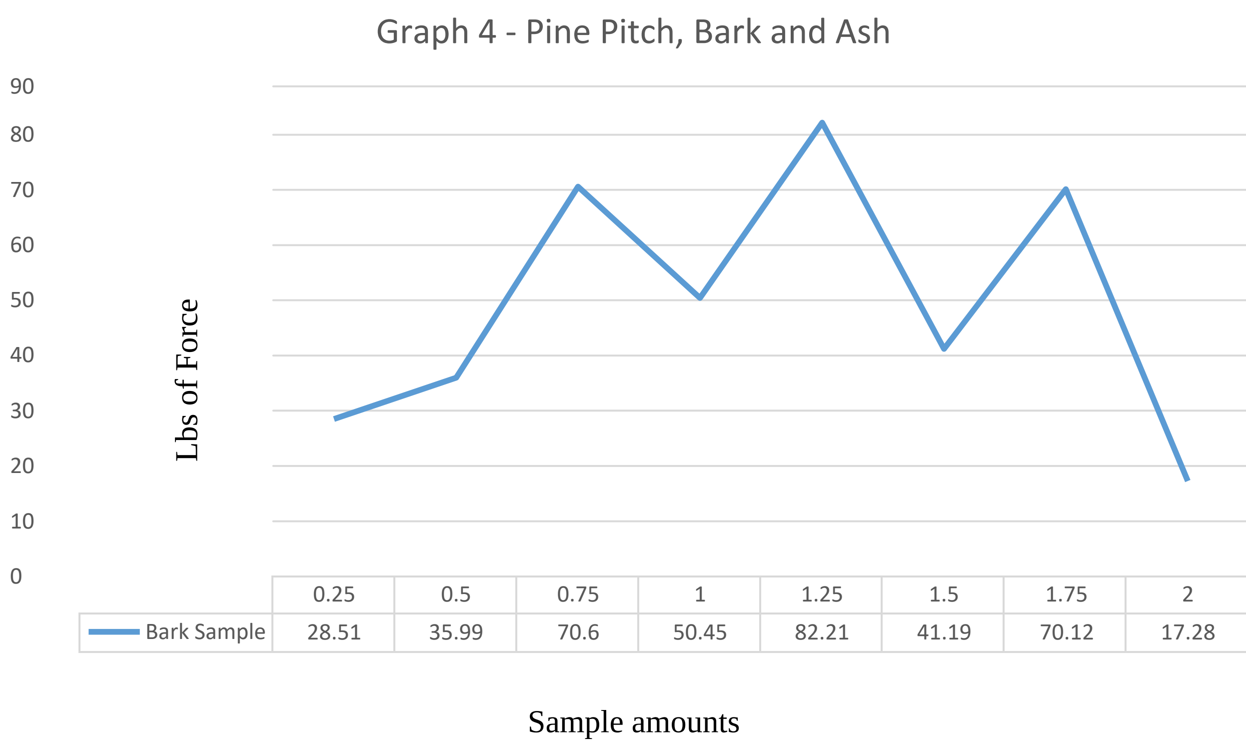
As Graph 2 shows the plain glue peaked at approximately 27.93 pounds of force. There were more experiments conducted past this point to see if there was a stronger peak, but all of those tests did not provide measurable data. When creating more samples, the pine pitch and ash glue dried up and did not hold any adhesive factor. The new pine pitch and ash glues were more of a hard powder of ash and pitch rather than glue. Having this hard powder there was no way to test it reliably, so the data would be negligible for this experiment.



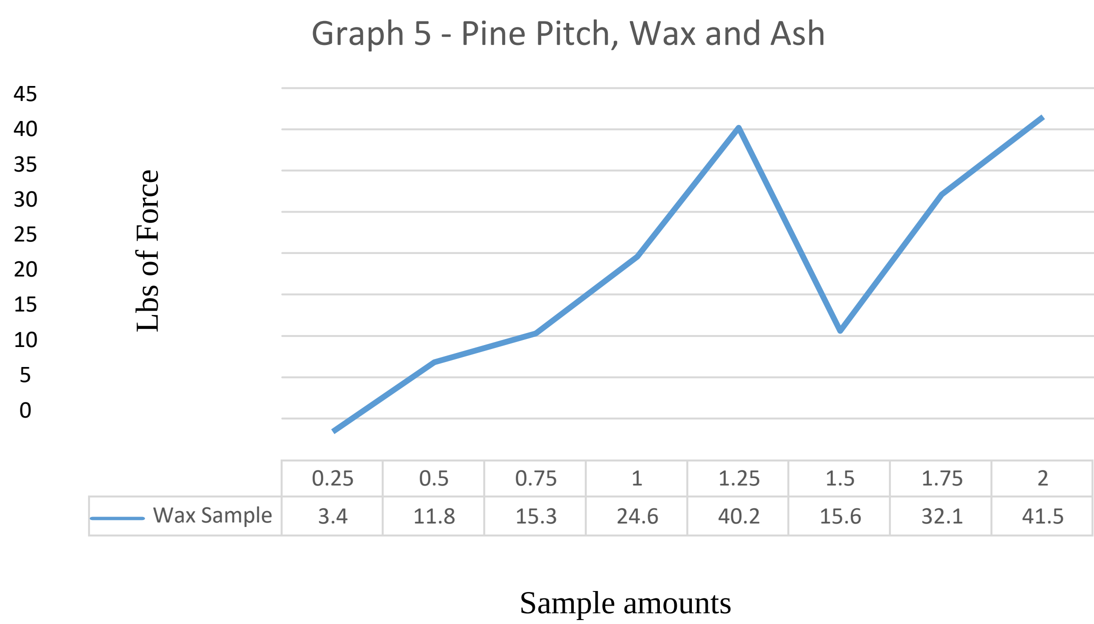
Pine pitch, leaf, and ash were the next samples and it had the ideal looking results as far as how the graph acted. It gave a standard bell curve shape which is typically ideal for situations like this. Graph 3 shows that the pine pitch, leaf, and ash glue had a peak of approximately 57.21 pounds. This is double that of just the pine pitch and ash samples. This sample set was created with 10 grams pitch, 1.25 grams ash, and 1.25 grams dried leaf. All of these samples were sanded with rough sand paper to create a course body for the glue to adhere to. Most store-bought boards are smooth on the outer surface and this would not lead to a reliable test. Even the board that the plugs were glued onto had the face of it sanded to create this course surface. This eliminates the possibility for one piece to be glued to a smooth surface versus a course one. The only board that was not sanded was the guide board but nothing was being glued to it so there was not much of a need for it to be sanded.



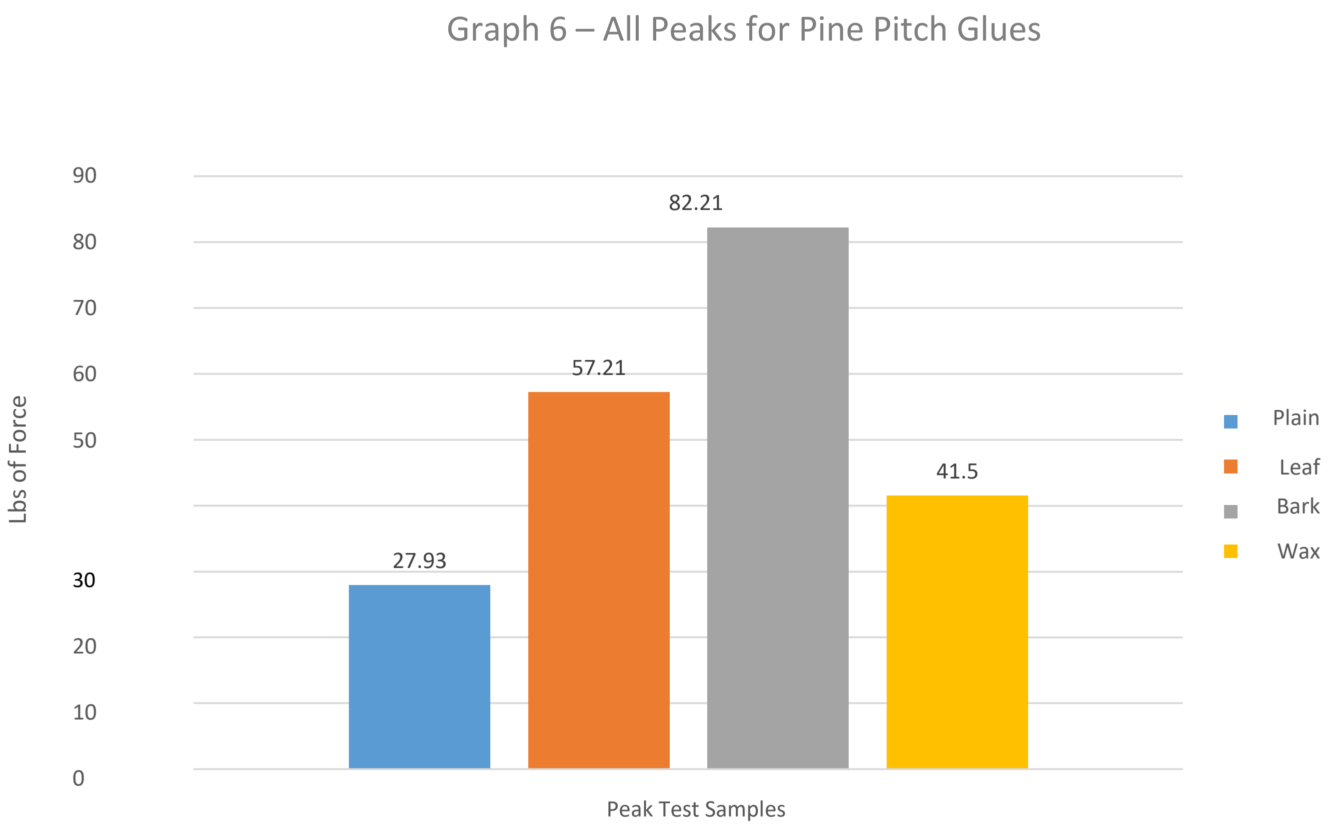
There was a hope that the pine pitch, bark and ash glue would give similar results to the pine pitch, leaf and ash samples but this was not the case. The ideal graph would have been another bell curve, but as Graph 4 shows this did not happen. Even though the graph did not have the ideal results the pine pitch, bark and ash glue did show interesting characteristics. The peak force for this glue was approximately 82.21 pounds of force (Graph 4). From the way that graph 5 looks there appears to be a combination that performs better than others. For this sample set it seems that 1.25 grams of ash and bark are the ideal amounts to be added to create the strongest hold. The one sample set that was exciting to test and disappointing at the same time was the wax samples.



The pine pitch, wax and ash samples were exciting at first because the wax seemed to give the glue a tacky feel and allowed the adhesive to flow easier. As Graph 5 shows the peak that is recorded is only 41.5 pounds of force. There were two tests conducted with the pine pitch, wax and ash samples but the first set was unreliable so the data was scrapped. With unreliable data a second test was conducted for every sample with the 600 pound scale.



Graph 6 shows all the peaks for the pine pitch glues. This graph shows that with slightly different ingredients there is a difference with their abilities. One of the interesting data points about all these glues is when compared to hide glue and modern wood glue. As expected the wood glue would hold a lot of force to be able to break it free from the wood plugs. During the hide glue it was not expected that the steel hooks used would bend exceeding more than 250 pounds of force. The wood plugs that were glued with wood glue never released from the wood and bent all the steel hooks that were used on the testing. The hide glue had similar results to the wood glue. When tested using steel hooks all of them that were tested had been bent from the amount of force used. One of the hooks even ripped out of the wood and the other wood plug broke in half just above where the hide glue was placed.



Discussion

Some of the oldest known evidence for adhesive comes from the Middle Paleolithic and were found around Campitello, Italy (Cârciumaru, 2012). This is later discovered to be birch tar-based adhesives, but this is a similar form to the adhesives used within this experiment. As described in the background in the America's the adhesives were more of a pine pitch base and in Europe birch tar was used more frequently likely due to the hardiness levels of the trees. There is some evidence showing that pitch adhesives are found across the Earth. The hardest part about conducting research on these adhesives is finding them. The purpose for this experiment was to try and find a peak mixture that held the best over the others within their sample type. During the pilot study it was thought that bees wax gave a certain type of flexibility to the samples where everything else as more brittle. At this point it is known that they bees wax samples should show higher amounts of force compared to the other samples. The only thing is that it is not known how much stronger it is compared to the others in terms of a binder for a quick force as opposed to a slow pulling force.

As previously mentioned, in 2016, Kozowyk developed an experiment that did lap shear testing on adhesives. The largest difference was the material for the adhesives and the equipment used. A Zwick-Roell 1455 tensile bench with a 20 kiloNewton (kN) was used for Kozowyk's experiment. This allows for a lot of extra control over the samples and accurate readings (Kozowyk, 2016). An advantage to using the tensile bench over the custom design for this experiment is that it can add force at a slower and more constant rate than that of the custom design. This could be considered ideal because there is more control over the equipment and it can be viewed with more attention. The original design for the custom jig was to hold the force gauge and manually pull straight up. It was decided that the best course of action would be to have the jig set up at a 90-degree angle to have the best support. This would also make it so that the samples would not be torqued at an off angle and release the samples before the glue failed.

It is difficult to compare hide glue to the pine pitch glue because it is not a plant-based adhesive. It should be analyzed and compared to, but not to the point that it should be looked at more than that of pine pitch glues. The process of making hide glue is long and time consuming; where that of pine pitch glues are quick if the resources are near. When harvesting an animal and boiling its hide it is very different from retrieving some pine pitch and ash to make an adhesive. To create pine pitch glue all that is needed is pine pitch, ash, heat, and an area to mix the two ingredients. Hide glue on the other hand, an animal needs to be harvested, skinned, the skin turned into strips, the skin boiled for several hours, and finally the water/collagen mix needs to be reduced into a thick paste.

Most of the graphs show an increase in the samples strength and then there is a noticeable decrease with the strength as well. For the pine pitch and ash samples, the graph simply just shows an increase in strength. When further samples were being made the pine pitch and ash would simply not combine after 2.25 grams and up of ash were added. As mentioned above it would just crumble and could not create a mixture that would adhere anything together. This made it impossible to test and collect data from.

The pine pitch, leaf and ash samples had a better result, because there is a distinctive peak that was shown in Graph 2. Everything before and after this point would not benefit the strength or use of the adhesive. The process for creating this adhesive first requires drying of the leaf component before grinding and application to the pine pitch. The idea for grinding the leaf up is to make the fiber sizes small so that they could combine properly to the pine pitch. From experience within this experiment it seems that the finer the material is the more likely it will mix with the other ingredients. It seemed for dried leaf the best way to grind it into a fine powder was to push it through a strainer. A mortar and pestle were used at first, but it did not seem to make it fine grained enough for the adhesive. From that moment a fine mesh cooking strainer was used to push the dried leaf through the mesh and ‘grind’ the leaf.

Pine pitch, bark and ash have a very similar effect to that of the pine pitch, leaf and ash combinations. At first it was attempted to grind the bark in a blender to create small grains of material, but it was quickly learned that this would not work. The blades would bind on the bark and stop the motor. The best method for this experiment was to use a wood file and hand grind the bark into a powder to later be added into the pine pitch and ash. Using the file was quick and easy to control how fine the bark would be. Pine pitch, bark and ash shows that it held the greatest amount of force of 82.21 pounds of force. The hard part to interpret is what properties does bark contain that allows it to hold this amount of force. One possible difference between the bark and leaf samples is that it could be is the amount of volume they each hold, and this created the difference in their strength, though it is not confirmed. When the bark and dried leaf are in a powder the leaf appears to be larger in size. Even though they are the same weight they are not the same volume.

It was hopeful that the pine pitch, wax, and ash sample would be able to handle more force than the other samples. As Graph 5 showed this was not the case because the highest force held was only 41.5 pounds of force. This was even less than that of the pine pitch, leaf, and ash samples. This was unexpected because the feel of this adhesive was very tacky and would stick to the human skin more than the other adhesives. Once this adhesive had dried within the mixing plates it could be marked with a finger nail where the other samples seems more crystalline in nature. In order to determine the mechanism behind the holding strength of these adhesives it will be necessary to conduct more experiments. Potentially, this may require examination of each sample for microstructural details.

Applications

This experiment does not show how prehistoric people made these glues or even in the mixtures modern people may think they are applied but it will allow for an alternate view of how it could have been done. There are many modern survivalist and craftsman that have learned how to create this form of glue and use it for many items in their tool kits, but all of their recipes are different and are not made in an exact amount style. Typically, it is just bits and pieces put together until a certain consistency is made and they let it cool to be later used for whatever purpose they may need of it.

Not only should testing be done to find the ideal pine pitch glue but it should also be tested against birch tar glue, fish glue, and more hide glue. They may be different types of glue, but this will demonstrate what each of these glues are capable of and what their ideal use would be. Briefly mentioned above hide glue exceeded the limits of the equipment used. The hooks that were attached to the oak plugs either bent or were ripped out from the plug. All the pine pitch samples did not have results similar to this, so they almost should not be compared to hide glue. Hide glue a slightly different material it will give results that are not like that of pine pitch glue. One possible fault to pine pitch glue is that all of the materials have to be mixed together in order to form a proper adhesive. Hide glue just needs to have animal hide reduced down in order to gain the adhesive property from it. With some analyses it could be tested to see if hide glue has a much finer mixture within its microstructure allowing it to adhere to the wood. The rough surface on the wood allowed it to adhere to it and create a stronger hold to the wood itself. Pine pitch glue would possibly have a larger mixture structure which would make it slightly more difficult to properly adhere to the wood and allow it to create as strong of a hold to it as the hide glue had done.

With the help of using Fourier Transform Infrared Spectroscopy (FTIR) it could be possible to analyze the pine pitch glues and see if it is possible to see the chemical makeup of the glues. FTIR spectroscopy is a powerful analytical technique commonly used to identify molecular compounds and minerals and it often requires extensive sample preparation (Monnier, 2013). Several methods were used by Monnier on bifacially flaked points to discover that they had bitumen on them (Monnier, 2013). Not only did they use microscopy to discover the location on the flakes to but using FTIR they were able to find the chemical makeup of their samples in order to define them as bitumen. It could be possible to use a similar method on several modern samples and then compare them to prehistoric known samples. In doing this a database would be established that would start to define what each of these prehistoric samples are composed of and possible variations included in them.

FTIR spectra of pitch and wood tar show a rich composition in highly oxidized and dehydrogenated molecules with respect to fresh colophony obtained from pine resin (Font, 2007: 124). Having the knowledge that there is both pitch and wood within the adhesive would give some insight to what the compound is made of and all for information to alter current research data. It could also strengthen other research that are similar to this experiment as well as strengthen this experiment. Once the FTIR data was collected it would just be a matter of figuring out which chemical makeup defines the pine pitch, ash and the possible other substances that are involved. Simply defining what the pine pitch would be is a large step because then it could become a process of testing samples and how they are similar or different to the original test.

Other things to possibly keep in mind is what type of evidence is there for these pine pitch glues. There is a large amount of evidence that shows pine pitch or birch tar glue being used to haft items together. Being an organic material, it is hard to find within the archaeological record so most times adhesives are found on the bifacially flake points. Discovering where adhesive remains are on stone tools could provide an idea on what type of hafting prehistoric people used (Yaroshevich, 2013: 4012). Being an organic material, it is not very common to find the foreshaft at this point. With this type of adhesive it would not be uncommon for remnants of it to appear on the retouched edge of tools or even partially stain the surface (Yaroshevich, 2013: 4015). These are all parts of a bifacially flaked point that keep material within them better than any other part of the point. Helwig (2008) talks about having an antler point that was used as a projectile point that also had some adhesive within the notching for it.

FTIR was one of the methods used to identify the chemical compound to discover which type of adhesive was used on it. Even though hafting adhesives have been found before in the archaeological record there has been very little undertaking to analyze them (Helwig, 2008: 281). With the aid of FTIR it was concluded that the adhesive residue was pine pitch based. It was also dated to be approximately 7,000 years old. Trying to find ingredients that prehistoric people would reveal a lot of information when it comes to this experiment. It would allow for more accurate samples to be made and it would allow modern people to potentially understand why people chose those ingredients. Having knowledge of the ingredients though could also place confusion into the mix because they may not be the best ingredients to use to create a strong glue.

Conclusions

The pine pitch glue tested within this experiment shows that the slight change in material weight can alter the adhesive in a positive or negative manner. When applied in the correct proportions it could be rather beneficial for the adhesive but adding too much or too little will alter the strength potentially a great amount. Adding beeswax to the mixture seemed to make the adhesive less brittle. Where adding more ash into the mixture it created strength but also added brittleness. Graph 5 shows that pine pitch, bark, and ash held the most force. This possibly could be because there was a balance between bark and ash to the pine pitch. Allowing it to create the ideal amount of brittleness and strength for the ingredients added to the mixture. There are other factors to why these adhesives may work better than other mixtures, but the experiment conducted did not test enough of those factors.

To truly understand how these adhesives will act against each other they will all have to be tested a great number more times and in different situations. A temperature test would be a great option for these because there is such a large temperature range in North America and a slight change could alter how the adhesive works. There are several tests that could be produced that would aid in the discovery of which prehistoric adhesive is best. One of the first steps that should happen is learn what the artifacts are made of first. Use FTIR and other chemical analyzers to discover what the chemical makeup is and use them as a base sample. Once the ingredients are discovered it could be trial and error to create a database of samples that are modern made with the same samples but different amounts of each ingredient. After a large group of samples are created it would be a matter of then analyzing them to discover which of the modern samples could possibly match the prehistoric samples. There is a chance that this method would not work but there is always that chance that it could.

After conducting the experiment over pine pitch glue there has been several other tests that have been thought up to test these samples even further. As just mentioned in the previous paragraph conducting a similar test but within different climates to see how the adhesive reacts to heat and cold. Find different coniferous pitch samples to create the glues and test them among each other to see how they compare. Testing each of these samples against different types of force such as lap shear and pulling force and even various pull speed of force such as quick versus steady as one of the experiments mentioned within this paper. Seeing if there could be a difference with slow force applied or even fast force applied to the adhesive.

In future tests extensive planning and preparation would be necessary to test the many scenarios where these glues could have been implemented including material types, climate, tool function, and numerous other testing possibilities. One possible way to conduct tests like this is to use experimental methods in various applications from prehistory such as hide scraping using a particular glue and whether it works and the duration of the use. In doing this it should be possible to back track every step of the experiment and be explainable for what may have caused the results. Not only this but it would allow others to test the method to see if it really is viable and re-test the experiment to analyze the results and apply them to archaeological problems.

Experiments over these adhesives are difficult to get ‘just right’ because as shown within this experiment the simplest changes within the mixture can alter the results greatly. One of the possibly more challenging parts is to acquire the proper amount of heat. From personal experience if heat is applied to quickly not all the pine pitch melts. If it is heated to slowly it takes a significant amount of time for the pine pitch to melt and the adhesive to be made. Then the issue of finding the proper ratio of pine pitch to ash and any other ingredient that may be used for the adhesive. There is much planning and experimentation that would have to be done for an ideal adhesive to be made and discovered in the past through trial and error. Defining 'ideal' in this manner is the most difficult part of this experiment because what may be ideal to the experiment may not be ideal for the practical use of the adhesive.

There are many variables to choose from when deciding how to make similar adhesives to the ones used within this experiment set. As mentioned earlier the hardiness of the plants is one of the first variables to look at. Just the simple changes of 4-6 for Douglas Fir and 2-7 for Birch trees is enough to make a different choice. When it is easier to acquire pine pitch by just collecting it from damaged trees, rather than de-barking a tree to obtain the pitch, it comes down to a matter of work smarter not harder.

When birch trees are all that is around in the living area than the choice is limited but when there is the option of a coniferous it gives the user another option to choose from. Creating these types of adhesives is not a recent invention. Prehistoric people have been making adhesives for thousands of years and adhesives are not slowing down in manufacturing. Conducting this experiment begins the path to understanding more about prehistoric adhesives and brings light to the unknowns for the adhesive itself as well as many new, exciting research questions. With more research and experimentation for this and similar adhesives there will be more that is known, and a database will start to form. There are many databases that have been created in today's world, but prehistoric adhesives have not been a top priority for that list. Even if a database is not complete just having criteria to follow and analyze would be enough to help define what these adhesives are and how to analyze future findings. A difficult part of creating this database is which criteria is going to be followed to allow it to be used as a general rule for prehistoric adhesives.

This experiment needs more refinement to create reliable data. With the few restrictions that were in place the experiment was a success, but the methods could have been sounder. This experiment is easily reproducible and simple to follow how the methods were put into placement. Therefore, with proper time and resources available the results possibly could have more accurate statistical outcomes. Additionally, with more accurate equipment available it would just allow this experiment to improve data collection and show more information about prehistoric adhesives. Prehistoric glues are more complicated than first thought and it is hopeful that future research is conducted to analyze and understand how this adhesive works. The use of FTIR and other equipment will do nothing but further the knowledge gained from prehistoric glues and how they act to wood and other material.

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