

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

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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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Paul R.B. Kozowyk
Faculty of Archaeology, Leiden University
Van Steenis Building, Office C1.06

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.

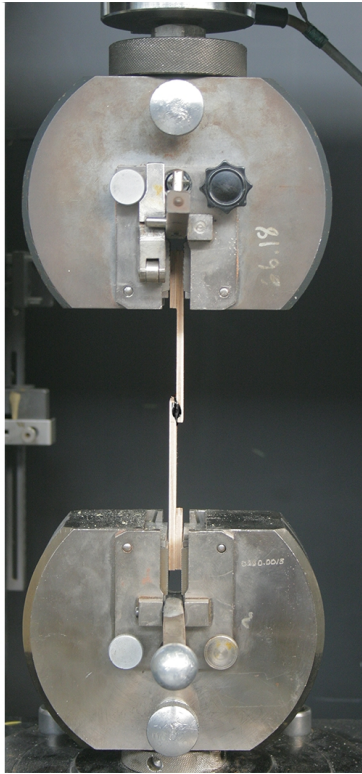
We have no opposed reviewers, and there have been no prior interactions with any other journal regarding the submission or publication of this manuscript and the data therein. All authors have approved this manuscript and the submission to JAS Reports.

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

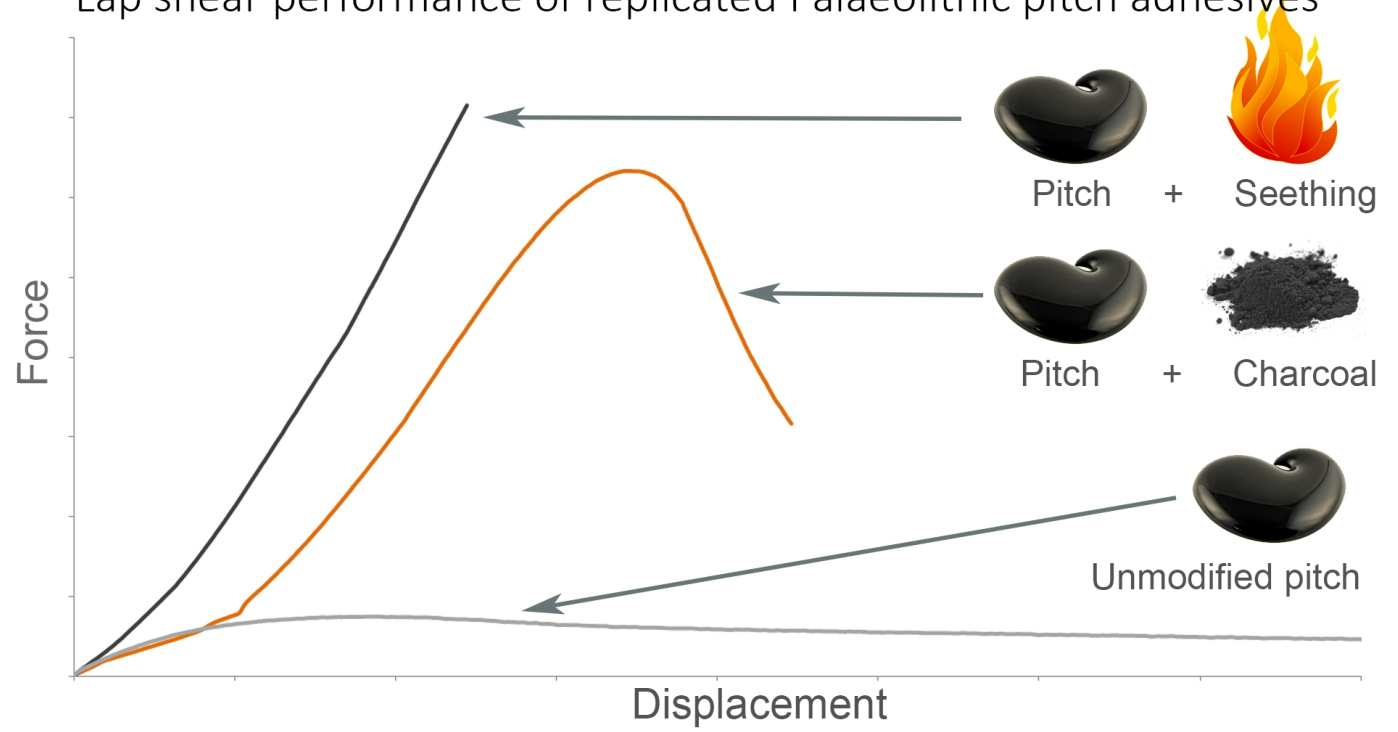
Sincerely,



Paul Kozowyk



Lap shear performance of replicated Palaeolithic pitch adhesives



1 **Full title**

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

4 **Short title**

5 Laboratory strength testing of pitch adhesives

6

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8

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19 **Highlights**

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

25 Abstract

26 Adhesives are an important yet often overlooked aspect of human tool use. Previous experiments have
27 shown that compound resin/gum adhesive production by anatomically modern humans was a cognitively
28 demanding task that required advanced use of fire, forward planning, and abstraction among other traits.
29 Yet the oldest known adhesives were produced by Neandertals, not anatomically modern humans. These
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41 performance. Similarly, pine pitch is sensitive to ambient temperature changes and it is strongest at 0°C
42 and weakest at 38°C. Adhesive failures occur in a similar manner on flint and wood suggesting the
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44 Finally, pine pitch adhesives may be better suited to resisting high-load rate impacts than shear forces. Our
45 experiments show that pitch production and post-production manipulation are sensitive processes, and to
46 obtain a workable and strong adhesive one requires a deep understanding of the material properties. Our
47 results validate previous archaeological adhesive studies that suggest that the manufacture and use of
48 adhesives was an advanced technological process.

49

50 Keywords

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

52

53 1.0 Introduction

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

65 Adhesives are used as a proxy to understand the technological and cognitive abilities of hominins
66 [2, 3, 6, 25, but see also 26]. This research has been dominated by compound resin/gum-ochre adhesives
67 made by anatomically modern humans in Africa [5-8, 27-29]. In this scenario, it is hypothesised that the
68 production and application of compound glues require advanced working memory, the ability to multi-
69 task, an understanding of abstract terms (e.g. miscibility, stiffness, viscosity and tack) and fluid
70 intelligence (as exemplified in transformative technology). The production of compound glues is complex
71 and the end product does not resemble the individual ingredients. Moreover, the process is
72 transformational and irreversible [6, 8, 30]. Neandertal tar production, although different from compound
73 adhesive manufacture, may have required similar cognitive abilities [2]. For example, the pyrolytic

74 production process is possible testimony to an understanding of abstract terms and fluid intelligence
75 (Wragg Sykes 2015) and is used to illustrate the technological abilities of Neandertals [31].

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

92 Here we present a first attempt to understand the effect of post-production manipulation on shear
93 strength and impact resistance of wood and bark tar pitches. We explore adhesive strength in relation to
94 tree species, climate, substrate material and force/activity. Pine tar is more ubiquitous in later periods than
95 birch tar [47]. and it might be that these two adhesives had different (additional) functions. It is possible
96 that one is stronger than the other, and therefore more/less preferred. To this end we conducted strength
97 tests on pine and birch tar pitch. Strength tests were also conducted to understand the influence of post-
98 production refinement and manipulation. In these tests charcoal was added in set increments to mimic
99 increased charcoal contamination. Similarly, we tested tar in different stages of reduction. Prehistoric tar

100 was used under variable environmental circumstances and it is possible that one of the attractions of this
101 adhesive over resin was that it performed well under a wide temperature range [29]. We therefore tested
102 tar for strength under different temperatures. Some adhesive may perform better on specific adherends or
103 substrate materials. Standard strength tests generally use aluminium and wood adherends; we added flint
104 to understand how tar strength on wood and flint compare. Finally, different force load-rates were at work
105 in different prehistoric tasks and an adhesive may react differently to one than another. Prehistoric peoples
106 may have selected glues based on these differences. We therefore compare the strength of tar under two
107 different forces: static lap shear and impact.

108

109 2.0 Materials

110 2.1 *Pine pitch, birch pitch, and charcoal*

111 Tar is a dark coloured viscous liquid produced through the pyrolysis or gasification of biomass
112 [48-50]. Tar can also be obtained from coal [49], or occur naturally as a material commonly known as
113 bitumen or asphalt [48]. When tar is in a liquid state, containing higher percentages of volatiles it is
114 referred to simply as ‘tar’. The term ‘pitch’ or ‘tar pitch’ refers to the more viscous, semi-solid or solid
115 fraction of tar [48, 49, 51]. Pitch is also sometimes confusingly used to refer to natural resin exudates
116 collected from conifers [52, 53], although this is more of a colloquial use of the term [54] and will be
117 avoided here.

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

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

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

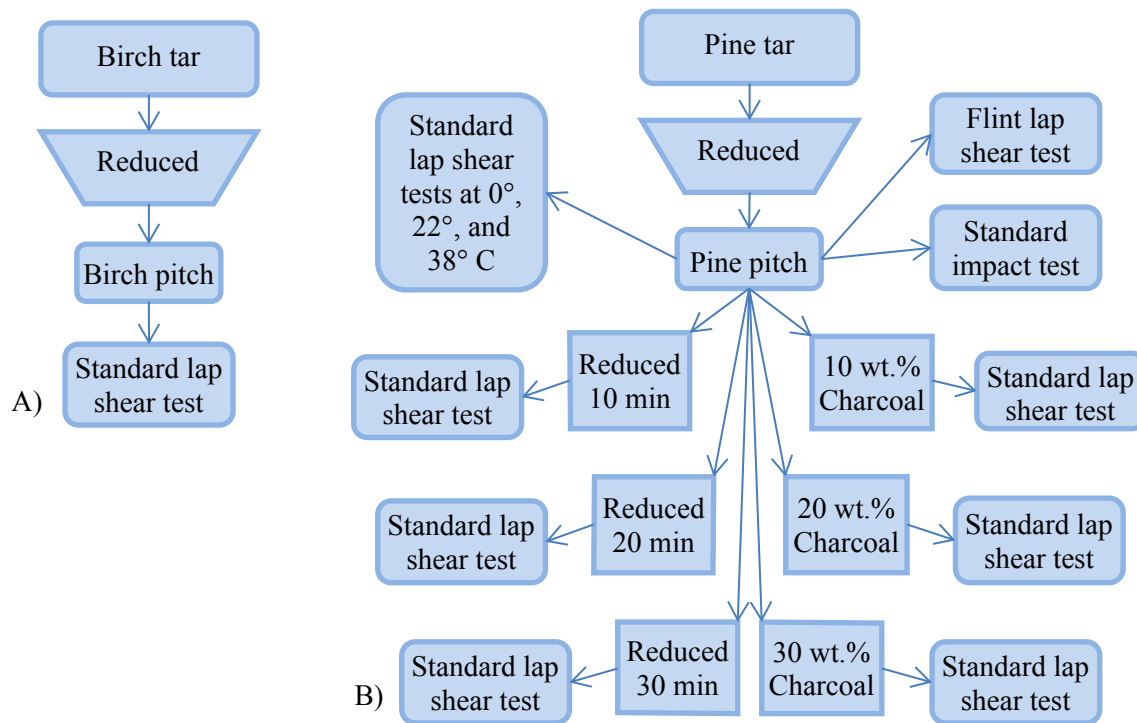
133 To test the influence of production-related contamination we added commercially available
134 powdered charcoal. This is pure charcoal made from beech (*Fagus* sp.) and ground into a fine powder
135 (<30 μ m). Without the use of ceramics or metal containers to isolate the tar end-product from fire by-
136 products, it is probable that charcoal would be a leading contaminant. There are other materials that could
137 and probably did contaminate adhesives, including plant material from the bark or wood, soil, sand, or ash
138 [43], but charcoal is perhaps the most significant and is thus the one we have chosen to test here.

139

140 *2.1 Sample preparation*

141 The sample preparation is the same for both lap shear and impact tests. Once the tar had been
142 reduced to pitch it was possible to break apart into separate amounts for further tests (Fig. 1). Table 1 lists
143 each adhesive and test applied. Unmixed birch pitch was used in one set of standard lap shear tests (LS1,
144 Fig. 1A), and the pine pitch experiments consisted of four parts (Fig. 1B). Part one was used to conduct
145 lap shear tests at a range of temperatures and on flint adherends (LS2, LS9, LS10). Part two was mixed
146 with 10, 20, and 30 wt.% charcoal and then used for standard lap shear tests (LS3, LS4, LS5). Part three
147 was further reduced by seething at approximately 150-200°C for 10, 20, and 30 additional minutes and
148 then used for standard lap shear tests (LS6, LS7, LS8). Part four was used for a standard impact test (IR1)
149 [cf. 29]. Before each test small glass beads (90 to 130 μ m) were added to the adhesives to ensure

150 uniformity among the set bondline thickness of each test piece [cf. 29]. The adhesives were stirred
 151 constantly for two minutes over an electric hot-plate before use and again briefly in between each
 152 application on every specimen. Once melted and thoroughly mixed, both adherend surfaces to be bonded
 153 were dipped in the adhesive at the same time. Then they were immediately squared and clamped until the
 154 adhesive had cooled and set. The wooden lap shear test specimens are 4.0 mm × 25.4 mm × 100.0 mm
 155 long. The bond overlap was 12.7 mm, making a bond surface area of 322.6 mm² in each experiment.



156
 157 *Figure 1. A) Workflow of sample preparation and experiments for birch bark pitch, and B) pine wood pitch adhesives.*

158
 159 *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	Rijkholt flint
IR1	Pine pitch	None	Impact resistance	22+/-2	Unknown hardwood

160

161 We also conducted one set of tests on Rijkholt flint from southern Limburg, the Netherlands

162 (LS11). This test was to ensure that the adhesive would behave similarly on flint. The flint was cut by a

163 professional mason into rectangular tabs to create a bond surface area that was also 25.4 mm × 12.7 mm.

164 To ensure maximum adhesion, the substrate materials were degreased with acetone, abraded with 100 grit

165 sandpaper, degreased again and left to dry for five minutes prior to the application of the adhesive (Fig. 2).



166

167 *Figure 2. Flint lap shear sample in test apparatus clamps. Sandpaper was placed between clamps and flint to ensure they would*

168 *not slip. This photo was taken during the test, and displacement can be witnessed by the distance the ends of the flint have moved*

169 *from the horizontal black lines.*

170

171 For the impact resistance test (IR1), the samples were made from solid pieces of tropical

172 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,

173 creating a bonded surface area of 216.0 mm² [cf. 29].

174

175 3.0 Methods

176 3.1 Lap shear experiments LS1-11

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

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

198 Lap shear test results are interpreted in several ways. First, a stress/strain graph is plotted that
199 gives an indication of the maximum force withstood by the adhesive. In this case a higher maximum force,
200 recorded as N/bonded surface area (mm²), or MPa, means that the adhesive was stronger. The stress/strain
201 curve can also describe the nature of the adhesive failure. A long low curve (larger displacement and
202 lower maximum force) typically signifies that the adhesive was less strong, highly ductile and easily
203 deformed. A steep sharp curve (lower displacement and higher maximum force), or one ending abruptly
204 indicates a stiffer adhesive, or one that failed in a brittle manner. Further, the location of adhesive residues
205 on the adherends after failure can indicate either a cohesive or an adhesive failure. If residue is evenly
206 distributed among both surfaces, the failure was cohesive – within the adhesive matrix itself. If the residue
207 is found only on one surface the failure was likely adhesive – occurring along the bond interface between
208 adhesive and adherend.

209

210 *3.2 Impact test IR1*

211 Materials can behave differently under different forces. For example, ductile materials can shatter
212 abruptly under impacts and high and low load rates also correspond to different prehistoric tasks; hafted
213 spear points were probably subjected to high load rates, whereas hafted scrapers were subjected to low
214 load rates [29]. To compare the results from the low load rate lap shear test and to determine if some
215 adhesive recipes are better suited to one task over another, we also tested pitch at high load rates (impact,
216 experiment number IR1). The most common tests for material impact resistance are the Charpy and Izod
217 tests [65]. We selected the variant described by ASTM D950 [62]. Impact tests were performed using a
218 Zwick 5113 pendulum impact tester. A pendulum hammer is released from a swing angle of 124.4 degrees
219 and accelerates to a speed of 3.46 m/s before impacting the specimen locked in the clamps. In our impact
220 test the adherend is struck with a velocity of 3.46 metres per second. This is faster than the loading speeds
221 estimated for stabbing, and slower than those for spear throwing [66]. The hammer impacted the 18 mm
222 wide face of the sample less than 1 mm from the bondline. Impact tests were conducted at an ambient air

223 temperature of 22–23°C and a relative humidity of 45+/-6%. Impact resistance is measured by the height
 224 of the pendulum swing after colliding with the adhesive sample and is given in Joules as the amount of
 225 energy required to break the adhesive bond. No stress stain curve is generated, but as in lap shear tests,
 226 impact failures can occur adhesively or cohesively.

227

228 4.0 Results

229 4.1 Room temperature lap shear LS1 – LS8

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

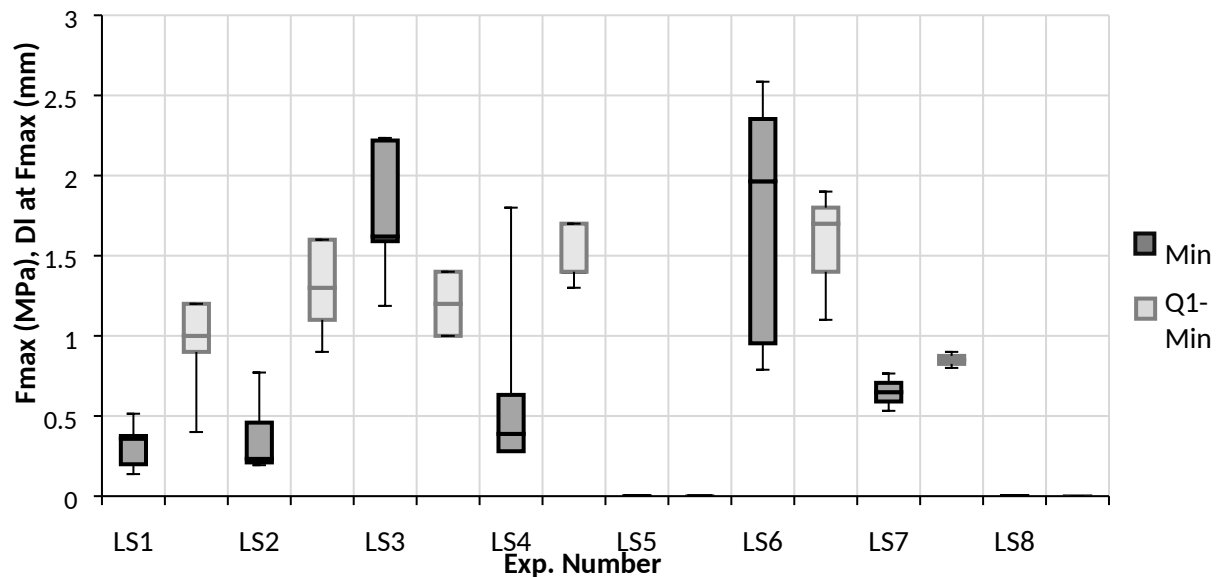
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237 *Table 2. Results of the lap shear tests. Including the mean, maximum, and minimum maximum force (Fmax), and the mean,*
 238 *maximum, and minimum displacement at maximum force (Dl at Fmax) for each adhesive recipe.*

Exp	Primary material	Secondary manipulation	Adherend type	Fmax (Mpa)			Dl at Fmax (mm)		
				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

239



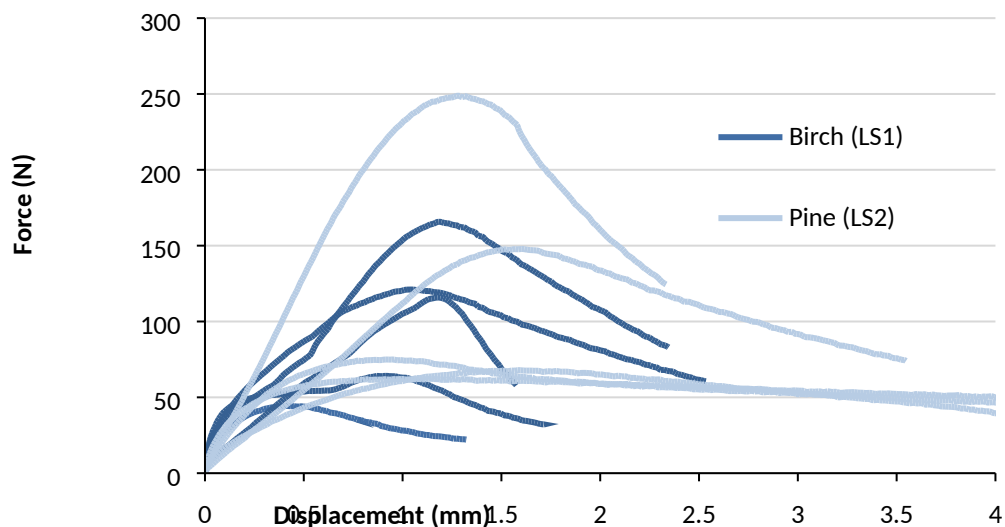
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241 *Figure 3. Lap shear results for experiments LS1 - LS8. Fmax = maximum force; DI at Fmax = displacement at maximum force.*

242

243 First, birch pitch performed in a similar manner to pine pitch (Table 2). The mean maximum
 244 strength of birch pitch was 0.32 MPa and the mean maximum strength of pine pitch was 0.37 MPa, the
 245 ranges of which overlap considerably. Birch and pine pitch were both highly ductile materials under static
 246 load rates, and were displaced an average of 0.9 mm and 1.3 mm respectively. The stress/strain curves
 247 appear similar for birch and pine pitch, although pine pitch was slightly more ductile (Fig. 4). Both
 248 adhesives shared a relatively high variation in maximum force. Neither failed abruptly, and both failed
 249 cohesively within the matrix of the adhesive rather than along the bond interface. As the physical
 250 characteristics of birch and pine pitches proved to be similar with this test, the other experiments were

251 conducted using commercially available pine pitch. This allowed us to control the variables resulting from
252 birch bark production in an open fire and thus aided the reproducibility.

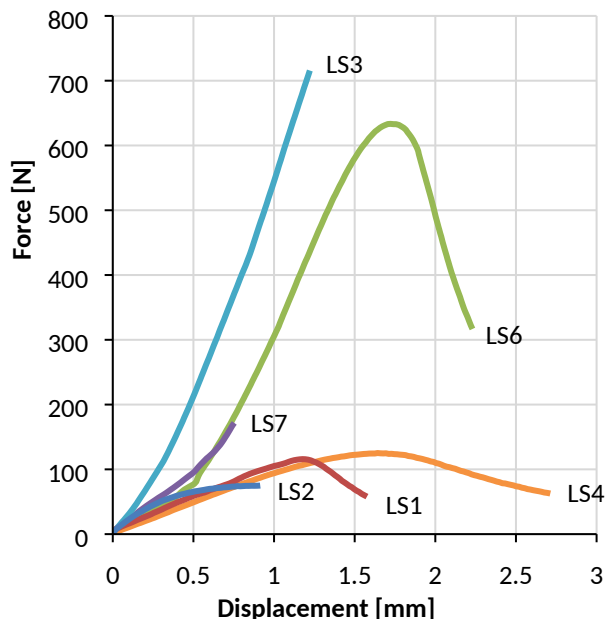


253
254 *Figure 4. Stress strain curves from each individual specimen for unmodified birch and pine pitch at room temperature on wood*
255 *adherends.*

256
257 When charcoal was added to pine pitch the properties changed significantly (Fig. 5). With the
258 addition of 10 wt% charcoal the mean Fmax of LS2 to LS3 increased from 0.37 MPa to 1.77 MPa, a mean
259 Fmax increase of 378 %, and mean displacement remained approximately the same. Charcoal therefore
260 improved the strength under static load, and increased the relative stiffness of the material. With an
261 additional 20 wt% charcoal, the mean Fmax of LS4 fell to 0.68 MPa (an increase of 84 % from LS2).
262 With 30 wt% charcoal LS5 was not useable as an adhesive as it became saturated with filler and lost
263 nearly all of its ‘tack’. The substrates could not be successfully bonded, and no lap shear test could be
264 conducted.

265 Further reducing pitch by seething [cf. 44] had a similar affect as adding charcoal (Fig. 5). After
266 10 extra minutes at 150-200°C the mean Fmax of LS6 was 1.73 MPa (an increase of 367% from LS2) and
267 mean the displacement was 1.6 mm. Twenty minutes of seething resulted in a mean Fmax for LS7 of 0.65
268 MPa (an increase of 76 % from LS2) and a mean displacement of 0.85 mm. However, it must be noted

269 that due to increased brittleness three out of five of the specimens for LS7 failed during preparation before
 270 the test could be started. Thirty minutes of seething created an extremely brittle material in LS8 that failed
 271 to bond successfully and cracked or broke on every specimen before the test could be started.



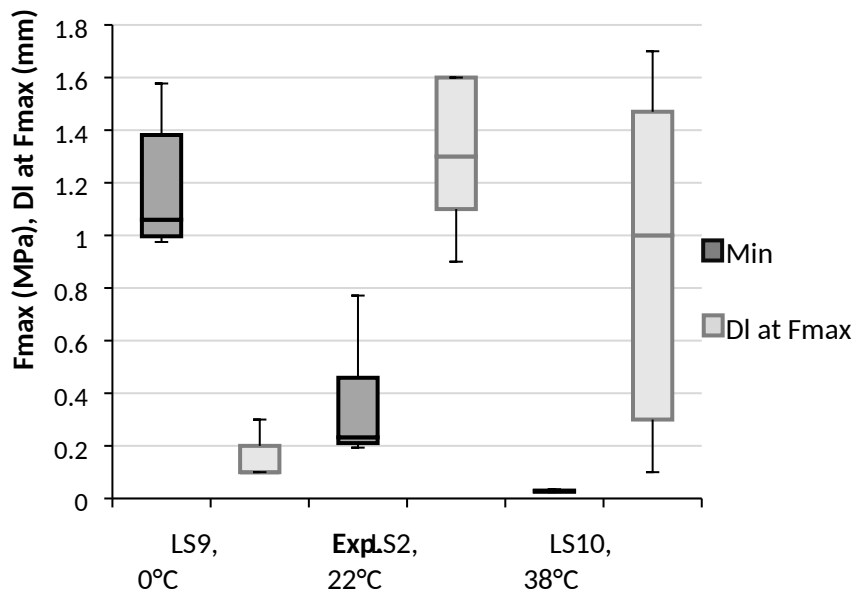
272
 273 *Figure 5. Stress/strain curves for median results of tests LS1, LS2, LS3, LS4, LS6, and LS7 to give approximation of variation*
 274 *between recipes. LS5 and LS8 gave no results. Of the five specimens tested for LS4, two were successful and the lowest of the two*
 275 *is visualized here.*

276

277 4.2 Climate chamber lap shear: LS9-LS10

278 These experiments include those conducted in the climate chamber at 0°C and 38°C to determine
 279 how pitch adhesives are affected by changes in temperature. They will be primarily compared with LS2 –
 280 the same unaltered adhesive tested at 22°C. This pine pitch performed significantly better at 0°C than at
 281 22°C (mean 1.20 MPa and 0.37 MPa respectively that is a mean Fmax increase of 224 %). It performed
 282 significantly worse at 38°C (0.03 MPa, or a mean Fmax decrease of 92 %) (Fig. 6). At this high
 283 temperature the pitch was so soft that it deformed under the 10 N preload of the test machine, and final
 284 test results are negligible (Fmax of near zero, and DI at Fmax is highly variable). At 0°C all of the pine
 285 pitch failures were brittle, rather than ductile as they were at room temperature and 38°C.

286



287

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

290

291 *4.3 Flint lap shear: LS11*

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

302

303 4.4 Impact resistance: IRI

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



309
310 *Figure 7. Bonded surfaces after impact test failures. Even presence of tar on upper and lower adherends indicates failures were*
311 *cohesive in nature.*

313 5.0 Discussion

314 5.1 Discussion of results

315 The preliminary comparison in this pilot study indicates that under static lap shear forces at room
316 temperature there is little difference in performance between birch and pine pitch. In this respect, and as it
317 has been described elsewhere, although tars from different tree species do differ chemically [67] their
318 composition is not altogether dissimilar and their physical properties may also be similar [68, 69]. It must
319 still be noted that the sensitivity of natural adhesives to additives, as seen here and in previous studies [5, 6,
320 29] may mean that birch and pine pitch behave differently when mixed with charcoal. The different
321 chemical components, such as the resin acids in pine pitch and betulin in birch bark pitch may also have
322 an effect on how these adhesives react to heat or re-use.

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

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

349 post-production refinement. More research would be required to test the quality and consistency of pitch
350 adhesives produced using Palaeolithic technology to accurately describe what reduction processes would
351 be necessary.

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

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

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

373

374 *5.2 Comparison with resin and gum based adhesives*

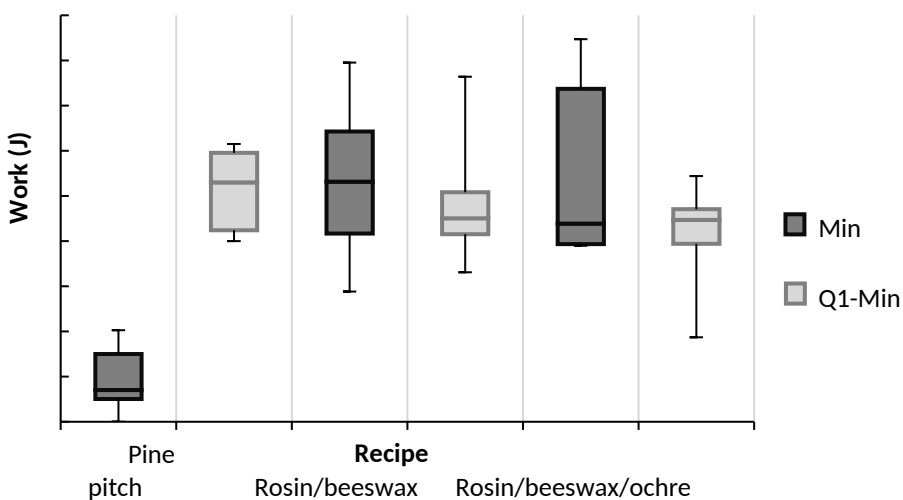
375 In a previous lap shear study we tested how sensitive rosin and gum based adhesives are to recipe
376 changes [29]. We found that, up to a particular optimum, pine rosin glues increase in strength when
377 beeswax and ochre are added. Small changes in the amount of ingredients had a big effect on strength.
378 Our unrefined pine pitch adhesive here was weaker under lap shear forces than any combination of rosin
379 with beeswax and ochre. The same pitch, however, outperformed rosin adhesives in the impact test. The
380 task being performed is therefore prevalent to the performance of the adhesive. With the addition of 10 wt.%
381 charcoal, or reduction for 10 additional minutes, the lap shear performance of pitch was comparable to
382 50/50 rosin-beeswax mixtures containing ochre. Or 80/20 rosin-beeswax ochre mixtures [29]. At 0°C the
383 unreduced pitch (mean Fmax 1.20 MPa) performed better than pure rosin (failed prior to any test due to
384 brittleness), 50/50 rosin-beeswax (mean Fmax 1.02 MPa), and 70/30 rosin-beeswax (mean Fmax 0.98
385 MPa). Each of these 3 rosin based adhesives outperformed pine pitch at 38°C, however, suggesting pitch
386 adhesives may be better suited to colder climates [72]. It must still be noted that this varies on the method
387 of production, and the level of reduction. Some experimentally produced birch pitch has been recorded as
388 being resistant to warm temperatures as well [46].

389 The addition of charcoal in 10 wt.% increments to pine pitch adhesives had more pronounced
390 effects in the shear tests than did ochre in the same wt.% increments to rosin-beeswax compound
391 adhesives [29]. A difference from 20 wt.% to 30 wt.% charcoal changed the adhesive from highly plastic
392 and soft to being so over-saturated that it would not adhere to either substrate. This difference may result
393 from the mass of charcoal powder compared to red ochre powder. Charcoal is much less dense, less than
394 1 g/ml, compared to red ochre/hematite, approximately 5 g/ml [73], so when the recipes are mixed by
395 weight, as was done here, the volume of charcoal used is considerably more than the volume of ochre, and
396 the particles simply cover more surface of the adhesive.

397 The action of seething pitch adhesives to change the performance properties may be comparable
398 to using heat from a fire to dry gum adhesives [5], or to boil down pine resin and produce rosin. Both of
399 these processes can damage the adhesive if too much heat is applied too quickly, and maintaining control
400 over the heat source is necessary. It is possible that a soft pitch could dry and harden over time, simply on

401 exposure to air or sunlight, as with gum or resin, but the practicality of this is questionable. As was seen
402 with gum adhesives, even after several days of air drying, when the adhesive was used it would break and
403 reveal wet and tacky gum in the centre [5]. Further, if the adhesive is too soft when left to dry it can easily
404 run out of its haft or drip off the tool.

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



412
413 *Figure 8. Relative work done (J) to maximum force (lap shear) and adhesive failure (impact) during tests.*

414
415 The variable nature of pitch adhesives, ranging from highly ductile to very brittle, suggests that
416 the addition of beeswax would not be required to act as a plasticising agent in the way that it is often
417 described for rosin adhesives [29, 74]. However, when pitch is over-heated, or boiled for too long it can
418 become brittle, and beeswax or animal fats can potentially improve/revert the quality (personal
419 observation). Additionally, pitch can exhibit viscoelastic properties [49, 75] and ‘flow’ at extremely low

420 rates over time. It is possible that the addition of a solid with high miscibility in tar may help to reduce this
421 unwanted property. Although it may not be necessary for hafting stone tools, especially if a binding
422 material was also used, it could be prevalent for purposes such as repairing pottery, where the bond would
423 be required to remain in exactly the same position under a low level of static stress for a prolonged period
424 of time.

425

426 *5.3 High-tech pitch?*

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

439 Alternative uses of adhesives during the Palaeolithic must also be considered, including the use
440 as a handle or backing material itself. The appearance of the flint flake from Campitello Quarry, Italy,
441 gives the impression of a simple back to improve prehension [17]. In this situation, pitch may have been
442 used in a manner similar to spinifex resin on Australian 'leiliras', a type of stone knife. It could be applied
443 as a backing to protect the users hands from the sharp edges of the flint, or melted and reapplied to bind
444 the same blade to a wooden handle when needed [76, 77]. Use-wear evidence from Inden-Altendorf suggests

445 tools were re-used and possibly re-hafted for different purposes [18]. In order to act as a backing material,
446 cohesive and adhesive strength are less important, and weak or brittle materials would likely suffice.
447 However, if the material were to be re-used as a binding medium to place the flint in a handle, the physical
448 strength and adhesive quality of pitch must be higher than for a backing alone.

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

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

471

472 6.0 Conclusion

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

488 These variations in performance resulting from small changes in ingredients or refinement
489 processes, combined with the effect of temperature and load-rate on adhesive performance suggest the
490 manufacturers were highly skilled with an intricate knowledge of the materials they were working and of
491 the techniques to do so. Depending on the outside temperature and the task at hand their manufacture
492 methods and/or post-production processes may have had to vary in order to produce the most effective
493 adhesive. Results here are parallel to those of gum and resin-based compound adhesives [6, 8, 29] and
494 thus imply high levels of analogous reasoning, technical and cognitive abilities. Yet, without direct

495 evidence of tar production methods by Neandertals in the archaeological record there is still much more
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727

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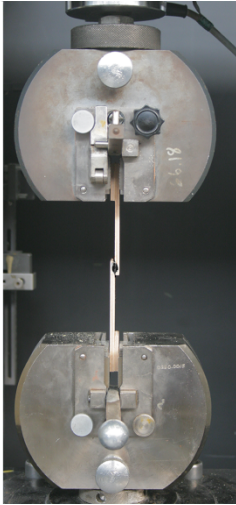
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744 Graphical Abstract

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Lap shear performance of replica Palaeolithic pitch adhesives

