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Short title	Laboratory strength testing of pitch adhesives
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Abstract

Adhesives are an important yet often overlooked aspect of human tool use. Previous experiments have shown that compound resin/gum adhesive production by anatomically modern humans was a cognitively demanding task that required advanced use of fire, forward planning, and abstraction among other traits. Yet the oldest known adhesives were produced by Neandertals, not anatomically modern humans. These tar or pitch adhesives are an entirely different material, produced from a distinct, albeit similarly complex process. However, the material properties of these adhesives and the influence of the production process on performance is still unclear. To this end we conducted a series of laboratory based lap shear and impact tests following modern adhesive testing standards and at three different temperatures to measure the strength of pine and birch pitch adhesives. We tested eight different recipes that contain charcoal as an additive (mimicking contamination) or were reduced by boiling for different lengths of time. Lap shear tests were conducted on wood and flint adherends to determine shear strength on different materials, and we conducted high load-rate tests to understand how the same material behaves under impact forces. Our results indicate that both pine and birch pitch adhesives behave similarly at room temperature. Pine pitch is highly sensitive to the addition of charcoal and further heating. Up to a certain extent charcoal additives increases performance, as does extra seething. However, too much charcoal and seething will reduce performance. Similarly, pine pitch is sensitive to ambient temperature changes and it is strongest at 0°C and weakest at 38°C. Adhesive failures occur in a similar manner on flint and wood suggesting the weakest part of a flint-adhesive-wood composite tool may have been the cohesive strength of the adhesive. Finally, pine pitch adhesives may be better suited to resisting high-load rate impacts than shear forces. Our experiments show that pitch production and post-production manipulation are sensitive processes, and to obtain a workable and strong adhesive one requires a deep understanding of the material properties. Our results validate previous archaeological adhesive studies that suggest that the manufacture and use of adhesives was an advanced technological process.

Keywords	Pine pitch; birch bark pitch; tar; adhesive; lap shear; Neandertal; Palaeolithic

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Leiden, 16 November 2016

Dear Editors,

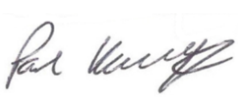
We hereby submit our research article entitled 'Laboratory strength testing of pine wood and birch bark adhesives: a first study of the material properties of pitch' for consideration by JAS Reports. This is an experimental archaeological study into the performance effects of the application of heat and the addition of charcoal to replicated tar-based Palaeolithic adhesives.

Throughout prehistory tar-pitch from birch bark and pine wood was used as an adhesive. Evidence of this technology is used in discussions about Neandertal cognitive and technological complexity, yet we know very little about how the material behaves, and how difficult it was to produce. In this paper we conducted 12 distinct adhesive performance tests. We applied industrial lap shear, climate chamber, and impact tests following ASTM International guidelines. The results of our study show that pitch adhesives are highly sensitive and precision is required to create the most effective adhesive. It therefore supports previous work, that hypothesizes the cognitive complexity of the early modern humans who produced the first compound adhesives. By detailing the performance of pitch adhesives using standardized methods our study also expands on research previously published about the Stone Age use of ochre in adhesives, and will aid in the comparison of Neandertal and modern human technologies.

We have no opposed reviewers, and there have been no prior interactions with any other journal regarding the submission or publication of this manuscript and the data therein. All authors have approved this manuscript and the submission to JAS Reports.

Also on behalf of my coauthors, thank you for considering this manuscript.

Sincerely,



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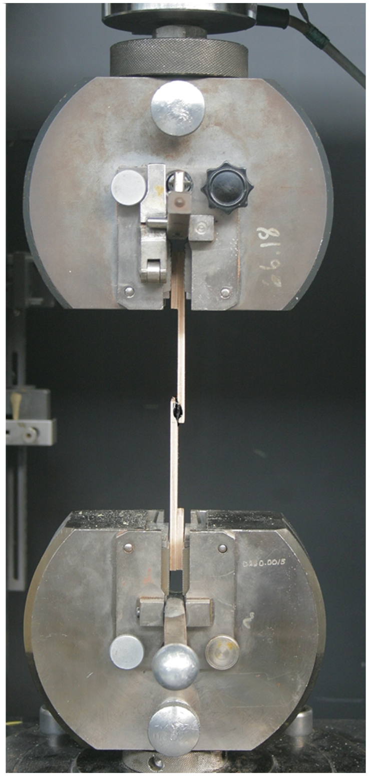
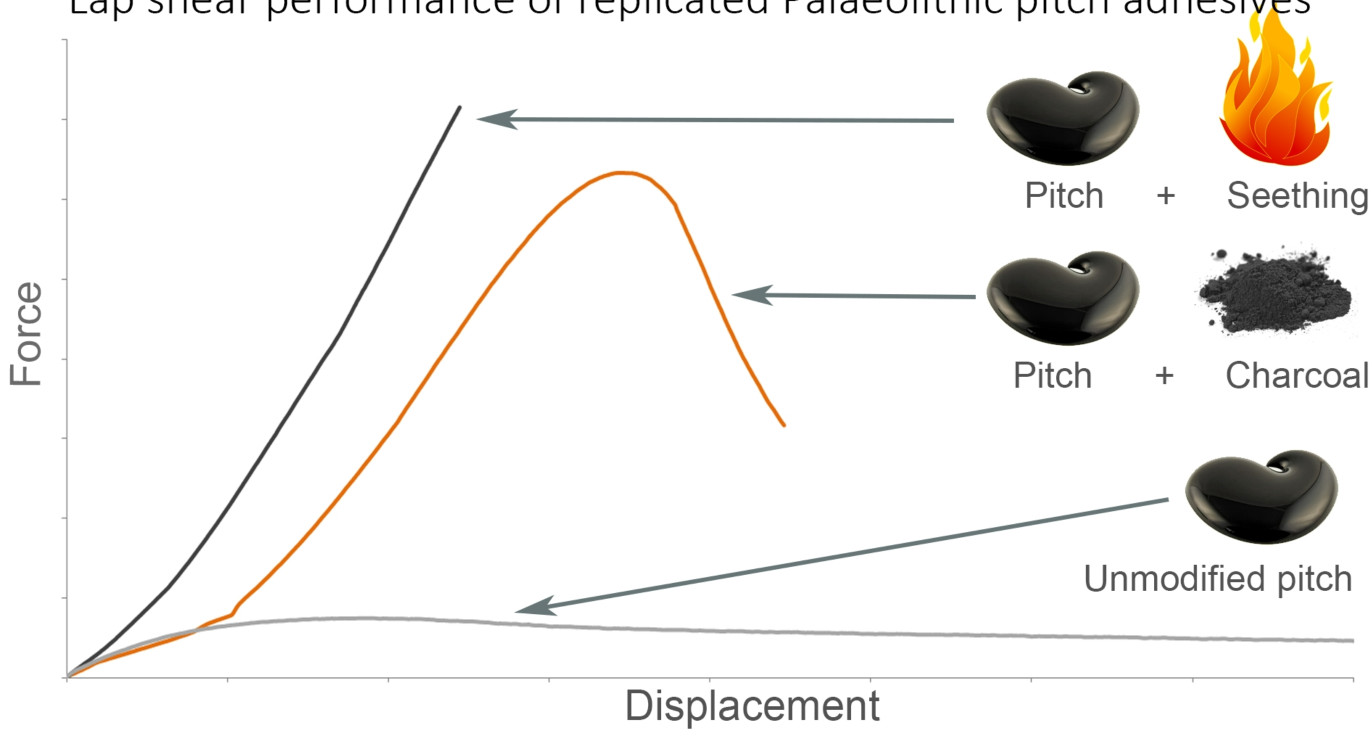


Lap shear performance of replicated Palaeolithic pitch adhesives



Full title

Laboratory strength testing of pine wood and birch bark adhesives: a first study of the material properties of pitch

Short title

Laboratory strength testing of pitch adhesives

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Highlights

- Unmodified pine and birch bark pitch adhesives resist similar lap shear forces.
- Pitch adhesive strength is improved with the addition of charcoal or by seething.
- Too much charcoal or seething can reduce the lap shear strength of pitch adhesives.
- Pitch is better suited to withstand impact than quasi-static lap shear forces.
- Pitch adhesives are similarly complex to rosin-based compound adhesives.

Abstract

Adhesives are an important yet often overlooked aspect of human tool use. Previous experiments have shown that compound resin/gum adhesive production by anatomically modern humans was a cognitively demanding task that required advanced use of fire, forward planning, and abstraction among other traits. Yet the oldest known adhesives were produced by Neandertals, not anatomically modern humans. These tar or pitch adhesives are an entirely different material, produced from a distinct, albeit similarly complex process. However, the material properties of these adhesives and the influence of the production process on performance is still unclear. To this end we conducted a series of laboratory based lap shear and impact tests following modern adhesive testing standards and at three different temperatures to measure the strength of pine and birch pitch adhesives. We tested eight different recipes that contain charcoal as an additive (mimicking contamination) or were reduced by boiling for different lengths of time. Lap shear tests were conducted on wood and flint adherends to determine shear strength on different materials, and we conducted high load-rate tests to understand how the same material behaves under impact forces. Our results indicate that both pine and birch pitch adhesives behave similarly at room temperature. Pine pitch is highly sensitive to the addition of charcoal and further heating. Up to a certain extent charcoal additives increases performance, as does extra seething. However, too much charcoal and seething will reduce performance. Similarly, pine pitch is sensitive to ambient temperature changes and it is strongest at 0°C and weakest at 38°C. Adhesive failures occur in a similar manner on flint and wood suggesting the weakest part of a flint-adhesive-wood composite tool may have been the cohesive strength of the adhesive. Finally, pine pitch adhesives may be better suited to resisting high-load rate impacts than shear forces. Our experiments show that pitch production and post-production manipulation are sensitive processes, and to obtain a workable and strong adhesive one requires a deep understanding of the material properties. Our results validate previous archaeological adhesive studies that suggest that the manufacture and use of adhesives was an advanced technological process.

Keywords

Adhesives, Pine pitch, Birch bark pitch, Palaeolithic, Hafting, Neandertal, lap shear, impact

1.0 Introduction

The use of adhesives for hafting in prehistory was a significant technological advancement [1-8]. Three primary materials were used to make adhesives in the Palaeolithic: Naturally sticky resins exuded from trees [9, 10], a naturally sticky petroleum product known as bitumen [11-15], and manufactured tars or pitches produced from the destructive distillation (pyrolysis) of plant matter [4, 16-19]. The earliest known adhesives are tars, dated to approximately 200,000 years ago, and were made from birch (*Betula* sp.) [4, 16-18]. Tar can be produced from any organic matter, and in recent times was more commonly made from pine (*Pinus* sp.) wood [20-23]. The pyrotechnical challenges associated with tar production have placed it at the forefront of a debate on Neandertal cognition [2, 24], however little is known about the sensitivity of tar in relation to the production process. The laboratory performance experiments conducted here provides valuable data for understanding the material properties of tar-based adhesives, moving the discussion about Neandertal cognition and technical abilities forward.

Adhesives are used as a proxy to understand the technological and cognitive abilities of hominins [2, 3, 6, 25, but see also 26]. This research has been dominated by compound resin/gum-ochre adhesives made by anatomically modern humans in Africa [5-8, 27-29]. In this scenario, it is hypothesised that the production and application of compound glues require advanced working memory, the ability to multi-task, an understanding of abstract terms (e.g. miscibility, stiffness, viscosity and tack) and fluid intelligence (as exemplified in transformative technology). The production of compound glues is complex and the end product does not resemble the individual ingredients. Moreover, the process is transformational and irreversible [6, 8, 30]. Neandertal tar production, although different from compound adhesive manufacture, may have required similar cognitive abilities [2]. For example, the pyrolytic production process is possible testimony to an understanding of abstract terms and fluid intelligence (Wragg Sykes 2015) and is used to illustrate the technological abilities of Neandertals [31].

Tar is made by heating biomass under reducing conditions and experiments confirm that wood tar production [32-35] and birch bark tar production [36-41] are sophisticated processes. Both can be made using aceramic technology (without pots), similar to what might have been available during the Palaeolithic [41, 42]. To produce tar organic material must be heated to a high enough temperature, under sufficiently reduced environments, and it must be collected without allowing it to burn or become over-saturated with ash, soil, or other contaminants [43]. When tar is produced it may still need further refinement before it is suitable to use as an adhesive. This may be in the form of additional heat treatment to evaporate and remove the more volatile liquid components (water, methanol, acetic acid) rendering what is more accurately described as ‘pitch’ [44]. Alternatively the tar may be thickened with an additive, such as charcoal, in a similar manner to ochre and gum [cf. 5]. Experimental re-production of tar resulted in contamination with plant products and fire by-products including charcoal [33, 43, 45, 46]. Although a current theoretical framework details the complexities of tar production (Wragg-Sykes and refs therein), it is presently unknown how complex the post-production process is and how sensitive the performance of pitch adhesives are to refinement with heat or to contamination. As with other natural adhesives, we know little about the adhesive performance of tar under different circumstances. Insight into these issues may help reveal prehistoric choices and add to the existing cognitive framework.

Here we present a first attempt to understand the effect of post-production manipulation on shear strength and impact resistance of wood and bark tar pitches. We explore adhesive strength in relation to tree species, climate, substrate material and force/activity. Pine tar is more ubiquitous in later periods than birch tar [47]. and it might be that these two adhesives had different (additional) functions. It is possible that one is stronger than the other, and therefore more/less preferred. To this end we conducted strength tests on pine and birch tar pitch. Strength tests were also conducted to understand the influence of post-production refinement and manipulation. In these tests charcoal was added in set increments to mimic increased charcoal contamination. Similarly, we tested tar in different stages of reduction. Prehistoric tar was used under variable environmental circumstances and it is possible that one of the attractions of this adhesive over resin was that it performed well under a wide temperature range [29]. We therefore tested tar for strength under different temperatures. Some adhesive may perform better on specific adherends or substrate materials. Standard strength tests generally use aluminium and wood adherends; we added flint to understand how tar strength on wood and flint compare. Finally, different force load-rates were at work in different prehistoric tasks and an adhesive may react differently to one than another. Prehistoric peoples may have selected glues based on these differences. We therefore compare the strength of tar under two different forces: static lap shear and impact.

2.0 Materials

2.1 Pine pitch, birch pitch, and charcoal

Tar is a dark coloured viscous liquid produced through the pyrolysis or gasification of biomass [48-50]. Tar can also be obtained from coal [49], or occur naturally as a material commonly known as bitumen or asphalt [48]. When tar is in a liquid state, containing higher percentages of volatiles it is referred to simply as 'tar'. The term 'pitch' or 'tar pitch' refers to the more viscous, semi-sold or solid fraction of tar [48, 49, 51]. Pitch is also sometimes confusingly used to refer to natural resin exudates collected from conifers [52, 53], although this is more of a colloquial use of the term [54] and will be avoided here.

The two states, tar and pitch, may have different functions. Historically, fluid tar materials were used for waterproofing and preserving wooden roofs and boats [55-57] and more solid pitch-like varieties were used as glue and for caulking ships [44]. Prehistorically, tars could have possibly served as a waterproof coating to protect sinew, raw-hide, or vegetable fibre bindings from moisture [58] and pitches could have been used as the bonding agent itself [4, 16, 18]. Although there is no precise classification that separates 'tar' from 'pitch', we will use the word 'tar' from here on to refer to the unrefined material obtained through the pyrolysis of woody plant materials, being in a liquid state at room temperature.

‘Pitch’ will be used to refer specifically to the refined fraction of tar that has been reduced to a semi-solid or solid at room temperature.

To control the material properties and to conduct a reproducible experiment we used commercially available pine tar, otherwise known as ‘Stockholm tar’ as our primary ingredient. Because birch bark tar is not commercially available we produced it using the ‘two pot’ method [33, 35, 59] in an open fire with metal containers. This method is quite refined, and produces a liquid tar with little charcoal contaminates. Both the pine and birch tar were reduced to pitch by boiling over a hot plate until they appeared solid at to room temperature [cf. 23].

To test the influence of production-related contamination we added commercially available powdered charcoal. This is pure charcoal made from beech (*Fagus* sp.) and ground into a fine powder (<30μm). Without the use of ceramics or metal containers to isolate the tar end-product from fire by-products, it is probable that charcoal would be a leading contaminant. There are other materials that could and probably did contaminate adhesives, including plant material from the bark or wood, soil, sand, or ash [43], but charcoal is perhaps the most significant and is thus the one we have chosen to test here.

2.1 Sample preparation

The sample preparation is the same for both lap shear and impact tests. Once the tar had been reduced to pitch it was possible to break apart into separate amounts for further tests (Fig. 1). Table 1 lists each adhesive and test applied. Unmixed birch pitch was used in one set of standard lap shear tests (LS1, Fig. 1A), and the pine pitch experiments consisted of four parts (Fig. 1B). Part one was used to conduct lap shear tests at a range of temperatures and on flint adherends (LS2, LS9, LS10). Part two was mixed with 10, 20, and 30 wt.% charcoal and then used for standard lap shear tests (LS3, LS4, LS5). Part three was further reduced by seething at approximately 150-200°C for 10, 20, and 30 additional minutes and then used for standard lap shear tests (LS6, LS7, LS8). Part four was used for a standard impact test (IR1) [cf. 29]. Before each test small glass beads (90 to 130 μm) were added to the adhesives to ensure uniformity among the set bondline thickness of each test piece [cf. 29]. The adhesives were stirred constantly for two minutes over an electric hot-plate before use and again briefly in between each application on every specimen. Once melted and thoroughly mixed, both adherend surfaces to be bonded were dipped in the adhesive at the same time. Then they were immediately squared and clamped until the adhesive had cooled and set. The wooden lap shear test specimens are 4.0 mm × 25.4 mm × 100.0 mm long. The bond overlap was 12.7 mm, making a bond surface area of 322.6 mm^2 in each experiment.

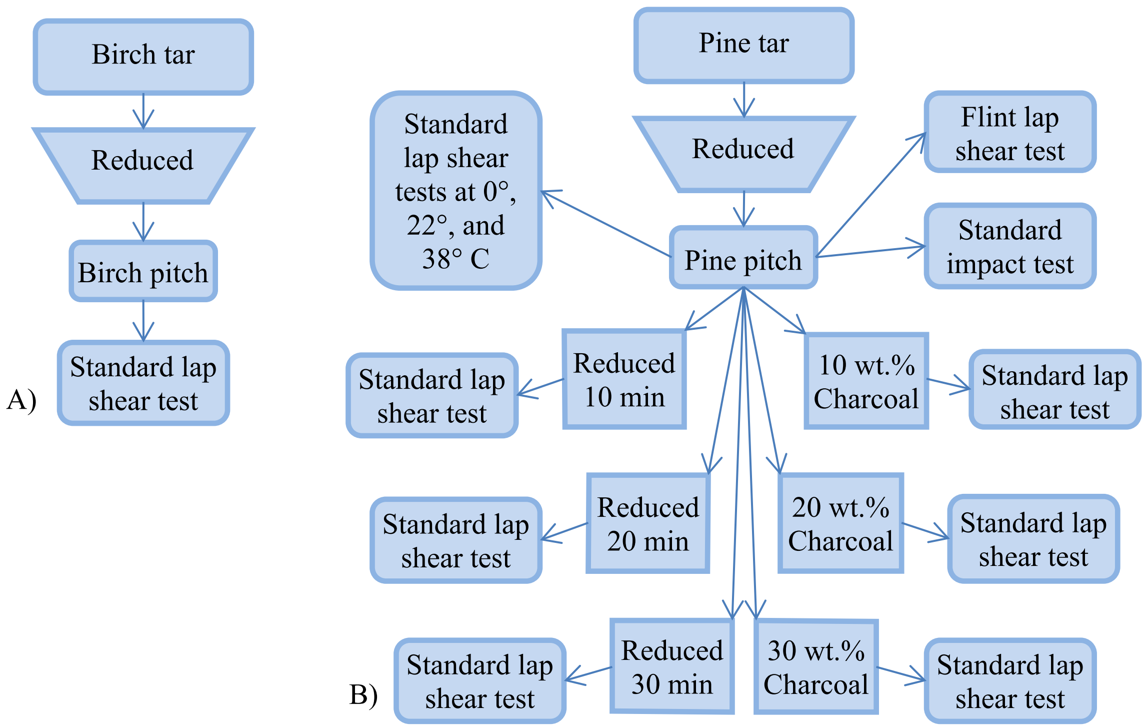

Figure 1. A) Workflow of sample preparation and experiments for birch bark pitch, and B) pine wood pitch adhesives.

Table 1. List of experiment number (Exp.) of all adhesives and test types used.

Exp.	**Primary material**	**Secondary manipulation**	**Test type**	**Temperature**	**Adherend type**
LS1	Birch pitch	None	Lap shear	22+/-2	Beech
LS2	Pine pitch	None	Lap shear	22+/-2	Beech
LS3	Pine pitch	10 wt.% charcoal	Lap shear	22+/-2	Beech
LS4	Pine pitch	20 wt.% charcoal	Lap shear	22+/-2	Beech
LS5	Pine pitch	30 wt.% charcoal	Lap shear	22+/-2	Beech
LS6	Pine pitch	Boiled 10 minutes	Lap shear	22+/-2	Beech
LS7	Pine pitch	Boiled 20 minutes	Lap shear	22+/-2	Beech

LS8	Pine pitch	Boiled 30 minutes	Lap shear	22+/-2	Beech
LS9	Pine pitch	None	Lap shear	0+/-2	Beech
LS10	Pine pitch	None	Lap shear	38+/-2	Beech
LS11	Pine pitch	None	Lap shear	22+/-2	Rijckholt flint
IR1	Pine pitch	None	Impact resistance	22+/-2	Unknown hardwood

We also conducted one set of tests on Rijkholt flint from southern Limburg, the Netherlands (LS11). This test was to ensure that the adhesive would behave similarly on flint. The flint was cut by a professional mason into rectangular tabs to create a bond surface area that was also 25.4 mm × 12.7 mm. To ensure maximum adhesion, the substrate materials were degreased with acetone, abraded with 100 grit sandpaper, degreased again and left to dry for five minutes prior to the application of the adhesive (Fig. 2).

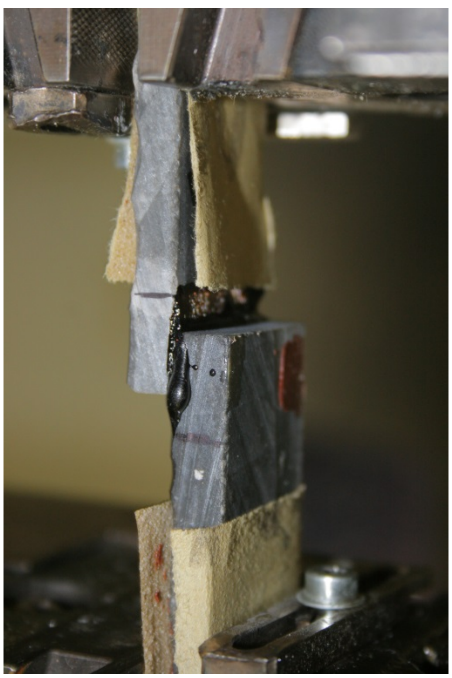

Figure 2. Flint lap shear sample in test apparatus clamps. Sandpaper was placed between clamps and flint to ensure they would not slip. This photo was taken during the test, and displacement can be witnessed by the distance the ends of the flint have moved from the horizontal black lines.

For the impact resistance test (IR1), the samples were made from solid pieces of tropical hardwood, and cut to 12.0 mm × 18.0 mm × 55.0 mm. The top 10.0 mm was cut off and glued back on, creating a bonded surface area of 216.0 mm^2 [cf. 29].

3.0 Methods

3.1 Lap shear experiments LS1-11

To test material properties in a reproducible manner we used the internationally recognised ASTM International standards [60]. Of these standards, we selected two tests: lap hear and impact, D-1002 and D-950 [61, 62]. Lap shear tests are widely used as adhesive joint strength tests because they are easy to conduct and closely resemble the geometry of many practical joints, including the cleft haft [28, 63]. The ASTM D1002 test standard was therefore selected for the quasi-static shear strength (or low load rate) of a single-lap joint. Due to the relatively weak nature of the adhesives (compared with modern glues) and to improve the likelihood of cohesive, rather than adhesive failures one aspect of the standard was changed. For the majority of the tests we used beech (*Fagus* sp.) plywood instead of aluminum as the substrate material. In one set of experiments we used Rijkholt flint.

The lap shear tests were conducted using a Zwick Roell 1455 tensile loader with a 20kN load cell at a rate of 1.3mm/minute and a pre-load of 10N (also see Kozowyk et al. 2016). Specimens were mounted vertically between two clamps, which are then moved apart from one another at a constant speed until bond failure. If the adhesive does not fail completely, tests are ended automatically when the force decreases to one-half that of the maximum obtained force. Five individual specimens were tested for each adhesive recipe. Tests were conducted at an ambient air temperature of 21–23°C and the relative humidity during the experiments was 45+/-6%. Experiments LS9 and LS10 were conducted using a Zwick Roell EC 1760 250kN tensile loader and climate chamber with the same load rate and protocol. To facilitate the larger flint test samples, experiment LS11 was also conducted using this apparatus, but with the climate chamber removed. Temperatures of 0°C and 38°C were selected as extreme, yet conceivable highs and lows. These temperatures also correspond with set protocols, test exposure numbers 4, 5, and 7 in ASTM D 1151-00 Standard practice for effect of moisture and temperature on adhesive bonds [64].

Lap shear test results are interpreted in several ways. First, a stress/strain graph is plotted that gives an indication of the maximum force withstood by the adhesive. In this case a higher maximum force, recorded as N/bonded surface area (mm^2), or MPa, means that the adhesive was stronger. The stress/strain curve can also describe the nature of the adhesive failure. A long low curve (larger displacement and lower maximum force) typically signifies that the adhesive was less strong, highly ductile and easily deformed. A steep sharp curve (lower displacement and higher maximum force), or one ending abruptly indicates a stiffer adhesive, or one that failed in a brittle manner. Further, the location of adhesive residues on the adherends after failure can indicate either a cohesive or an adhesive failure. If residue is evenly distributed among both surfaces, the failure was cohesive – within the adhesive matrix itself. If the residue is found only on one surface the failure was likely adhesive – occurring along the bond interface between adhesive and adherend.

3.2 Impact test IR1

Materials can behave differently under different forces. For example, ductile materials can shatter abruptly under impacts and high and low load rates also correspond to different prehistoric tasks; hafted spear points were probably subjected to high load rates, whereas hafted scrapers were subjected to low load rates [29]. To compare the results from the low load rate lap shear test and to determine if some adhesive recipes are better suited to one task over another, we also tested pitch at high load rates (impact, experiment number IR1). The most common tests for material impact resistance are the Charpy and Izod tests [65]. We selected the variant described by ASTM D950 [62]. Impact tests were performed using a Zwick 5113 pendulum impact tester. A pendulum hammer is released from a swing angle of 124.4 degrees and accelerates to a speed of 3.46 m/s before impacting the specimen locked in the clamps. In our impact test the adherend is struck with a velocity of 3.46 metres per second. This is faster than the loading speeds estimated for stabbing, and slower than those for spear throwing [66]. The hammer impacted the 18 mm wide face of the sample less than 1 mm from the bondline. Impact tests were conducted at an ambient air temperature of 22–23°C and a relative humidity of 45+/-6%. Impact resistance is measured by the height of the pendulum swing after colliding with the adhesive sample and is given in Joules as the amount of energy required to break the adhesive bond. No stress stain curve is generated, but as in lap shear tests, impact failures can occur adhesively or cohesively.

4.0 Results

4.1 Room temperature lap shear LS1 – LS8

Here we discuss the lap shear tests conducted at room temperature using wooden adherends. They show how pine and birch pitch adhesives compare, how pitch is affected by contamination from charcoal, and by post production refinement using additional heating. The strength of lap shear tests is recorded as the maximum force over the surface area of the bond (MPa). Table 2 displays the maximum, minimum, and mean values for each adhesive recipe. Fig. 3 displays all the results of lap shear test on wood at room temperature.

Table 2. Results of the lap shear tests. Including the mean, maximum, and minimum maximum force (Fmax), and the mean, maximum, and minimum displacement at maximum force (Dl at Fmax) for each adhesive recipe.

				Fmax (Mpa)			Dl at Fmax (mm)		
Exp	**Primary material**	**Secondary manipulation**	**Adherend type**	**Mean**	**Max**	**Min**	**Mean**	**Max**	**Min**
LS1	Birch bark pitch	None	Beech	0.32	0.51	0.14	0.94	1.2	1
LS2	Pine pitch	None	Beech	0.37	0.77	0.19	1.3	1.6	0.9
LS3	Pine pitch	10 wt.% charcoal	Beech	1.77	2.23	1.19	1.2	1.4	1
LS4	Pine pitch	20 wt.% charcoal	Beech	0.68	1.80	0.28	1.5	1.7	1.3
LS5	Pine pitch	30 wt.% charcoal	Beech	-	-	-	-	-	-
LS6	Pine pitch	Boiled 10 additional minutes	Beech	1.73	2.59	0.79	1.58	1.9	1.1

LS7	Pine pitch	Boiled 20 additional minutes	Beech	0.65	0.77	0.53	0.85	0.9	0.8
LS8	Pine pitch	Boiled 30 additional minutes	Beech	-	-	-	-	-	-
LS9	Pine pitch	None	Beech	1.20	1.58	0.97	0.16	0.3	0.1
LS10	Pine pitch	None	Beech	0.03	0.04	0.02	0.914	1.7	0.1
LS11	Pine pitch	None	Rijckholt flint	0.86	1.18	0.39	0.344	1	0.05

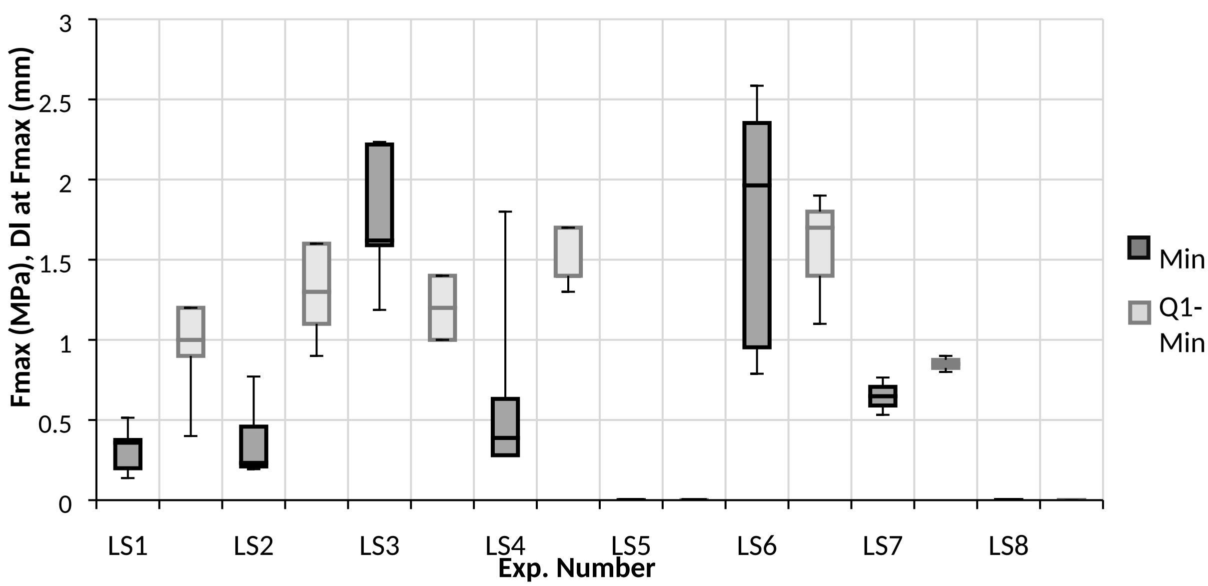

Figure 3. Lap shear results for experiments LS1 - LS8. Fmax = maximum force; Dl at Fmax = displacement at maximum force.

First, birch pitch performed in a similar manner to pine pitch (Table 2). The mean maximum strength of birch pitch was 0.32 MPa and the mean maximum strength of pine pitch was 0.37 MPa, the ranges of which overlap considerably. Birch and pine pitch were both highly ductile materials under static load rates, and were displaced an average of 0.9 mm and 1.3 mm respectively. The stress/strain curves appear similar for birch and pine pitch, although pine pitch was slightly more ductile (Fig. 4). Both adhesives shared a relatively high variation in maximum force. Neither failed abruptly, and both failed cohesively within the matrix of the adhesive rather than along the bond interface. As the physical characteristics of birch and pine pitches proved to be similar with this test, the other experiments were conducted using commercially available pine pitch. This allowed us to control the variables resulting from birch bark production in an open fire and thus aided the reproducibility.

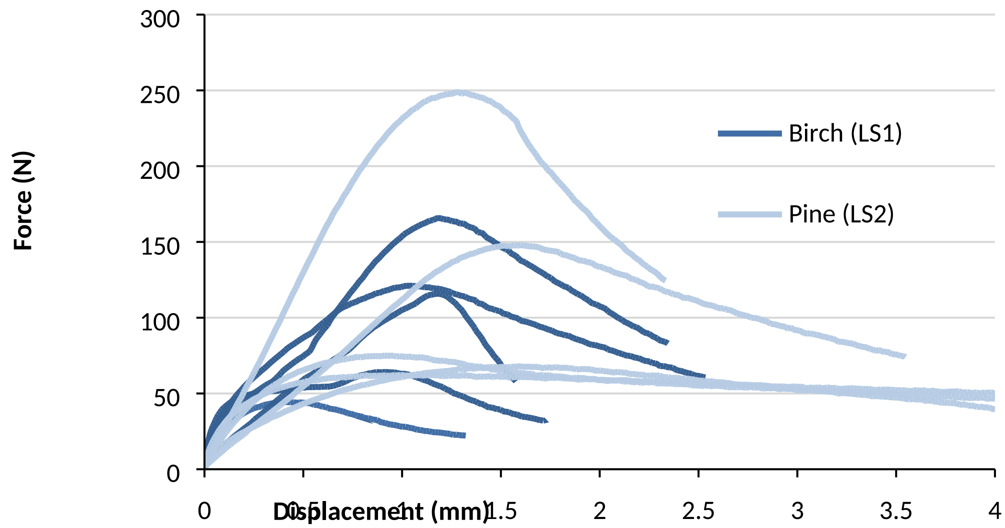

Figure 4. Stress strain curves from each individual specimen for unmodified birch and pine pitch at room temperature on wood adherends.

When charcoal was added to pine pitch the properties changed significantly (Fig. 5). With the addition of 10 wt% charcoal the mean Fmax of LS2 to LS3 increased from 0.37 MPa to 1.77 MPa, a mean Fmax increase of 378 %, and mean displacement remained approximately the same. Charcoal therefore improved the strength under static load, and increased the relative stiffness of the material. With an additional 20 wt% charcoal, the mean Fmax of LS4 fell to 0.68 MPa (an increase of 84 % from LS2). With 30 wt% charcoal LS5 was not useable as an adhesive as it became saturated with filler and lost nearly all of its ‘tack’. The substrates could not be successfully bonded, and no lap shear test could be conducted.

Further reducing pitch by seething [cf. 44] had a similar affect as adding charcoal (Fig. 5). After 10 extra minutes at 150-200°C the mean Fmax of LS6 was 1.73 MPa (an increase of 367% from LS2) and mean the displacement was 1.6 mm. Twenty minutes of seething resulted in a mean Fmax for LS7 of 0.65 MPa (an increase of 76 % from LS2) and a mean displacement of 0.85 mm. However, it must be noted that due to increased brittleness three out of five of the specimens for LS7 failed during preparation before the test could be started. Thirty minutes of seething created an extremely brittle material in LS8 that failed to bond successfully and cracked or broke on every specimen before the test could be started.

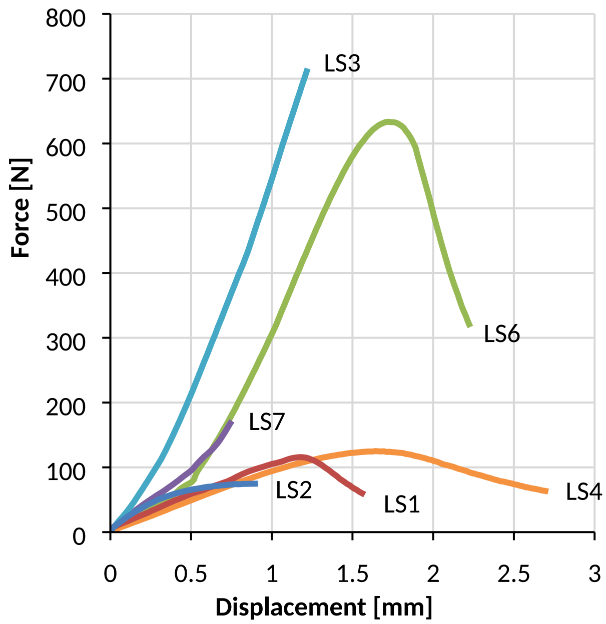

Figure 5. Stress/strain curves for median results of tests LS1, LS2, LS3, LS4, LS6, and LS7 to give approximation of variation between recipes.LS5 and LS8 gave no results. Of the five specimens tested for LS4, two were successful and the lowest of the two is visualized here.

4.2 Climate chamber lap shear: LS9-LS10

These experiments include those conducted in the climate chamber at 0°C and 38°C to determine how pitch adhesives are affected by changes in temperature. They will be primarily compared with LS2 – the same unaltered adhesive tested at 22°C. This pine pitch performed significantly better at 0°C than at 22°C (mean 1.20 MPa and 0.37 MPa respectively that is a mean Fmax increase of 224 %). It performed significantly worse at 38°C (0.03 MPa, or a mean Fmax decrease of 92 %) (Fig. 6). At this high temperature the pitch was so soft that it deformed under the 10 N preload of the test machine, and final test results are negligible (Fmax of near zero, and Dl at Fmax is highly variable). At 0°C all of the pine pitch failures were brittle, rather than ductile as they were at room temperature and 38°C.

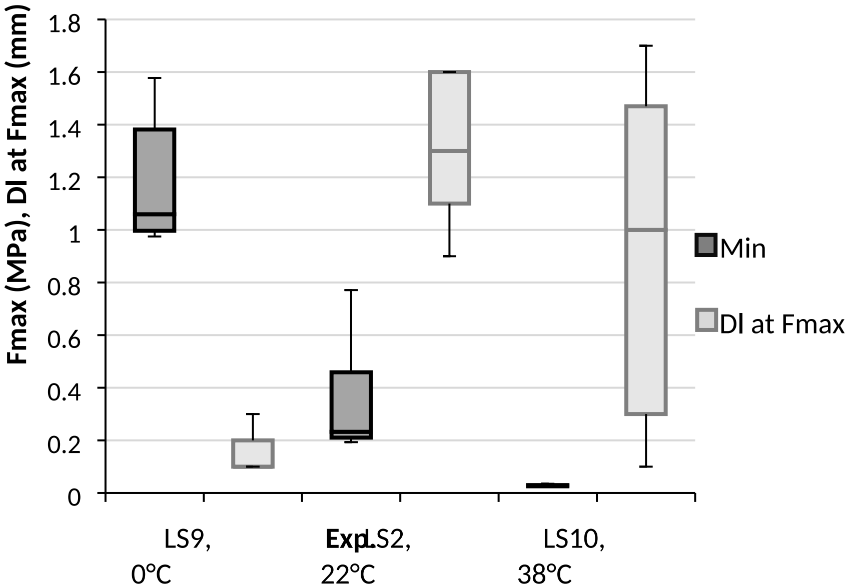

Figure 6. Maximum force (Fmax) and displacement at maximum force (Dl at Fmax) of climate chamber experiments LS9 (0°C) and LS10 (38°C) in comparison with LS2 (22°C).

4.3 Flint lap shear: LS11

These experiments include those using flint adherends to determine how the adhesive behaves when applied to different surfaces. The adhesive for these tests was pure pine pitch that has not been further reduced, and it will be compared primarily with LS2, the unreduced pine pitch at room temperature. On Rijckholt flint LS11 resisted a maximum force of 0.86 MPa. The increase in strength over LS2 may be a result of the time between experiments. LS11 was conducted at a later date and the pitch may have dried/hardened additionally. The most important result here, however, is that the failure types on flint were all cohesive. This means that on both flint and wood, the bond strength between the adhesive and adherend is greater than the internal strength of the adhesive matrix. The weakest point in a wood-pitch-flint compound tool may therefore be the adhesive material, and not the bond between any of these materials.

4.4 Impact resistance: IR1

In the impact test we used pure pine pitch that has not been further reduced and the results are thus comparable to experiment LS2. This test was conducted to determine how different load rates affect the performance of pitch adhesives. The test was repeated on seven specimens and the mean impact resistance was 0.51J. The maximum and minimum were 0.40J and 0.61J respectively. Every test resulted in a cohesive failure, with adhesive residue clearly left on both adherend surfaces (Fig. 7).

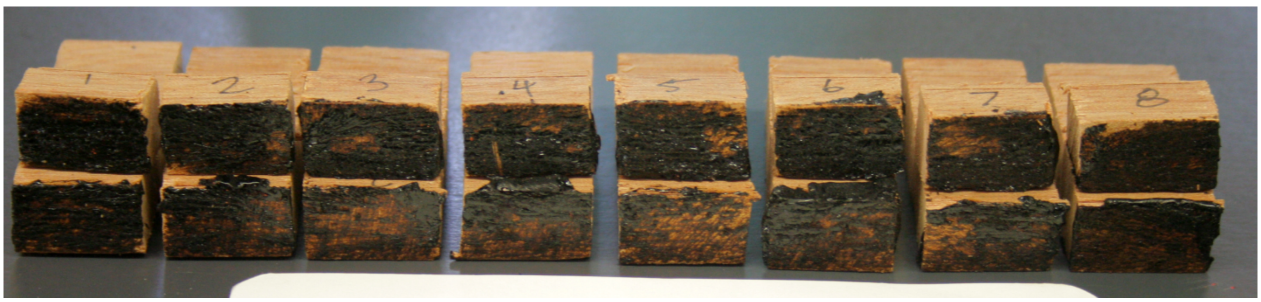

Figure 7. Bonded surfaces after impact test failures. Even presence of tar on upper and lower adherends indicates failures were cohesive in nature.

5.0 Discussion

5.1 Discussion of results

The preliminary comparison in this pilot study indicates that under static lap shear forces at room temperature there is little difference in performance between birch and pine pitch. In this respect, and as it has been described elsewhere, although tars from different tree species do differ chemically [67] their composition is not altogether dissimilar and their physical properties may also be similar [68, 69]. It must still be noted that the sensitivity of natural adhesives to additives, as seen here and in previous studies [5, 6, 29] may mean that birch and pine pitch behave differently when mixed with charcoal. The different chemical components, such as the resin acids in pine pitch and betulin in birch bark pitch may also have an effect on how these adhesives react to heat or re-use.

Pine pitch strength proved to be highly sensitive to charcoal. For the pine pitch used in this study the strongest mixture would likely contain somewhere just over 10 wt% charcoal powder. Anything less and it will be too plastic and soft, and anything more and it will lose tack, both of which will reduce its strength as an adhesive. If the production method used by prehistoric humans created uncontaminated tar, then the intentional addition of charcoal would be beneficial. Alternatively, as evidence of contamination during experimental reproduction suggests, charcoal contamination may have occurred naturally during production [43]. Some contamination would in this case be beneficial to the performance, and a perfectly clean production method is not necessary. However, as too much charcoal (LS4 and LS5) clearly hampers the adhesive qualities, the *amount* of contamination would still be very important to control. Today, adhesive formulators adjust adhesive properties with additives such as carbon black [70] to similar ends. Fillers are used to control rheology or deformation and balance physical properties that are necessary to suit the intended use of the adhesive such as tack and viscosity [71]. Finding such a balance with ancient pitch and charcoal adhesives shares many similarities may have been a homologous affair.

The effects of seething pine pitch have a similar result on performance as contamination. Pine pitch is highly sensitive to change, and seething for 10 to 20 minutes is enough to improve the strength four-fold and then decrease it to something unusable. The reduction of pine pitch from the LS2 consistency would therefore reach a maximum strength somewhere around 10 minutes. Anything less and the material is too plastic and soft, and anything more and the material becomes too brittle. Like the contamination from charcoal, this says something about the sophistication of the production processes. As the manufacture of commercial pine tar is highly refined, and the product is much less viscous than the final pitch adhesive, it requires considerable effort to reduce it to a solid pitch ideal for the application at hand. Such refinement, seen here as boiling at a controlled temperature for a specific time, would require considerable pyro-technic dexterity, along the same lines as using fire to dry acacia gum adhesives [6, 7], or to melt and mix rosin with beeswax or ochre [29]. With a less refined production many of the liquid fractions of tar may escape during manufacture and the resulting product would be more pitch-like from the start. This would lead to the production of a stronger adhesive such as LS3 or LS6 without the need for post-production refinement. More research would be required to test the quality and consistency of pitch adhesives produced using Palaeolithic technology to accurately describe what reduction processes would be necessary.

Ambient temperature has a strong influence on the behaviour of pine pitch adhesives. At 0°C, LS9 was comparable, though not quite as strong as the mixed and reduced pitches in LS3 and LS6 respectively. At lower temperatures it may therefore not be necessary to add charcoal or further reduce pitch to make it stronger. At 38°C, LS10 was extremely soft and ductile, likely too soft to serve any purpose as an adhesive. From these tests it appears that this pine pitch is strongest between 22°C and 0°C. As it stands, it is unclear whether the strength would continue to increase below 0°C. However, at 0°C all of the pine pitch failures were brittle, rather than ductile, so it is likely that as the temperature continued to decrease the adhesive would become increasingly brittle until the point where it is unusable.

The cohesive nature of the failure on flint adherends shows that regardless of surface (porous wood, or smooth flint) pitch adhesives perform similarly and do not delaminate along the bond interface. Under lap-shear conditions it can then be said that the weak-point is not necessarily the surface between adhesive and adherend, but rather the bulk adhesive itself. This may be different with other materials such as bone or antler points, so testing a wider array of Palaeolithic materials could be useful in the future.

Pine pitch adhesive IR1, the same material used in experiment LS2, behaved differently under impact. This material was likely too ductile to be a useful adhesive for purposes with repeated or continual use at low load-rates, such as hide scraping and cutting, yet would be well suited to impact-related uses such as projectile or spear points [cf. 18]. It is likely that as refinement by seething, additive content, or ambient temperature change the lap shear performance, the optimum impact-resistance of pitch adhesives would change in a similar way. As temperature decreases, for example, a pitch that is less viscous at room temperature would need to be produced in order to maintain a high impact resistance and avoid becoming too brittle.

5.2 Comparison with resin and gum based adhesives

In a previous lap shear study we tested how sensitive rosin and gum based adhesives are to recipe changes [29]. We found that, up to a particular optimum, pine rosin glues increase in strength when beeswax and ochre are added. Small changes in the amount of ingredients had a big effect on strength. Our unrefined pine pitch adhesive here was weaker under lap shear forces than any combination of rosin with beeswax and ochre. The same pitch, however, outperformed rosin adhesives in the impact test. The task being performed is therefore prevalent to the performance of the adhesive. With the addition of 10 wt.% charcoal, or reduction for 10 additional minutes, the lap shear performance of pitch was comparable to 50/50 rosin-beeswax mixtures containing ochre. Or 80/20 rosin-beeswax ochre mixtures [29]. At 0°C the unreduced pitch (mean Fmax 1.20 MPa) performed better than pure rosin (failed prior to any test due to brittleness), 50/50 rosin-beeswax (mean Fmax 1.02 MPa), and 70/30 rosin-beeswax (mean Fmax 0.98 MPa). Each of these 3 rosin based adhesives outperformed pine pitch at 38°C, however, suggesting pitch adhesives may be better suited to colder climates [72]. It must still be noted that this varies on the method of production, and the level of reduction. Some experimentally produced birch pitch has been recorded as being resistant to warm temperatures as well [46].

The addition of charcoal in 10 wt.% increments to pine pitch adhesives had more pronounced effects in the shear tests than did ochre in the same wt.% increments to rosin-beeswax compound adhesives [29]. A difference from 20 wt.% to 30 wt.% charcoal changed the adhesive from highly plastic and soft to being so over-saturated that it would not adhere to either substrate. This difference may result from the mass of charcoal powder compared to red ochre powder. Charcoal is much less dense, less than 1 g/ml, compared to red ochre/hematite, approximately 5 g/ml [73], so when the recipes are mixed by weight, as was done here, the volume of charcoal used is considerably more than the volume of ochre, and the particles simply cover more surface of the adhesive.

The action of seething pitch adhesives to change the performance properties may be comparable to using heat from a fire to dry gum adhesives [5], or to boil down pine resin and produce rosin. Both of these processes can damage the adhesive if too much heat is applied too quickly, and maintaining control over the heat source is necessary. It is possible that a soft pitch could dry and harden over time, simply on exposure to air or sunlight, as with gum or resin, but the practicality of this is questionable. As was seen with gum adhesives, even after several days of air drying, when the adhesive was used it would break and reveal wet and tacky gum in the centre [5]. Further, if the adhesive is too soft when left to dry it can easily run out of its haft or drip off the tool.

Previous impact tests on compound rosin adhesives [29] showed a relative decrease in performance when compared with pine pitch adhesives. The mean lap shear Fmax of rosin-beeswax-ochre was (3.49 MPa) and the mean impact resistance was (0.48 J). While pine pitch (LS2 and IR1) mean lap shear Fmax was (0.37 MPa) and the mean impact resistance was (0.51 J). Although it is difficult to directly compare lap shear to impact performance, when the area under the lap shear stress-strain curve is calculated giving a measurement in Joules, it is clear that pine pitch is noticeably weaker than compound rosin adhesives during the shear tests and remains comparable in strength under impact forces (Fig. 8).

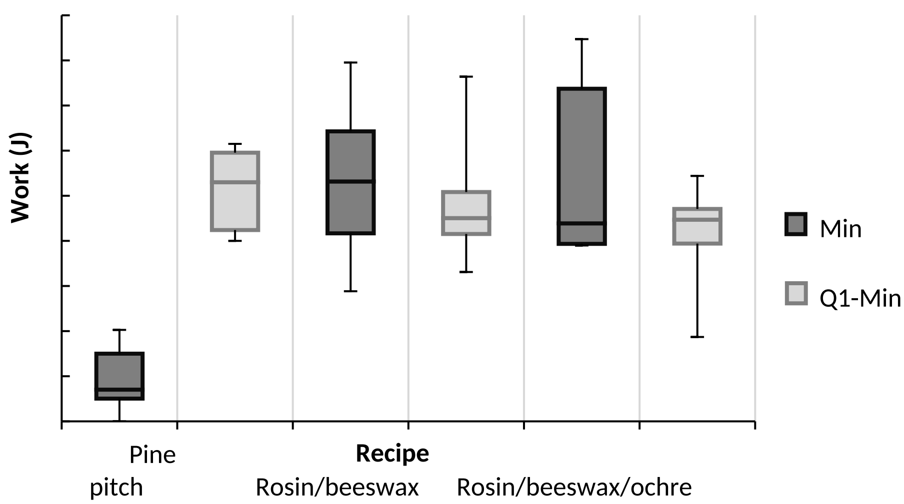

Figure 8. Relative work done (J) to maximum force (lap shear) and adhesive failure (impact) during tests.

The variable nature of pitch adhesives, ranging from highly ductile to very brittle, suggests that the addition of beeswax would not be required to act as a plasticising agent in the way that it is often described for rosin adhesives [29, 74]. However, when pitch is over-heated, or boiled for too long it can become brittle, and beeswax or animal fats can potentially improve/revert the quality (personal observation). Additionally, pitch can exhibit viscoelastic properties [49, 75] and 'flow' at extremely low rates over time. It is possible that the addition of a solid with high miscibility in tar may help to reduce this unwanted property. Although it may not be necessary for hafting stone tools, especially if a binding material was also used, it could be prevalent for purposes such as repairing pottery, where the bond would be required to remain in exactly the same position under a low level of static stress for a prolonged period of time.

5.3 High-tech pitch?

To define the complexity of pitch based only on the method of production, as is often done, is too simplistic. There are a number of conditions that must be met to produce a strong adhesive. Whatever the method of production, it must result in high enough yields of a suitable adhesive material. The control of contamination during production would be necessary, as would the controlled application of heat to reduce tar to pitch. Too much charcoal may yield an unusable adhesive, while not enough may result in one that is too liquid or soft. Seething at too low heat, or for too short a time and the adhesive will not be hard enough, while too much heat for too long will produce one that is brittle and crumbly. These two processes may also play off one another. A material with a high degree of charcoal contamination will likely require less seething and vice versa. Either the production process must be so refined as to produce an optimum material from the onset, or a good understanding of how to manipulate the properties post-production would be necessary. And likely, depending on the season, temperature, or task, some combination of the two would be necessary.

Alternative uses of adhesives during the Palaeolithic must also be considered, including the use as a handle or backing material itself. The appearance of the flint flake from Campitello Quarry, Italy, gives the impression of a simple back to improve prehension [17]. In this situation, pitch may have been used in a manner similar to spinifex resin on Australian 'leiliras', a type of stone knife. It could be applied as a backing to protect the users hands from the sharp edges of the flint, or melted and reapplied to bind the same blade to a wooden handle when needed [76, 77]. Use-wear evidence from Inden-Altdorf suggests tools were re-used and possibly re-hafted for different purposes [18]. In order to act as a backing material, cohesive and adhesive strength are less important, and weak or brittle materials would likely suffice. However, if the material were to be re-used as a binding medium to place the flint in a handle, the physical strength and adhesive quality of pitch must be higher than for a backing alone.

Tar and pitch was also used in historic times for waterproofing and protection. It was produced and used on a very large scale to caulk and waterproof pots, wooden ships and even protect wooden churches [22, 44, 55, 78, 79]. It may have served a similar purpose in prehistory as well. Many hafting methods rely on some form of fibre or cordage for binding [58, 80, 81]. Natural plant and animal fibres are highly susceptible to moisture, and tar or pitch is an obvious choice for waterproofing. In this situation the strength of the material is again not very important. Materials with lower viscosity could be applied easily. Highly ductile materials may be beneficial, as flexibility would help prevent the waterproof coating from cracking and breaking. But even for waterproofing the consistency and production methods effect the performance. It has been suggested that pine pitches produced at lower temperatures are more suited to surface protection, and pine pitches produced at higher temperatures are better for impregnation and caulking [44]. Although this might not be as relevant for a small stone tool, it still further illustrates the sensitivity of the production and post-production refinement process for the task at hand.

The variable nature of pitches and adhesives used in different tasks means that there is still much work to be done. Lap shear tests, although an industry standard, are not an accurate representation of all practical joints, especially with regards to Palaeolithic style hafts. Furthermore, greater comparison needs to be made with actual adhesives found in the archaeological record. Using the production method alone as a discussion point for Neandertal cognitive complexity is too simplistic, and more aspects should be taken into account. This study has shown that, like compound adhesives, wood tar based pitch adhesives can be greatly affected by changes in ambient temperature, tool type and hafting arrangements, as well as to production and post-production processes such as contamination or heating. The sensitivity of pitch adhesives to these factors suggests that ancient manufacturers understood the material properties and had the technical abilities to manipulate the material as necessary.

6.0 Conclusion

As with other natural adhesives, we know little about the adhesive performance of tar under different circumstances. It is presently unknown how complex the post-production process is and how sensitive the performance of pitch adhesives are to refinement with heat, to contamination during production, or to ambient air temperatures. Insight into these issues may help reveal prehistoric choices and add to the existing cognitive framework for Neandertals and early modern humans. The results from this study show several features along these lines: Adhesive materials obtained from reducing birch bark and pine wood tar to pitch behave similarly under static lap shear tests. Adhesive qualities of pitch from pine wood pyrolysis tars are highly sensitive to changes due to charcoal additive content and 10 wt.% additions significantly alter the maximum strength during static lap shear. Likewise, the refinement of tar and pitch by seething at temperatures below 200°C for 10 minute intervals can significantly alter the plasticity and strength of the material. Changes in ambient temperature also have profound effects on the performance. A pine pitch that is brittle yet strong at 0°C will behave entirely different and be ductile and weak at 38°C. Further, while pitch may be highly ductile during static or low load-rate applications, it behaves entirely differently under high-load rate impacts. Under such circumstances (impact), pitch is comparable in strength to compound rosin-beeswax-ochre adhesives [29].

These variations in performance resulting from small changes in ingredients or refinement processes, combined with the effect of temperature and load-rate on adhesive performance suggest the manufacturers were highly skilled with an intricate knowledge of the materials they were working and of the techniques to do so. Depending on the outside temperature and the task at hand their manufacture methods and/or post-production processes may have had to vary in order to produce the most effective adhesive. Results here are parallel to those of gum and resin-based compound adhesives [6, 8, 29] and thus imply high levels of analogous reasoning, technical and cognitive abilities. Yet, without direct evidence of tar production methods by Neandertals in the archaeological record there is still much more work than needs to be done.

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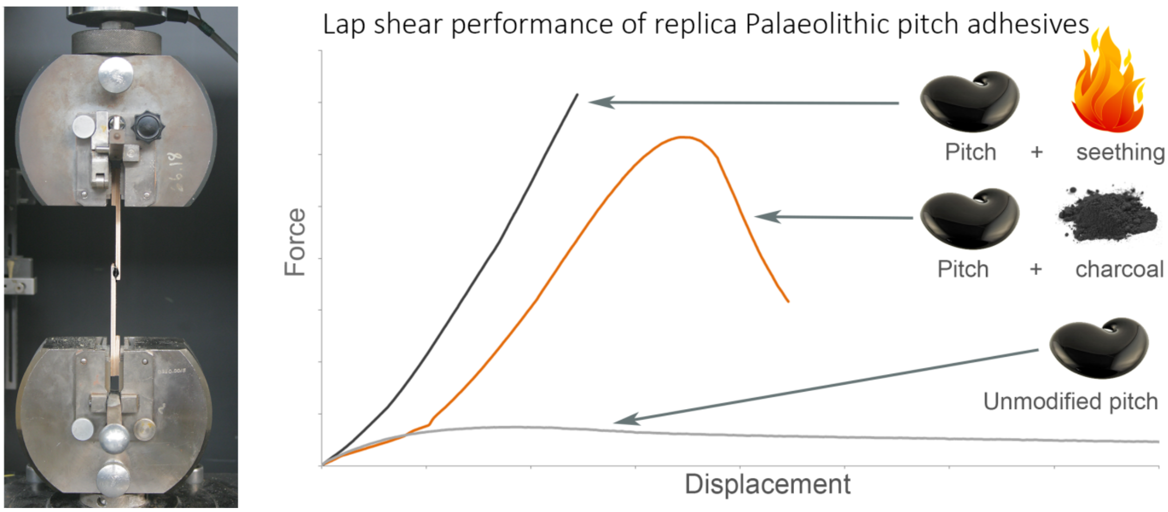
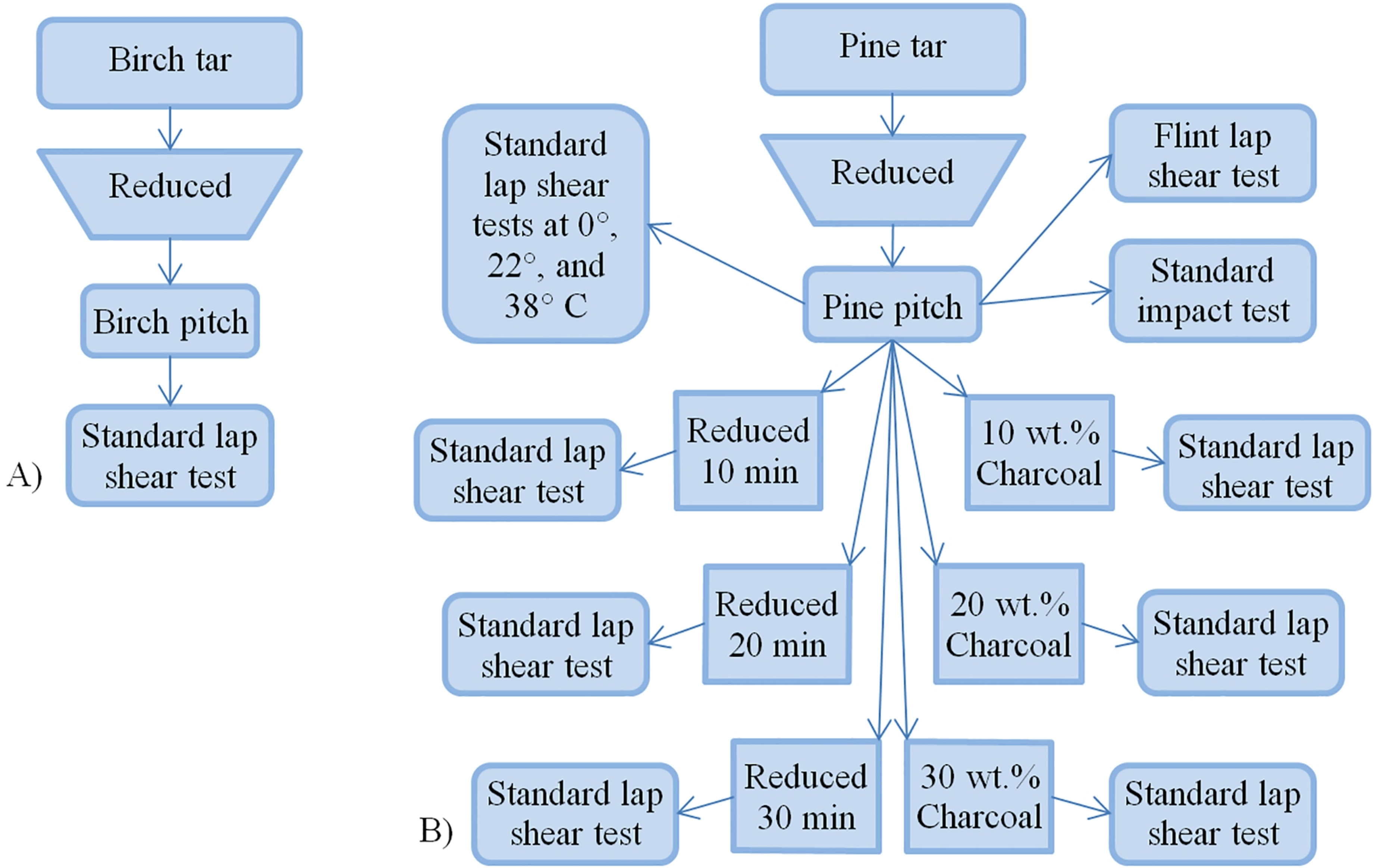
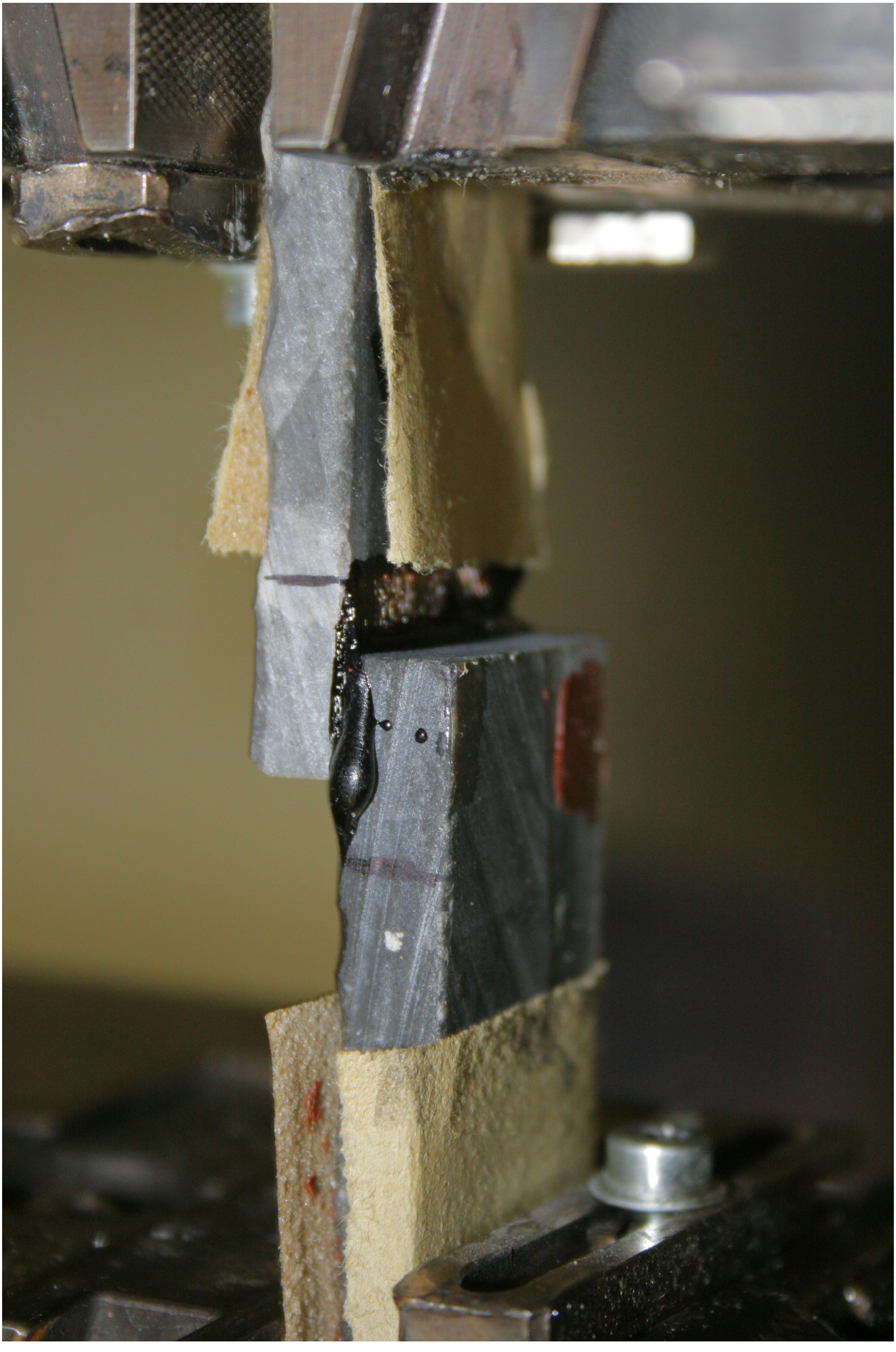
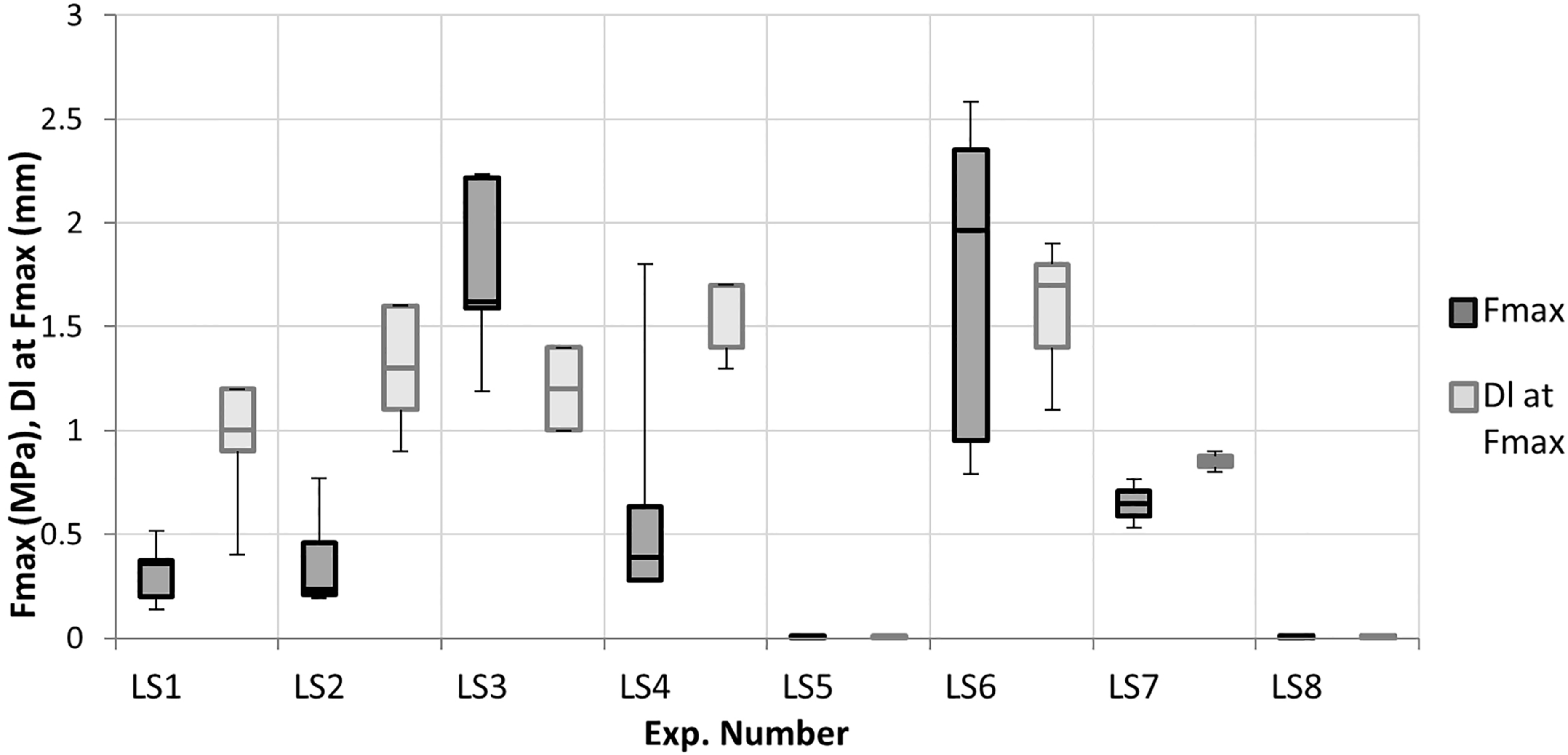
Graphical Abstract

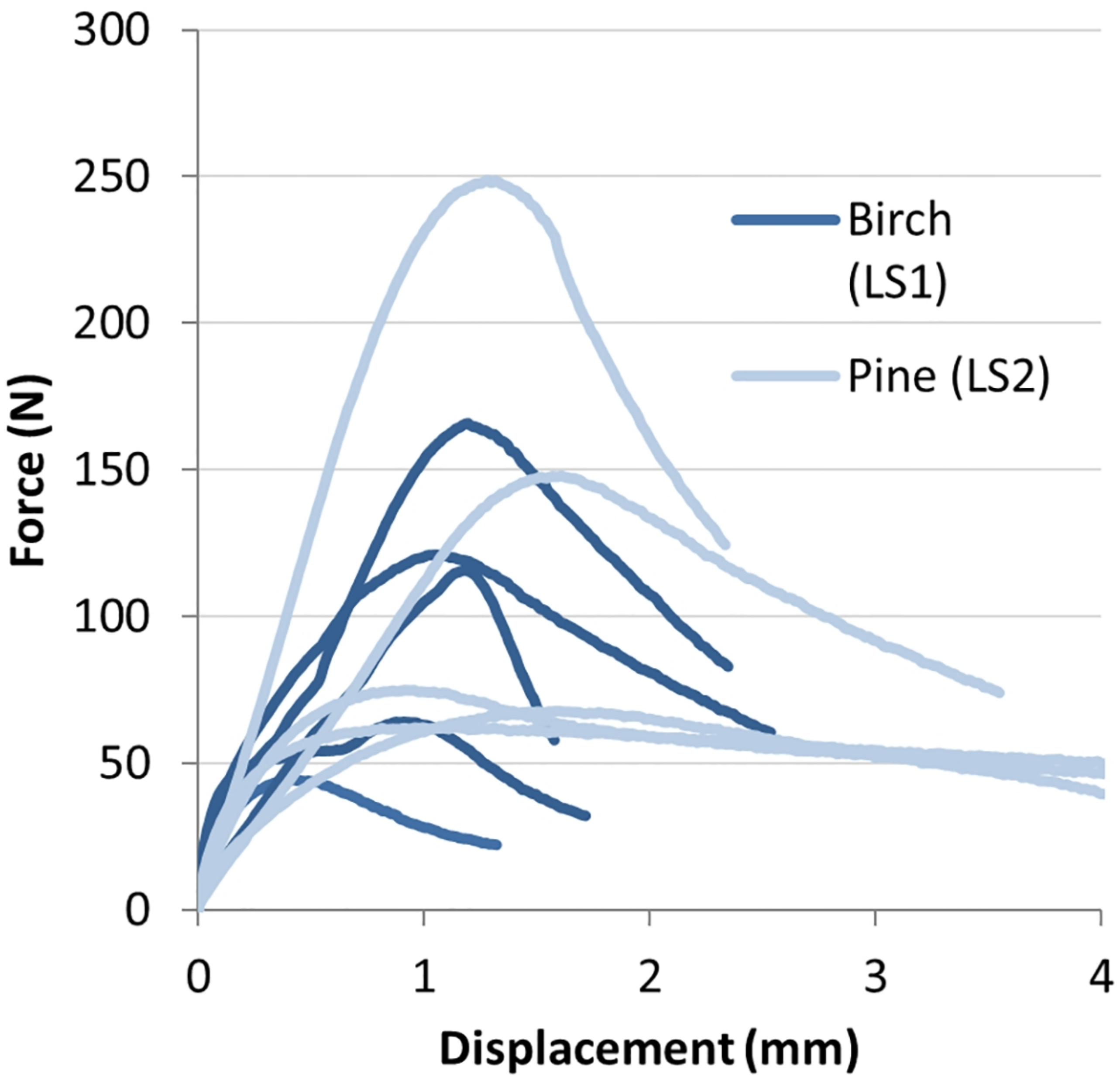

Lap shear performance of replica Palaeolithic pitch adhesives
Force
Displacement
Pitch + seething
Pitch + charcoal
Unmodified pitch

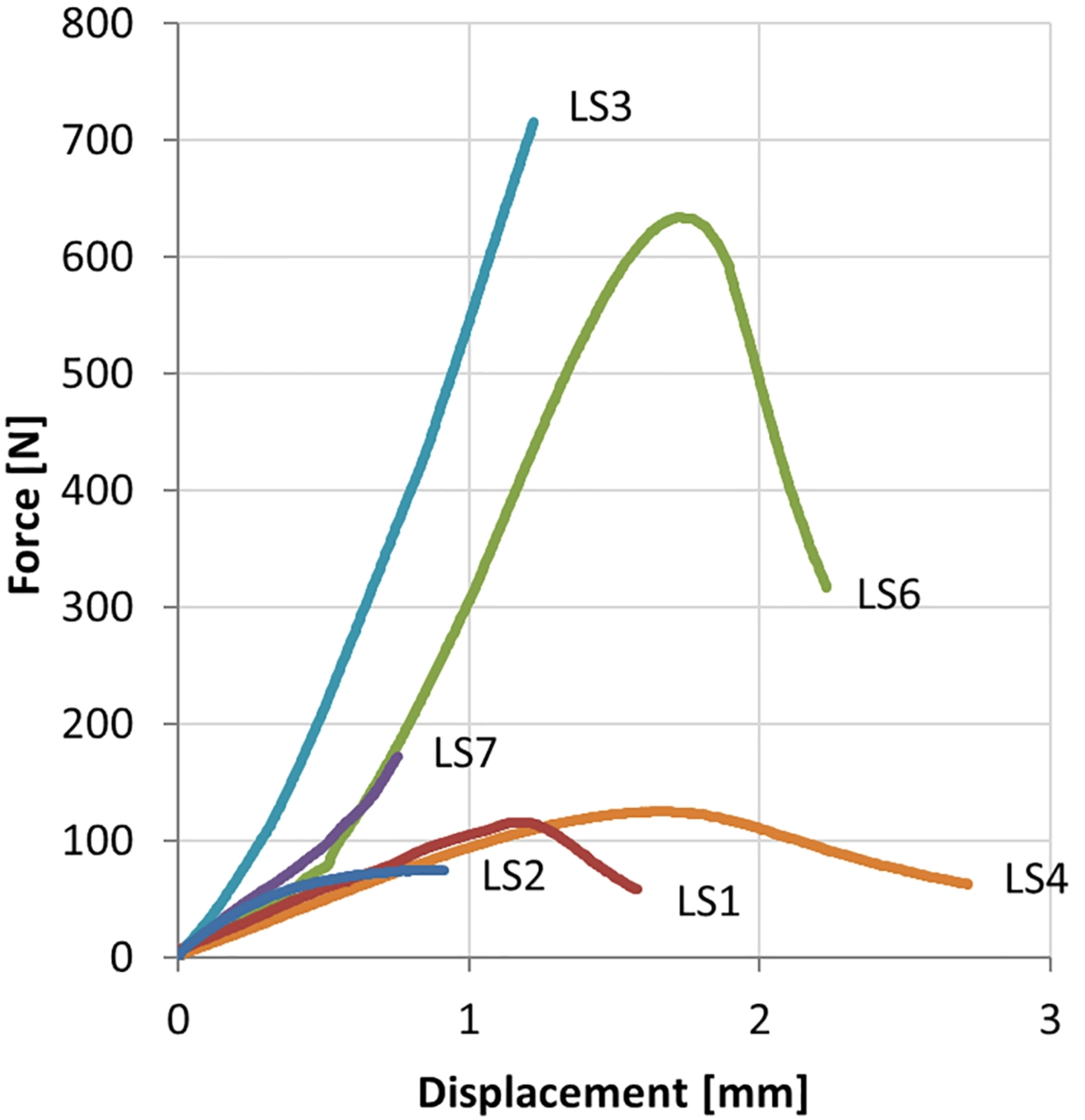

Birch tar
Reduced
Birch pitch
Standard lap shear test
A)
Pine tar
Reduced
Pine pitch
Standard lap shear tests at 0°, 22°, and 38° C
Flint lap shear test
Standard impact test
Reduced 10 min
Standard lap shear test
10 wt.% Charcoal
Standard lap shear test
Reduced 20 min
Standard lap shear test
20 wt.% Charcoal
Standard lap shear test
Reduced 30 min
Standard lap shear test
30 wt.% Charcoal
Standard lap shear test
B)



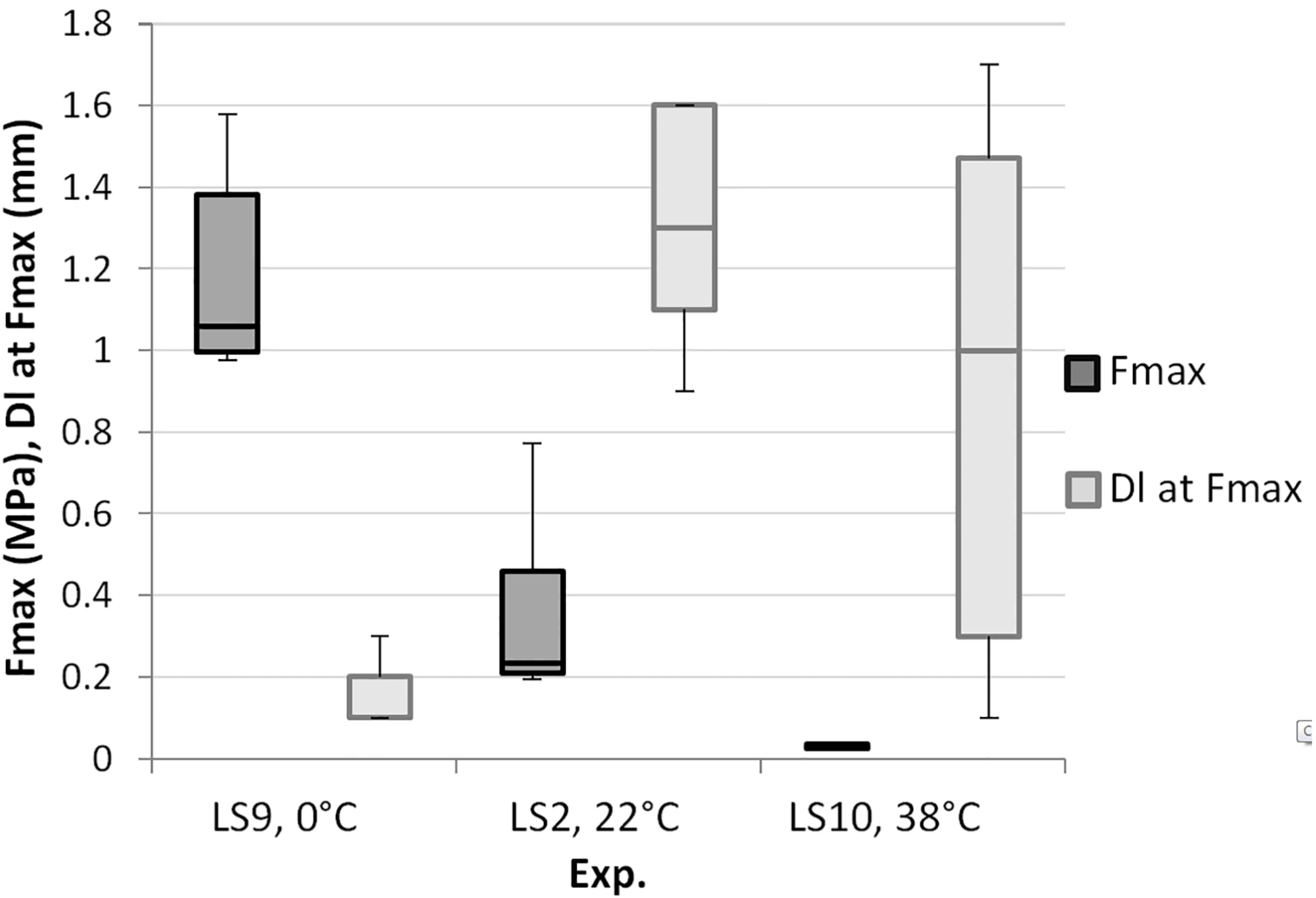


Fmax (MPa), Dl at Fmax (mm)
3
2.5
2
1.5
1
0.5
0
LS1
LS2
LS3
LS4
LS5
LS6
LS7
LS8
Exp. Number
Fmax
Dl at Fmax


300
250
200
150
100
50
0
Force (N)
0
1
2
3
4
Displacement (mm)
Birch (LS1)
Pine (LS2)

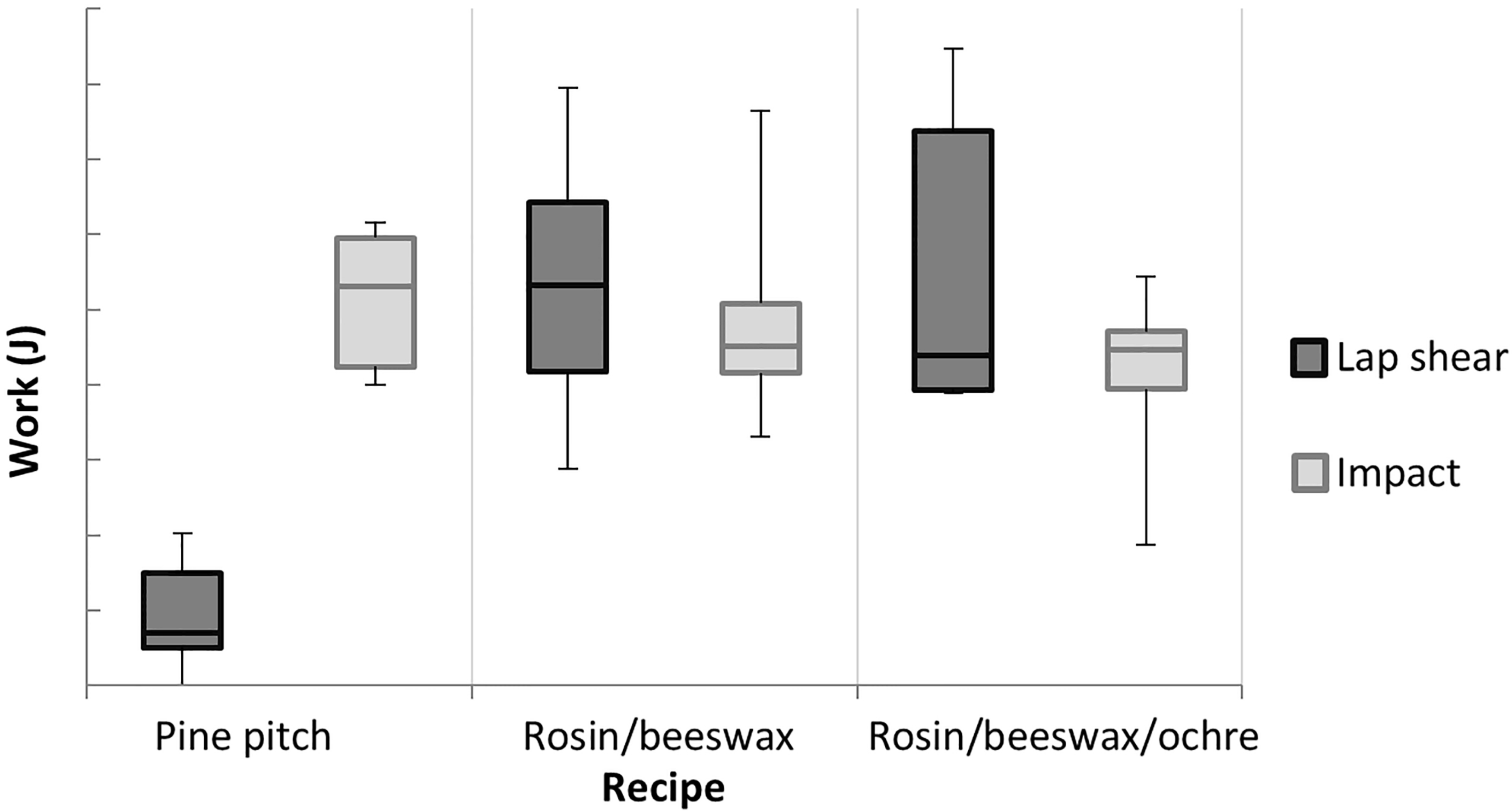


800
700
600
500
400
300
200
100
0
Force [N]
0
1
2
3
Displacement [mm]
LS3
LS6
LS7
LS2
LS1
LS4



1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Fmax (MPa), Dl at Fmax (mm)
LS9, 0°C
LS2, 22°C
LS10, 38°C
Exp.
Fmax
Dl at Fmax


1
2
3
4
5
6
7
8


Work (J)
Lap shear
Impact
Pine pitch
Rosin/beeswax
Rosin/beeswax/ochre
Recipe