Unlocking the **Secrets of Long-lasting Success**

Kurzfassung · Langfassung: www.tum.de/faszination-forschung-26

Was lange hält, ist gut

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Das Wissen über historische Klebstoffe ist zu einem Großteil verloren gegangen. Prof. Cordt Zollfrank und sein Team am TUM Campus Straubing holen es wieder ans Tageslicht. Ihr Ziel ist es, Klebstoffe zu entwickeln, die in der Herstellung und Anwendung umweltfreundlicher sind als die zurzeit am Markt dominierenden Epoxidharze auf Erdölbasis. In einem Projekt hat der Doktorand Johann Lang den wirksamen Klebstoff aus Birkenpech extrahiert. Dieser könnte als sogenannter Tackifier in modernen Heißklebstoffen eingesetzt werden. In seinen Eigenschaften ist er teils besser als bisher am Markt verfügbare Produkte.
In einem zweiten Projekt analysiert die Steinrestauratorin und Doktorandin Sophie Hoepner Klebstoffe, die vor hunderten von Jahren beim Bau von Kathedralen zum Einsatz kamen und seitdem ohne nennenswerte Alterungserscheinungen Wind und Wetter trotzen. Ihr Ziel ist es, eine Rezeptur für solch einen langlebigen Klebstoff auf Basis von Naturstoffen zu entwickeln. □

Most of what we used to know about ancient adhesives has been lost in the mists of time. Cordt Zollfrank and his colleagues at TUM's Straubing campus are shining a light on this long-forgotten knowledge once more. They are combing through old books, analyzing glue samples taken from cathedrals, and devising recipes for non-harmful adhesives made from sustainable raw materials.

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Picture credit: Magdalena Jooss, Unsplash/Dallas Reedy

Many materials to make ancient adhesives are harvested in nature, mostly in forests.

1 Rosin clear
2 Gum mastic
3 Sugarcane wax
4 Rosin super-transparent
5 Gum sandarac
6 Bonded tensile specimens from granite
7 Rosin from pinus nigra
8 Dammar gum
9 Carnauba wax
10 Marble powder
11 Bonded tensile specimens from sandstone
12 Brick powder
13 Birch-bark pitch

When Cordt Zollfrank went to visit his close school friend Mario Pfreundner, little did he know that he would be opening a new chapter in his research work that day. Pfreundner is a keen amateur archaeologist and also teaches schoolchildren about the subject, which is very dear to his heart. So his house is strewn with the kind of home-made arrows that hunters used as long ago as the Stone Age. Following the standard method of the time, he had used birch tar that he had mixed himself to stick the stone heads and wooden shafts of his arrows together. As soon as Zollfrank saw this, he was captivated.

Though he had never heard of birch tar, it sounded highly promising. This is because hot-melt adhesives, i.e. those that are solid at room temperature but turn liquid when heated, have become such an integral part of our lives that we cannot imagine doing without them. They are used in all areas of industry, such as packaging and wood processing. Nowadays, glues are primarily made from polyamide, polyurethane, and other copolymers. Although they work quite well as adhesives, they have many drawbacks: They are produced from fossil fuels, generating a lot of CO_2 in the process, and are harmful to health and the environment.

The world's only pitch drop experiment with birch-bark pitch: The original pitch drop experiment, started in 1930 (Prof. Dr. Thomas Parnell, University of Queensland, Australia) as a long-term investigation of the liquid characteristics of pitches. Zollfrank's team started their pitch drop experiment with birch-bark pitch in October 2016.

"[Birch tar] is just as good, or even better, than the products that are currently available on the market."

Cordt Zollfrank

Using birch tar as the hot-melt element

"Birch tar, on the other hand, is a sustainable raw material," says Zollfrank, who is Head of the Department of Biogenic Polymers at TUM's Straubing campus. "And, not only that, there's an abundant supply of it in Europe and Siberia." So he immediately set about reading up on the subject. He read how people used to go into the woods, gather birch bark, and put it on the fire inside a covered pot. How it would start to smolder inside until, finally, a pitch- or tar-like substance would begin to drip out – this was birch tar. "Archaeological research has given us a wonderfully clear picture of how birch tar is made and what it contains, but there's been virtually nothing on the material properties of the substance," Zollfrank explains. This prompted him and his doctoral student Johann Lang to find out for themselves.

They carbonized birch tar under controlled conditions in a laboratory furnace to extract the powerful adhesive. "Pure birch tar stinks like an overflowing ashtray," Zollfrank says. "So you couldn't use it for anything." However, the adhesive substance that they obtained from it is virtually odorless. ▷

Picture credits: Magdalena Jooss

Prof. Cordt Zollfrank

Cordt Zollfrank studied chemistry at TUM before moving to the university's Wood Research Institute, where his studies of wood chemistry led to a doctorate in forest sciences. Between 2000 and 2002, he conducted research into biomimetic material synthesis, initially as a postdoctoral researcher at the Institute of Glass and Ceramics at Friedrich-Alexander-Universität Erlangen-Nürnberg. In 2002, he began his work developing the "Bioengineered Ceramics and Biomaterials" research group. He acquired his postdoctoral teaching qualification (habilitation) in material sciences in 2009 and was appointed Professor for Biogenic Polymers at TUM's Straubing campus on October 1, 2011. As of December 2020 he was appointed to a lighthouse professorship for Biogenic Polymers.

"These kinds of bonds have to endure wind, rain, and snow […] – often for many hundreds of years."

Sophie Hoepner

Granite tensile specimens with different hot-melt adhesive formulations prepared for the determination of tensile strength of butt joints.

Picture credits: Magdalena Jooss

Modern hot-melt adhesives consist of three elements: The first is a polymer, a macromolecule that mainly provides the mechanical strength. Then comes a "tackifier", which improves the contact between the adhesive and the substrate – makes it "tackier", in other words. The final piece of the puzzle is a modifier, which can alter the adhesive's properties such as its viscosity (resistance), melting range, smell, or color. Birch tar can be made into a particularly good tackifier. "It's just as good, or even better, than the products that are currently available on the market," Zollfrank says.

Ever since he began his in-depth study of birch tar, he has been unable to get ancient adhesives out of his head. In a second project at his professorship, stone restorer and doctoral student Sophie Hoepner is investigating how stones used to be glued together when churches and cathedrals were built. "These kinds of bonds, particularly those outside, have to endure wind, rain, and snow and withstand continuous freeze-thaw cycles – often for many hundreds of years," Hoepner says. If you consider that epoxy resins often begin to crumble after just 50 years, the adhesives used back then – 600 years ago! – are far superior to our modern products. ▷

Universal testing machine for the determination of tensile lap-shear strength of bonded assemblies.

1

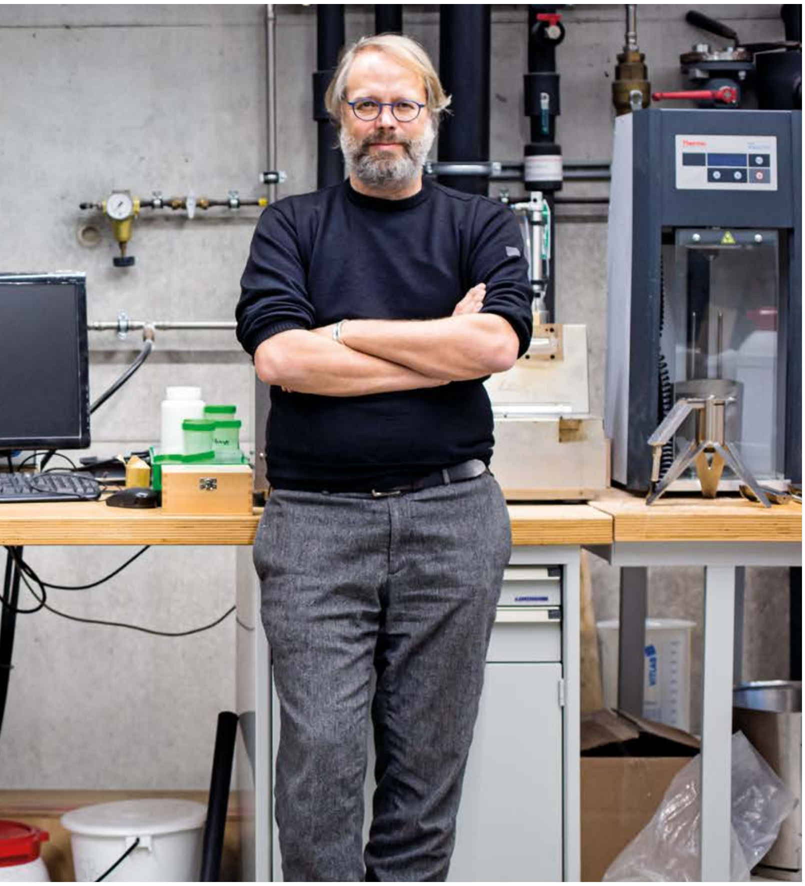
After applying hot-melt adhesive to the heated granite test specimens, glass beads of 400 µm in size are scattered on the bonding surface to achieve a constant reproducible joint thickness.

2

The adhesive-coated bonding surfaces are heated using a heat gun before joining.

3

After joining of the granite test specimens, they are loaded with 2 kg of weight until the hot-melt adhesive has cooled down.



Cordt Zollfrank and his doctoral student Sophie Hoepner share the passion for ancient adhesives.

Stone glues in cathedrals hold fast for centuries

But her research into the literature did not reveal a great deal either. In the past, much was not written down at all, but rather handed down orally from the master craftsman to his apprentice. The few recipes she did find were full of fantastical weights and measures: “two handfuls” of this, a “grain” of that. The verdict: entertaining, but thoroughly useless. “I can’t bear the fact that this knowledge has been lost,” says Zollfrank.

Sophie Hoepner now has to tackle the matter back to front. Instead of following a recipe, she creates one herself. To do this, she uses her scalpel to remove lentil-sized samples from the glued joints between cathedral stones and analyzes their composition. She is now familiar with the fundamental materials used to make most ancient adhesives.

These were based on pure wood tar from spruce or pine trees, which was distilled and mixed with mineral aggregates. Rosin, a substance left over when the pine wood resin is distilled, was also frequently used. Because it is very brittle, beeswax was added to make it elastic – but getting the right amount is crucial. “Too much beeswax makes the glue too soft, while not enough turns it brittle,” Hoepner says. Rock flour, a natural byproduct of stoneworking, was also added into the mix to give the adhesive a good level of sturdiness and viscosity and a certain coloration.

An adhesive stronger than many stones

After many rounds of analysis, Hoepner mixes the first few glues of her own, whose properties she then tests in the lab. One particularly important characteristic is tensile-shear strength, which measures the force required to pull apart two bodies glued together in an overlapping arrangement. “In the tests I ran on sandstone, the stones fractured before the adhesive came unstuck,” Hoepner reports. To find out exactly how tough her adhesives really were, therefore, she had to test them out on solid granite. By the end of her project, she is hoping to have come up with some detailed recipes for glues that are based on sustainable raw materials and that also last longer than the oil-based epoxy resins currently dominating the market. In the best-case scenario, we will soon see the same tried-and-tested adhesives used to restore the stonework on various historical buildings that have already been keeping one stone firmly on top of another for many hundreds of years. The construction industry will also benefit from an environmentally friendly stone adhesive that is less toxic and harmful.

Claudia Doyle

“I can’t bear the fact that this knowledge has been lost.”

Cordt Zollfrank about the old adhesive recipes

Picture credits: Magdalena Jooss